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REDOX MEASUREMENTS

their theory and technique

RADIOMETER A/S · EMDRUPVEJ 72 · DK2400 · COPENHAGEN NV · DENMARK

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FOREWORD

For the past 30-40 years redox measurements have been known and used for scientific investigations in many laboratories throughout the world. However, they have never become a really widespread success in practical life except in one particular field - namely, in connection with potentiometric titrations, where such measurements have gained considerable ground.

Very likely the limited success of redox measurements in practice is ascribable to one or all of the following three reasons:

The popular understanding of the theory underlying redox measurements is far from satisfactory.

The practical measuring technique is not always simple to master.

Our insight into this technique is highly inadequate.

As the subject literature is very plentiful, the cause of the inadequate understanding of redox measurements cannot be sought in a deficiency of information, but rather, perhaps, in the fact that the available information is very heavy reading and therefore is left unread.

The scope of this bulletin is to acquaint the reader with the commonly used redox symbols, with redox measurements and with the measuring technique underlying such measurements. It is not intended as a new contribution to the scientific literature on the subject, but will have fulfilled its mission if it serves to give the reader an impression of the significance of redox measurements and renders him capable of making rapid, skillful and accurate determinations.

The data contained in the bulletin is to a great extent extracted from the book of Professor Holger Jørgensen: Redox-Målinger (ref. 1), published in 1945. This highly readable publication must still be deemed a fair and easily understood introduction to redox measurements. Unfortunately it is available in Danish only.

Jan. 1966

G. Kokholm Petersen M.Sc.

A. INTRODUCTION

By a redox measurement is understood a measurement of the reduction-oxidation potential of a solution. A redox measurement is in fact very similar to a pH measurement, which latter certainly is widely understood to-day. Where a pH measurement gives an indication of the acid/base status of a solution, i.e. indicates the hydrogen ion activity, a redox measurement serves instead to determine the reduction-oxidation status of a solution, i.e. indicates the electron activity.

It is a well-known fact that the pH of a solution can be measured by immersing a pH-sensitive electrode, e.g. a glass electrode, and a second electrode (reference electrode), e.g. a calomel electrode, in the solution and then measuring the potential difference occurring between them on a special millivoltmeter, viz. a pH meter.

Similarly, it has been found that placing a so-called indifferent electrode - e.g. a platinum or gold electrode - and a reference electrode in a solution renders it possible to measure a potential difference, the magnitude of which is a measure of the strength of the solution with regard to reduction and oxidation substances.

It is known from the acid-base theory that an aqueous solution containing a strong acid in addition to its content of hydrogen ions also will include hydroxyl ions. Likewise, an aqueous solution containing a weak acid will always include the corresponding base. The ratio of acid to corresponding base is dependent on the pH-value of the solution.

This is also the case for redox systems.

An aqueous solution containing a reduction agent will invariably also contain the corresponding oxidation agent.

The ratio of reduction agent to oxidation agent depends on the strength of the reduction-oxidation system in the solution.

Originally the potential differences measured in a solution containing reduction agents were called reduction potentials, and, conversely, the potential differences measured in a solution containing oxidation agents were called oxidation potentials. As mentioned above, however, a solution will always contain both reduction agents and oxidation agents, so that the current term applied to such potentials is reduction-oxidation potentials, commonly abbreviated to redox potentials.

B. THE THEORY OF REDOX MEASUREMENTS

The Brønsted acid-base definition will serve admirably as a basis for a discussion on the theory of redox measurements. According to him, an acid is defined as a substance that is capable of liberating a hydrogen ion:

$$\underset{\text{acid}}{HA} \rightleftharpoons \underset{\text{base}}{A^-} + \underset{\text{hydrogen ion}}{H^+} \tag{1}$$

Accordingly, a base is a substance that is capable of absorbing a hydrogen ion. It is seen, then, that every acid has its complemental base.

It is possible to define the redox system in a form analogous to that of the acid-base definition. Thus, a reduction agent is definable as a substance capable of liberating an electron:

$$\mathrm{Red} \rightleftharpoons \mathrm{Ox} + e^- \tag{2}$$

Accordingly, an oxidation agent is definable as a substance capable of accepting an electron.

Two typical examples are:

$$\underset{\text{iodide}}{I^-} \rightleftharpoons \underset{\text{iodine}}{1/2\ I_2} + \underset{\text{electron}}{e^-} \tag{3}$$

$$\underset{\text{ferro ion}}{Fe^{+2}} \rightleftharpoons \underset{\text{ferri ion}}{Fe^{+3}} + \underset{\text{electron}}{e^-}$$

A reduction agent and its corresponding oxidation counterpart are commonly called a redox system.

If a platinum wire is placed in a solution containing such a redox system, the platinum wire will develop a potential which can be expressed as:

$$e = k + \frac{RT}{F} \ln \frac{a_{Ox}}{a_{Red}}$$

in which K is a temperature-dependent constant

R is a constant, the Gas Constant

T is the absolute temperature

F is the Faraday constant

a_{Ox} is the activity of the oxidation agent

a_{Red} is the activity of the reduction agent.

However, it is not possible to measure a single potential. On the other hand, potential differences can be measured by means of a millivoltmeter. In addition to the platinum wire (hereinafter called the platinum electrode), a reference electrode is consequently placed in the solution. The significance of this reference electrode when placed in the solution is the fact that it develops a potential that is not dependent on the composition of this solution.

Such reference electrodes are now commercially available from many sources. The commonest type of reference electrode for use in redox measurements is the calomel electrode.

The voltage- or potential difference existing between a platinum electrode and a reference electrode when both are immersed in a solution can now be expressed as:

$$E = K + \frac{RT}{F} \ln \frac{a_{Ox}}{a_{Red}} \qquad (4)$$

where E is the potential difference,

and K is a constant dependent on the temperature, the type of reference electrode used, and the nature of the redox system.

If the reference electrode is a standard hydrogen electrode, then K will equal the standard potential, E^{o}_{Ox-Red}, and the E-value measured will be designated E_h and called the redox potential, since the sub-index 'h' indicates that the potential is evaluated or measured against the standard hydrogen electrode:

$$E_h = E^{o}_{Ox-Red} + \frac{RT}{F} \ln \frac{a_{Ox}}{a_{Red}} . \qquad (5)$$

However, as the standard hydrogen electrode is not suitable as a reference electrode in actual practice, a calomel electrode is used instead (see above).

As the potential of the calomel electrode against the standard hydrogen electrode is +244.4 mV at 25°C, any measurement performed with the platinum electrode and the calomel electrode can be converted so as to yield the redox potential, E_h, by adding the potential of the latter:

$$E_h = E + E_{calomel} = E^o_{Ox-Red} + \frac{RT}{F} \ln \frac{a_{Ox}}{a_{Red}} \tag{6}$$

$$E_h \text{ mV} = E + 244.4 = E^o_{Ox-Red} + \frac{RT}{F} \ln \frac{a_{Ox}}{a_{Red}} \tag{7}$$

The terms included in equations 4-7 are based on the reaction defined by equation (2):

$$\text{Red} \rightleftharpoons \text{Ox} + e^- \; .$$

However, in actual practice processes frequently involve more than one electron, and quite often also hydrogen ions participate.

The equation defining the redox potential can as a rule be given as:

$$\text{Red} + qH_2O \rightleftharpoons \text{Ox} + m \cdot H^+ + n \cdot e^- \tag{8}$$

$$E_h = E^o_{Ox-Red} + \frac{RT}{n \cdot F} \ln \frac{a_{Ox} \cdot a^m_{H^+}}{a_{Red} \cdot a^q_{H_2O}}$$

Inasmuch as the activity of water in a dilute aqueous solution is constant and definable as unity, we obtain:

$$E_h = E^o_{Ox-Red} + \frac{RT}{n \cdot F} \ln \frac{a_{Ox} \cdot a^m_{H^+}}{a_{Red}} \tag{9}$$

It is seen, then, that the redox potential is dependent also on the hydrogen activity of the solution - in other words: on the pH-value.

By inserting the values for R and F, and setting ln = 2.3026·log, equation (9) can be rearranged as follows:

$$E_h \text{ (mV)} = E^o_{Ox-Red} + \frac{0.1983 \cdot T}{n} \log \frac{a_{Ox} \cdot a^m_{H^+}}{a_{Red}} \; .$$

Since $-\log a_{H^+} = \text{pH}$, we further obtain:

$$E_h \text{ (mV)} = E^o_{Ox-Red} + \frac{0.1983 \cdot T}{n} \log \frac{a_{Ox}}{a_{Red}} - \frac{0.1983 \cdot T \cdot m}{n} \text{pH} \tag{10}$$

Equation (10) is the normal equation for the redox potential when hydrogen ions are involved in the chemical reaction.

If hydrogen ions are not involved, the equation is reduced to:

$$E_h\,(\mathrm{mV}) = E^{o}_{Ox-Red} + \frac{0.1983 \cdot T}{n}\ \log \frac{a_{Ox}}{a_{Red}} \qquad (11)$$

Examples

Hydrogen ions are not involved in the reaction:

1) $Fe^{+2} \rightleftharpoons Fe^{+3} + e^{-}$
ferro ion ferri ion electron

$$E_h = E^{o}_{Fe^{+3},\ Fe^{+2}} + 0.1983 \cdot T \log \frac{a_{Fe^{+3}}}{a_{Fe^{+2}}}$$

2) $Tl^{+} \rightleftharpoons Tl^{+3} + 2e^{-}$
thallo ion thalli ion electron

$$E_h = E^{o}_{Tl^{+3},\ Tl^{+1}} + \frac{0.1983 \cdot T}{2} \quad \log \frac{a_{Tl^{+3}}}{a_{Tl^{+1}}}$$

Hydrogen ions are involved in the reaction:

1) $Mn^{+2} + 4\ H_2O \rightleftharpoons MnO_4^{-} + 8H^{+} + 5e^{-}$
mangano ion water permanganate ion hydrogen ion electron

$$E_h = E^{o}_{MnO_4^{-},\ Mn^{+2}} + \frac{0.1983 \cdot T}{5} \log \frac{a_{MnO_4^{-}}}{a_{Mn^{+2}}} - \frac{0.1983 \cdot T \cdot 8}{5}\ pH$$

2) $C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2 + 2H^{+} + 2e^{-}$
hydroquinone quinone hydrogen ion electron

$$E_h = E^{o}_{\text{quinone, hydroquinone}} + \frac{0.1983 \cdot T}{2} \log \frac{a_{\text{quinone}}}{a_{\text{hydroq.}}} - \frac{0.1983 \cdot T \cdot 2}{2}\ pH$$

$$= E^{o}_{\text{quinone, hydroquinone}} + \frac{0.1983 \cdot T}{2} \log \frac{a_{\text{quinone}}}{a_{\text{hydroq.}}} - 0.1983 \cdot T\ pH$$

Our exposition on the theoretical aspects of redox measurements is now partly concluded. The following sections will be devoted to a study of the practical problems of such measurements (electrode construction, application, potentiometric titrations), and a final section will discuss such terms as, for instance, rH and $E^{o'}$, in order to acquaint the reader with concepts occasionally referred to in the electro-chemical literature.

C. ELECTRODE CONSTRUCTIONS

As mentioned above in section B, a redox electrode need in principle consist of no more than a platinum wire. However, in actual practice it it normal to use a platinum electrode consisting of a platinum wire or platinum plate inlaid in or fused to a glass tube through which contact between the platinum body and the electrode cable is established. One advantage of this kind of electrode is that the entire platinum mass can be immersed in the solution whilst the rest of the electrode remains chemically inactive. The electrode is, moreover, rugged enough to withstand considerable mechanical shock.

Of such a design is the RADIOMETER Platinum Electrode, type P101. Its platinum body is formed as a plate.

Also gold electrodes can be used for this purpose, e.g. the RADIOMETER Gold Electrode, type P201. This electrode is excellently suited as a hydrogen electrode (see section F1).

A calomel electrode is usually employed as the reference electrode in this setup. The type normally preferred is equipped with a salt-bridge fitted with a porous pin through which the liquid junction between the electrode and the test solution is established. Such an electrode is the RADIOMETER type K401 Calomel Electrode.

A different type of calomel electrode must be recommended for very accurate redox measurements. In this model (K101), the salt-bridge is fitted with a capillary through which the liquid junction is made. In this type of electrode, the inevitable liquid junction potential existing between the electrode and the test solution will be very small and highly reproducible.

NOTE: In the theoretical exposition of section B, the reference electrode was defined as an electrode whose potential was not influenced by the test solution. However, at the interface between the salt-bridge of the electrode and the test solution a liquid junction potential will always be generated. This is due to the fact that the diffusion velocities of the negative and positive ions as a rule are different, such that a charge is created at the interface of the two solutions. An attempt has been made to reduce such a liquid junction potential by using an electrolyte in the salt-bridge of the reference electrode that is highly concentrated and contains positive and negative ions with almost identical velocity of diffusion.

For titration purposes it is possible to use a so-called combined platinum/calomel electrode, type PK149, in which the platinum electrode and the calomel electrodes are joined in one body. In addition, this type is fitted with a burette nozzle.

In the few instances where contamination of the solution by potassium chloride from the salt-bridge of the calomel electrode will corrupt measurements, a calomel electrode of the type K900 can be used instead, as its salt-bridge contains saturated ammonium nitrate. At suitable intervals, the NH_4NO_3-solution inside the salt-bridge must be renewed owing to the fact that potassium chloride from the calomel element will contaminate the salt-bridge.

A different type of reference electrode, viz. the Mercurous Sulphate Electrode, type K601, can also be used. The electrode potential of this kind of electrode against the standard hydrogen electrode is approx. +636 mV at 25°C - a fact that must be taken into account when E_h-measurements are performed. Its salt-bridge consists of a saturated potassium sulphate solution. The liquid junction potentials of this kind of electrode are substantially greater than those of the calomel electrode, and it should therefore only be used in an emergency.

Electrodes with physical dimensions different to the above mentioned types are available. To obtain full particulars, see the RADIOMETER electrode catalogues or consult the local RADIOMETER representative.

D. REDOX MEASUREMENTS IN PRACTICE

D1. The Technique of Redox Measurements

The redox potential, symbolized by E_h and defined as the potential difference existing between a platinum electrode placed in a solution and the standard hydrogen electrode, is, as previously mentioned, measured in practice by immersing a platinum electrode and a reference electrode in the solution and measuring their potential difference, E.

A millivoltmeter is used to measure value E. Since the total electrode resistance is of the order of 10 kΩ, it is necessary to use a millivoltmeter having an input resistance of minimum 10 MΩ. As a rule, however, an even greater input resistance will be required owing to the fact that the electrodes will sustain only a very low measuring current without becoming polarized. Because of this, it is normal practice to use a pH meter for the measurement as the majority of pH meters in addition to their pH measuring-range also are equipped with one or more mV-ranges.

This requirement is fulfilled by the following pH meters from RADIOMETER:

Type PHM4
- PHM22
- PHM25
- PHM26
- PHM27
- PHM28.

Moreover, the types PHM22, PHM25, and PHM27 can be supplemented with scale-expanders, and types PHM4 and PHM26 have built-in scale-expanders, so that the reproducibility on these meters is better than 0.3 mV.

Normally, a platinum electrode (P101) and a calomel electrode (K401) are used for measuring.

The electrodes can be connected to the Glass- and Calomel Electrode terminals on the pH meter. Either terminal will serve for each, but the sign of the measured potential difference will depend on the connection preferred. Connecting the platinum electrode to the Calomel Electrode terminal of the pH meter and the calomel electrode to the Glass Electrode terminal (when RADIOMETER pH meters with the exception of PHM4 are used) will ensure that the measured potential difference steadily grows as the oxidizing capacity of the test solution increases. All potential differences cited in this bulletin are based on the electrodes being connected in this manner.

The electrodes are next placed in the test solution, and a reading is made as soon as the meter pointer has settled.

The measured potential difference, E, can very often be used directly as an indication of the redox potential, provided that it be taken into account that the reference electrode used is a calomel electrode.

The E_h, when wanted, can be computed from:

$$E_h = E + E_{\text{reference electrode}} \qquad (12)$$

For the calomel electrode at 25°C:

$$E_h = E + 244.4 \text{ mV} \qquad (13)$$

D2. Special Considerations

D2.1 Influence of Temperature

It appears from equations (10) and (11) that the redox potential is reliant on temperature, and all measurements should consequently include a temperature reference. In cases where many measurements are to be compared, it will be an advantage to maintain a constant temperature during the entire operation.

D2.2 Influence of Atmospheric Air

When making redox measurements it should be borne in mind that atmospheric oxygen as a rule will influence the measurements.

In cases where measurements are to be made on solutions that beforehand have been exposed to atmospheric air, it is usually not necessary to take special measures. Nor, of course, will oxygen give cause for anxiety in highly oxidizing solutions.

However, in almost all other cases it will be necessary to take special precautions against the influence of oxygen.

The normal method for avoiding the influence of oxygen is to protect the solution by passing a protective gas - e.g. nitrogen - through or over the solution. It should be realized, however, that the protective gas employed must be absolutely free from oxygen. Commercially available nitrogen is not always oxygen-free, and it must therefore be purified before use - e.g. by leading it through an alkaline solution of pyrogallol or an alkaline solution of sodium hydrosulphite.

The purified gas can afterwards be passed through the solution whose redox potential is to be measured. In this manner, all dissolved gases are removed from the solution. However, in certain cases this is unfortunate or even wrong. If for instance, the solution contains dissolved carbon dioxide as well as a redox system whose redox potential is dependent on the pH of the solution (cf. equation (10)), the pH will change because a volatile acid (CO_2) is removed, and the redox potential will consequently also change.

Exactly what conditions are desirable for each particular measurement and how these will affect the measurement must therefore be considered in advance.

Should it not be desired to remove absorbed gases from the solution although the aim still is to protect it from atmospheric oxygen, it will be necessary to pass an inert gas over the solution and measure the redox potential at the bottom of a tall beaker that is nearly filled with the solution.

D2.3 The Course of a Redox Measurement

Quite often it will be noticed that it is impossible to obtain stable measurements. Instead, these will shift towards ever more negative values, and particularly so during redox measurements in biological fluids. The reason why a well-defined redox potential sometimes cannot be obtained is frequently that the redox system (or systems) contained in the solution only slowly exchanges electrons with the platinum electrode.

If such is the case, a rapid and accurate potential indication can be achieved by resorting to a finesse, that is: by adding a small quantity of a so-called "mediator" to the test solution.

A mediator is a redox system capable of making both rapid and simple exchange of electrons with the platinum electrode. In order that such a mediator can function satisfactorily, the activity (concentration) occurring in its oxidized form should be equal to that occurring in its reduced form.

Many ideally suited mediators can be found from among redox systems in which hydrogen ions participate in the reaction.

From equation (10) we obtain:

$$E_h = E^o_{Ox\text{-}Red} - \frac{0.1983 \cdot T}{n} \log \frac{a_{Ox}}{a_{Red}} - \frac{0.1983 \cdot T \cdot m}{n} \text{ pH}$$

A requirement for $a_{Ox} \simeq a_{Red}$ is that

$$E_h = E^o_{Ox,\text{-}Red} - \frac{0.1983 \cdot T \cdot m}{n} \text{ pH} = E^{o\prime}$$

The quantity $E^{o\prime}$ will be considered in detail in section 1.

As a simple rule for the mediator employed it may be stipulated that the measured redox potential, E_h, shall fall within the range $E^{o\prime} \pm 100$ mV.

In table 1 is listed a number of suitable mediators. Fig. 1 gives the $E^{o'}$ for varying values of pH.

Slowly indicating redox measurements are then handled in the following manner:

First a measurement is attempted without the use of a mediator, so that a rough estimate can be made of the expected redox potential. From a knowledge of the pH of the solution, an appropriate mediator, whose $E^{o'}$ -value at the said pH lies close to the estimated redox potential, is next selected by means of Fig. 1. If the subsequent measurement then yields a redox potential that deviates by more than 100 mV from the $E^{o'}$ of the mediator at the relevant pH-value, the measurement must be repeated with a second mediator that lies nearer to the measured redox potential.

The volume of mediator added must be small in comparison with the volume of redox system present in the test solution. If this is not the case, the admixture of mediator may cause the redox potential of the solution to become displaced.

Excellent results are often obtained with a mediator volume of a few drops of an 0.05% solution to 100 ml test solution.
As a means of deciding whether or not the addition of a mediator has changed the redox potential, it is possible - after completing the first addition and measurement - to add a little more of the mediator and then observe whether doing so changes the redox potential.

D2.4 Use of Redox Buffer Solutions

As a rule the redox potential is measured directly without a special calibration being made of the measuring system. If special circumstances seem to indicate that the measuring system should be controlled, this can be accomplished by immersing the electrodes in a solution whose redox potential is known. Such a solution is called a redox buffer solution.

Ideal for this purpose is a quinhydrone solution. It is prepared by adding quinhydrone crystals to a suitable acid-base buffer solution until a state of saturation is reached.

The redox potential, E_h, of this solution is dependent only on the solution pH and temperature.

Thus, at 25°C:

$$E_h = +699 - 59.2 \cdot \text{pH} \ \text{mV} \qquad (14)$$

As the solution can be used for all pH-values between 0 and 9, the redox range +699 to + 166 mV is adequately covered.

D2.5 Maintenance of the Platinum Electrode

Platinum electrodes intended for redox measurements must always be carefully cleaned before use. Frequently a thorough rinsing in clean water will suffice, but in many cases such a treatment is not enough.

One commonly used method is to rinse the electrode in concentrated sulphuric acid and afterwards place it for 10-20 minutes in an approx. 50°C warm 3% solution of potassium dichromate in 10% sulphuric acid. Finally, the electrode is swilled in clean water and left standing in the water for several hours. A subsequent conditioning (for a few hours) in a 10% solution of ascorbic acid in 0.1 normal hydrochloric acid will quite often further improve the electrode.

If the platinum electrode is very badly contaminated, it may be necessary to clean it with scouring powder or with a fine-grained emery cloth.

E. APPLICATIONS

The practical uses of redox measurements are manifold. However, in this bulletin only a few illustrative examples will be given to show how versatile the method is.

E1. Application in Biochemistry

It is a well-known fact that nutritious matter is metabolized in living cells. This metabolism, occurring at the temperature of the organism, is brought about by hydrogen being separated from the nutritious matter by means of enzymes (dehydrogenases). The hydrogen does not combine directly with the oxygen to form water, but passes through a series of redox systems. In a direction from the nutritious matter and towards the free oxygen, each of these redox systems will reduce the next one in the chain, and the last redox system will reduce the free oxygen.

In making a study of this mechanism it has, of course, been necessary to measure the redox potentials of the individual redox systems in order to understand the process.

Besides, any abnormality in such a mechanism will often be detectable as a blocking of one of the redox systems. Hence the reason for redox measurements always being closely associated with such studies.

E2. The influence of the Redox Potential on the Activity of Enzymes

In his doctor's thesis (ref. 2), professor Holger Jørgensen has given a practical example proving to what degree the activity of an enzyme is dependent on the redox potential.

It is shown here that the baking strength of wheat is improved by admixing small amounts of potassium bromate. The wheat flour contains an enzyme which breaks down the gluten so that it cannot bind the carbon dioxide developed in the dough to the same extent as it would if it remained intact. By utilizing potassium bromate to increase the redox potential, the activity of the enzyme is impeded so that bigger loaves are formed.

Beyond doubt, practical life could furnish many similar examples of the usefulness of this method.

E3. Anaerobic and Aerobic Organisms

The growth of micro-organisms is highly dependent on the redox level of the medium in which they exist. Thus, anaerobic micro-organisms require a low redox potential where they are found, whilst aerobic micro-organisms require a high redox potential.

An example of the practical value of such phenomena can be drawn from the cheese-making industry. The occurrence of butyric acid bacteria in cheese manufacture is hazardous as butyric fermentation may take place so that gases are developed, causing bubbles to be formed inside the cheese. However, as butyric acid bacteria are anaerobic, their activity can be arrested by increasing the redox potential in cheeses - e.g. by adding potassium bromate.

Another example is yeast-cells. If these are allowed to work in a sugar solution without the admission of oxygen (low redox potential), alcohol will be produced. On the other hand, if oxygen is admitted during their action (high redox potential), most of the culture medium will be consumed, carbon dioxide and water almost exclusively being formed, and the yeast-cells will multiply rapidly.

E4. Other Applications

The redox potential in soil is a factor of importance for the growth of many plants. However, as a rule redox potential and pH may be considered equally useful indicators of the quality of the soil.

It should also be mentioned that redox measurements in beer, wine and butter may play an important rôle in disclosing or preventing the occurrence of offensive flavours.

The textile industry, too, is showing a keen interest in redox measurements with respect to textile dyeing.

Many dye-stuffs are added in their reduced state (frequently as colourless compounds), and they are then oxidized so as to provide the desired colour.

F. SPECIAL APPLICATIONS

F.1 The Hydrogen Electrode

If a platinum electrode - or better still, a platinized gold electrode - is placed together with a reference electrode in a solution through which hydrogen is passed, a redox potential, E_h, will be measurable in accordance with the reaction:

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

$$E_h = K + \frac{0.1983 \cdot T}{2} \log \frac{a^2_{H^+}}{a_{H_2}}$$

Since a_{H_2}, the activity of hydrogen in the solution, according to Henry's law is proportional to the hydrogen tension, the equation can be rearranged as:

$$E_h = K + \frac{0.1983 \cdot T}{2} \log \frac{a^2_{H^+}}{k \cdot P_{H_2}}$$

Finally, $pH = -\log a_{H+}$ can be inserted, and all constants can be included in K - thus:

$$E_h = K' - \frac{0.1983 \cdot T}{2} \log P_{H_2} - 0.1983 \cdot T \cdot pH$$

According to definition, $K' = O$, so:

$$E_h = - \frac{0.1983 \cdot T}{2} \log P_{H_2} - 0.1983 \cdot T \cdot pH$$

which, then, is the equation expressing the redox potential of the hydrogen electrode.

For $P_{H_2} = 1$ atm. and pH = O, we have $E_h = 0$.

A platinum electrode (platinized gold electrode) that is placed in a solution through which hydrogen is bubbled is called a hydrogen electrode, and under the above standardized conditions: a standard hydrogen electrode.

The fact that the redox potential in the above computation equals 0 is natural considering that E_h originally was given as the potential relative to the standard hydrogen electrode.

As will be seen from the equation

$$E_h = \frac{-0.1983 \cdot T}{2} \log P_{H_2} - 0.1983 \cdot T \cdot pH$$

the hydrogen electrode can be used for pH measurements, as it also has been, since all basic investigations - e.g. determination of the pH values of acid-base buffer solutions - have been made with this electrode.

However, the electrode is not practical to use, one reason being that hydrogen must be bubbled through the solution, another that the solution must not contain redox systems that are able to take part in the electrode reactions. Consequently, the hydrogen electrode is now used only for purely scientific purposes. In practice, the pH glass electrode has replaced it.

NOTE: Some readers may find a description of the hydrogen electrode at this point in the survey somewhat out-of-place, deeming that it merited coverage at a much earlier stage in this bulletin. The reason for relegating it to a later section is, however, that very few readers are likely to require the electrode for any purpose and, consequently, need not be bothered with an account of it in the main sections.

F2. The Quinhydrone Electrode

Quinhydrone has been mentioned on several occasions in the previous sections, e.g. as a suitable redox buffer. This section will therefore be devoted to an examination of its theory.

The substance quinhydrone consists of equal parts of hydroquinone and quinone. Hydroquinone is the reduction counterpart of the oxidation agent quinone.

Since:

$$\text{Hydroquinone} \rightleftharpoons \text{quinone} + 2H^{+} + 2e^{-},$$

the redox potential in a solution containing quinhydrone can be written:

$$E_h = E^{o}_{\text{quinone, hydroquinone}} + \frac{0.1983 \cdot T}{2} \log \frac{a_{\text{quinone}}}{a_{\text{hydroq.}}} - 0.1983 \cdot T \cdot \text{pH}.$$

Inasmuch as the concentrations of quinone and hydroquinone are equal, their activities can also by approximation be considered equal. Hence:

$$E_h = E^{o}_{\text{quinone, hydroquinone}} - 0.1983 \cdot T \cdot \text{pH}$$

$$E_h = 699 - 59.2 \cdot \text{pH mV at } 25^{o}\text{C}.$$

It is seen, then, that a quinhydrone electrode, conceived as a platinum electrode immersed in a solution containing quinhydrone, can be used for pH measurements. This was also the case once, but it is seldom used now as the pH glass electrode in practice is better suited. The quinhydrone electrode can be used only in the pH range 0 - 9, as reactions other than the above mentioned will occur at pH values above 9, due to the fact that hydroquinone is a dibasic acid. Moreover, the solution to which the quinhydrone is added must not contain substances that are capable of reacting with either hydroquinone or quinone.

G. POTENTIOMETRIC TITRATIONS

G1. Theory

Perhaps the widest use of redox measurements lies within the field of potentiometric titrations. Its usefulness is based upon the fact that many substances, whose quantity the analyst is desirous of determining, can react with a second substance that is capable of oxidizing, respectively reducing, the former, whilst it itself becomes reduced, respectively oxidized.

The reactions taking place can be explained according to:

$$\mathrm{Red}_1 \rightleftharpoons \mathrm{Ox}_1 + e$$

$$\mathrm{Ox}_2 + e \rightleftharpoons \mathrm{Red}_2$$

Assume that the substance Red_1 is to be quantitatively determined. The substance Red_1 is then added to a solution, the potential of which now can be written as:

$$E_h = E^o_{\mathrm{Ox}_1-\mathrm{Red}_1} + 0.1983 \cdot T \log \frac{a_{\mathrm{Ox}_1}}{a_{\mathrm{Red}_1}} \qquad (15)$$

If only very small amounts of Ox_1 are present - which normally is the case at the commencement of a titration - then $a_{\mathrm{Ox}_1}/a_{\mathrm{Red}_1}$ will be very small and E_h therefore be low. If a suitable oxidation agent, Ox_2, of a known volume now is added, the following reaction will take place:

$$\mathrm{Red}_1 + \mathrm{Ox}_2 \rightleftharpoons \mathrm{Ox}_1 + \mathrm{Red}_2$$

By this, Ox_1 and Red_2 are formed. Provided that the oxidation agent Ox_2 has a sufficiently strong oxidizing capacity - high redox potential - the reaction will in practice only be a one-way movement to the extreme right. When enough Ox_2 has been added to oxidize all the Red_1 into Ox_1, the titration will be terminated, and the amount of Ox_2 used is then a measure of the quantity of Red_1.

A sequence study of the redox potential during titration is best made by slightly altering equation (15) through introducing a quantity $F = \frac{a_{\mathrm{Ox}}}{a_{\mathrm{Ox}} + a_{\mathrm{Red}}}$, which can be called the 'degree of oxidation':

$$E_h = E^o_{\mathrm{Ox}_1-\mathrm{Red}_1} + 59.2 \log \frac{F}{1-F} \text{ at } 25^\circ\mathrm{C}$$

If E_h is marked out as the abscissa on a diagram, and F is marked out as the ordinate, a curve as seen in Fig. 2 will be obtained.

It is seen from the diagram that for small values of F (in actual practice only Red_1 occurs), low values of E_h are had.

When half of Red_1 is oxidized, $F = 1/2$ and $E_h = E^o_{\mathrm{Ox}_1-\mathrm{Red}_1}$.

When 91% of Red_1 is oxidized, F = 0.91 and $E_h = E^o + 59.2$.

When 99% of Red_1 is oxidized, $F = \sim 0.99$ and $E_h = E^o + 2 \cdot 59.2$.

When 99.9% of Red_1 is oxidized, $F = \sim 0.999$ and $E_h = E^o + 3 \cdot 59.2$.

This shows that if only the Ox_2 added is capable of changing the redox potential to $E_h = E^o + 3 \cdot 59.2$, then the titration will be achieved with an error of only 0.1%.

An oxidizing substance can in like manner be titrated with a reducing solution.

If the electrode reaction involves more than one electron, the above values will differ, inasmuch as the factor 59.2 must be divided by the number of electrons involved in the reaction.

As a simple rule it may be assumed that in order to perform a titration with a theoretical error of less than 0.1%, a titrant must be used, whose E^o is at least 350 mV removed from the E^o of the substance examined.

It should be noted that it is $E^{o'} = E^o - \frac{0.1983 \cdot T \cdot m}{n}$ pH and not the E^o -value of the test solution which is to be compared with the E^o-value of the titrant in redox systems involving hydrogen ions.

The pH-value of the solution must consequently be known.

The majority of redox titrations are carried out in strongly buffered solutions, so that pH normally can be set down as constant during the titration.

If the titration is performed by recording correlated values of measured E and volume of titrant added, a curve - the titration curve - as seen in Fig.3 will be produced. Usually the equivalence point is established as the point of inflection on this curve.

This point (also called the end-point) can be computed theoretically, but as a rule it is determined through practical experiments.

G2. MANUAL TITRATIONS

In order to perform a manual titration, it is necessary to employ a pH meter from the series PHM22, PHM25, PHM26, PHM27 and PHM28. Also required is a titration assembly of the type TTA1.

The first step is to plot a titration curve by recording correlated values of measured E and ml titrant added. The end-point is then found as the point of inflection on this curve.

Note: When making titrations, it is not necessary to convert the measured E-values into E_h-values as long as the same type of reference electrode is used for all the titrations.

Subsequent titrations are simply discontinued when this point is reached, and the corresponding titrant consumptions is then measured.

Assuming that 'a' grams of test solution have been used in the titration, that 't' is the normality of the titrant, that 'b' ml is the volume of titrant added, and that 'n' is the number of electrons involved in the reaction, then the content 'x' of titrated substance of mol weight 'M' expressed in percentage by weight is found from:

$$x\ (\%) = \frac{M}{10 \cdot n} \cdot \frac{b \cdot t}{a}$$

The normality of the titrant is determined by performing a titration in which is used a known quantity of the substance which afterwards is to be titrated.

G3. AUTOMATIC TITRATIONS

In order to perform an automatic titration, it is necessary to use an automatic titrator - e.g. type TTT1 or type TTT11 in conjunction with a type PHM25, PHM26, 27, or 28.

As titration assembly, either type TTA1 with a Magnetic Valve, type MNV1, and a normal flow burette, or type ABU1 with digital read-out of the titrant consumption + TTA3 (or TTA31) is used.

The titration is carried out by first plotting a titration curve as described in section G2 and then automatically titrating to the end-point thus determined.

The most important titrator settings are:

End-point:	determined experimentally	
Proportional band:	usually: 2-5	
Delay of shut-off:	5 sec.	
Direction of titration:	titrant is oxidizing:	upscale
	titrant is reducing:	downscale

(platinum electrode: calomel electrode terminal)
(calomel electrode: glass electrode terminal)

G4. AUTOMATIC RECORDING OF TITRATION CURVES

For this purpose is used a titrigraph assembly of the type SBR2 together with an automatic titrator (TTT1 or PHM25, PHM26, 27, 28 + TTT11), a burette type SBU1 or type ABU1, and a titration assembly TTA3 or TTA31.

The equivalence point is found as the point of inflection on the titration curve recorded.

The most important settings are:

Titrator:	Proportional band:	0.1	
	Delay of shut-off:	∞	
	Direction of titration:	titrant is oxidizing:	upscale
		titrant is reducing:	downscale
Titrigraph, type SBR2:	Chart calibration:	titrant is oxidizing:	+10, 20 or 50 mV
		titrant is reducing:	-10, 20 or 50 mV

The volume of test solution used should be so chosen that as much of the paper width as possible is expended when titrating up to the point of inflection. An automatic recording of the titration is in all probability the most accurate form of titration in current use.

It should be remembered that an automatic recording of the titration curve may, when desired, simply be performed to determine the end-point, and subsequent titrations can then be accomplished by titrating to the end-point thus established, as explained in section G3.

G5. REDOX TITRATIONS

It falls beyond the scope of this bulletin to give an exhaustive account of all possible types of redox titrations. For complete information, the reader is referred to the subject literature, amongst which these deserve special mention:

1) J.J. Lingane: Electroanalytical Chemistry, section VII (ref. 3), and
2) Kolthoff & Furman: Potentiometric Titrations (ref.4), which brings accounts of many types of redox titrations.

Finally, it should be mentioned that 'Titrimetric Methods' (ref.5) especially emphasizes "Combined Potentiometric Determinations of Manganese, Chromium, and Vanadium in Steels".

If the reader wants to rely on his own judgment as to whether a special method of titration is liable to work, he will find W.M. Latimer's 'Oxidation Potentials', (ref.6), an invaluable aid in making his calculations.

H. THE rH CONCEPT

An account of the hydrogen electrode was given in section F1. It was shown there that the redox potential of a hydrogen electrode can be written:

$$E_h = \frac{-0.1983 \cdot T}{2} \log P_{H_2} - 0.1983 \cdot T \cdot pH \qquad (16)$$

where P_{H_2} is the hydrogen tension in the solution. As a rule a platinum electrode is called a hydrogen electrode only when hydrogen is led directly into the test solution and when the process $H_2 \rightleftharpoons 2H$ is able to take place, as the electrode has a very large platinum surface which is capable of catalyzing this process.

However, by rights any platinum electrode placed in an aqueous solution could be called a hydrogen electrode, and all aqueous solutions could be claimed to exhibit a certain hydrogen tension, although the process $H_2 \rightleftharpoons 2H$ will not equilibrate owing to the absence of a catalyzer.

Now, according to convention the negative logarithm of the hydrogen tension is designated rH:

$$rH = -\log P_{H_2}$$

By inserting this in equation (16), we obtain:

$$E_h = \frac{0.1983 \cdot T}{2} rH - 0.1983 \cdot T \cdot pH, \text{ or}$$

$$E_h = 0.1983 \cdot T \left(\frac{rH}{2} - pH\right) \qquad (17)$$

It is seen from equation (17) that rH serves only as an expression for the redox condition in the solution at constant pH.

The nature of many redox systems is such that their E_h changes with changing pH, but quite often rH will remain constant. In such cases, it will often be better to make an rH-measurement as rH expresses the composition of the redox system irrespective of the prevailing pH.

rH can always be computed by means of equation (17) from a measured E_h-value and the pH of the solution. It can, however, also be measured directly by immersing a glass electrode and a platinum electrode in the solution and connecting their cables to a pH meter.

The potential of a glass electrode can be written thus:

$$E_{glass} = K - 0.1983 \cdot T \cdot pH \qquad (18)$$

The measured potential difference between the platinum electrode and the glass electrode, E, can then be expressed as:

$$E = E_h - E_{glass} = 0.1983 \cdot T \left(\frac{rH}{2} - pH\right) - K + 0.1983 \cdot T \cdot pH$$

or

$$E = \frac{0.1983 \cdot T}{2} \cdot rH - K.$$

K is determined by immersing the electrodes in a redox buffer solution of known rH-value.

I. $E^{o'}$ - POTENTIAL (the potential of E^o at which a_{Ox} equals a_{Red})

The normal equation for the redox potential of a redox system in which hydrogen ions participate in the electrode reaction is as cited in equation (10):

$$E_h\ (mV) = E^o_{Ox-Red} + \frac{0.1983 \cdot T}{n} \log \frac{a_{Ox}}{a_{Red}} - \frac{0.1983 \cdot T \cdot m}{n}\ pH$$

in which 'm' is the number of hydrogen ions and 'n' is the number of electrons involved in the reaction.

It is seen that at constant pH also $E^o_{Ox-Red} - \frac{0.1983 \cdot T \cdot m}{n}$ pH is constant

This constant is usually denoted $E^{o'}_{Ox-Red}$. $E^{o'}$ equals E_h when a_{Ox} equals a_{Red}.

$$E^{o'}_{Ox-Red} = E^{o}_{Ox-Red} - \frac{0.1983 \cdot T \cdot m}{n} \, pH \qquad (19)$$

The literature frequently states $E^{o'}$-values at pH=7 for biological redox systems in preference to quoting E^{o}-values.

As shown in Fig.1, $E^{o'}$ - pH diagrams can be of use to the analyst, as it is simple by means of such diagrams to establish the redox potential at a given pH of a solution containing equal amounts of Ox. and Red.

APPENDIX

The following constants (with reference to source) have been used in this bulletin:

1. Gas Constant: $R = 8.3143$ joule/$^\circ$C · mol (ref. 7)
2. Faraday Constant: $F = 96487$ coulomb/equiv. (ref. 7)
3. Absolute Temperature: $T = t^\circ C + 273.15$ (ref. 7)
4. $\frac{RT}{F} \ln x = \frac{RT \ln 10}{F} \log x = \frac{RT \cdot 2.3026}{F} \log x$
5. $\frac{RT}{F} \ln x = 59.2 \log x$ mV at 25°C
6. Potential of saturated calomel electrode against standard hydrogen electrode:

   $E_{calomel} = 244.4$ mV at 25°C (ref. 8)
7. Potential of saturated mercurous sulphate electrode against standard hydrogen electrode:

   $E_{mercurous\ sulphate} = 636$ mV at 25°C
8. $E^{o'}$ for mediators (cf. table I) (ref. 1)
9. Standard potential of quinhydrone electrode:

   $E^o = 699$ mV at 25°C (ref. 9)

REFERENCES

Ref. 1 H. Jørgensen: Redox-målinger, J. Gjellerup, Copenhagen, 1945.

Ref. 2 H. Jørgensen: Studier over bromatvirkningens natur, J. Gjellerup, Copenhagen, 1941.

Ref. 3 J.J. Lingane: Electroanalytical Chemistry, Interscience Publishers, Inc., New York, 1953.

Ref. 4 Kolthoff & Furman: Potentiometric Titrations, John Wiley & Sons, New York.

Ref. 5 Titrimetric Methods, the Chemical Institute of Canada, Plenum Press, New York, 1961.

Ref. 6 W.M. Latimer: Oxidation Potentials, Prentice Hall, Inc., New York, 1953.

Ref. 7 R.G. Bates: Determination of pH, Theory and Practice, John Wiley & Sons, Inc., New York, 1964.

Ref. 8 D.J.G. Ives and G.J. Janz: Reference Electrodes, Theory and Practice, Academic Press, New York, 1961.

Ref. 9 Handbook of Chemistry and Physics, 44th ed., Chemical Rubber Publishing Co., Cleveland, 1963.

Additional Literature:

L. Michaelis: Oxydations - Reductions - Potentiale, J. Springer, Berlin, 1929.

A. Berka, J. Vulterin, and J. Zyka: Massanalytische oxydations-und Reduktionsmethoden, Akademische Verlagsgesellschaft, Geest & Portig K.-G. Leipzig, 1964.

TABLE 1		
No. (Fig. 1)	Mediator	$E^{0'}$ mV at pH 7
1	Quinhydrone	+ 275
2	2.6-dichlorophenol-indophenol	+ 217
3	1-naphthol-2-sulphonate-indophenol	+ 124
4	Lauth's violet (thionine)	+ 62
5	Methylene blue	+ 10
6	Indigo tetra sulphonate	- 46
7	Indigo carmine (indigo disulphonate)	- 124
8	Brilliant alizarin blue	- 173
9	Safranine T	- 285
10	Neutral Red	- 325

Fig. 1

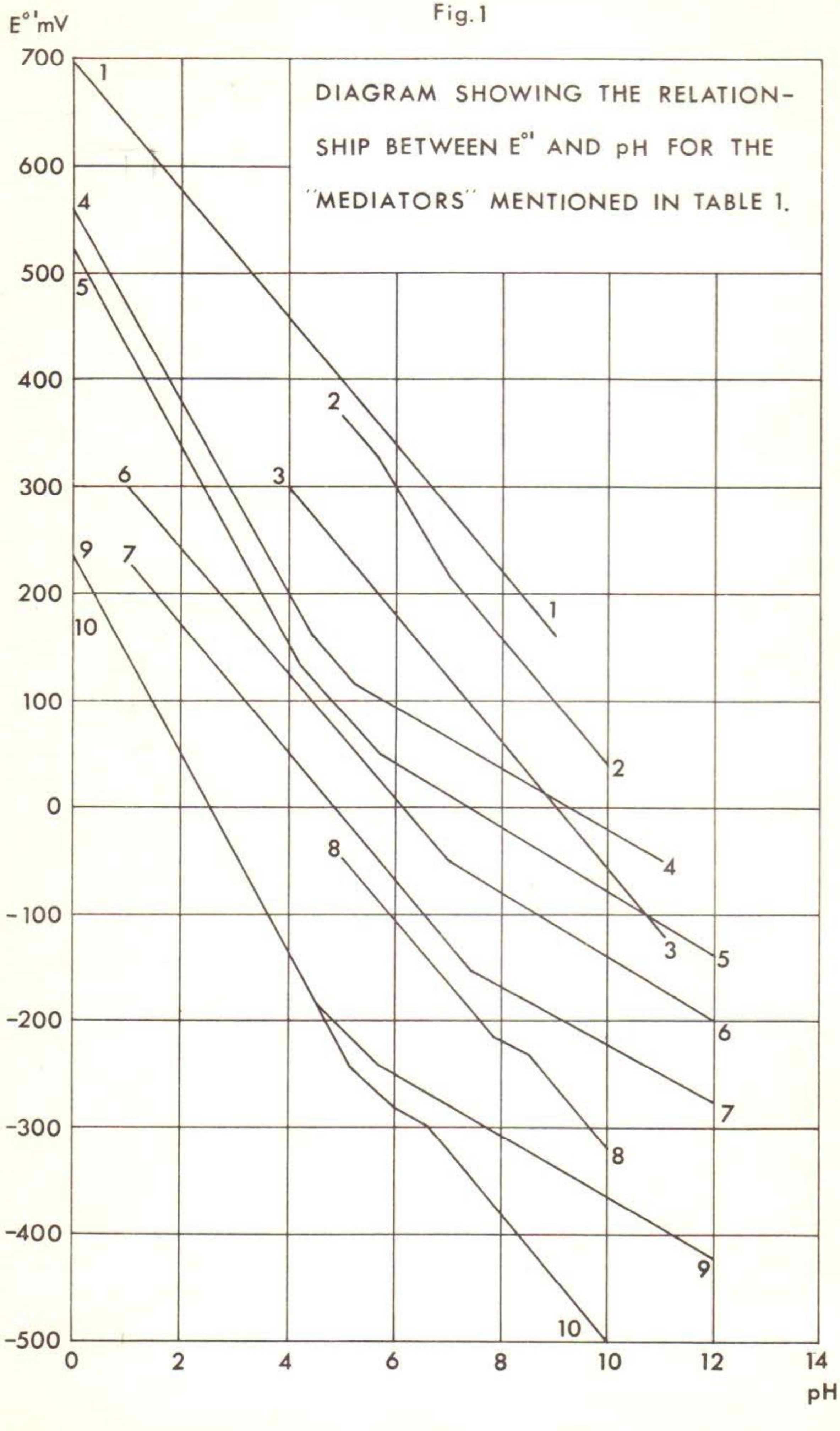


DIAGRAM SHOWING THE RELATIONSHIP BETWEEN $E^{o\prime}$ AND pH FOR THE "MEDIATORS" MENTIONED IN TABLE 1.

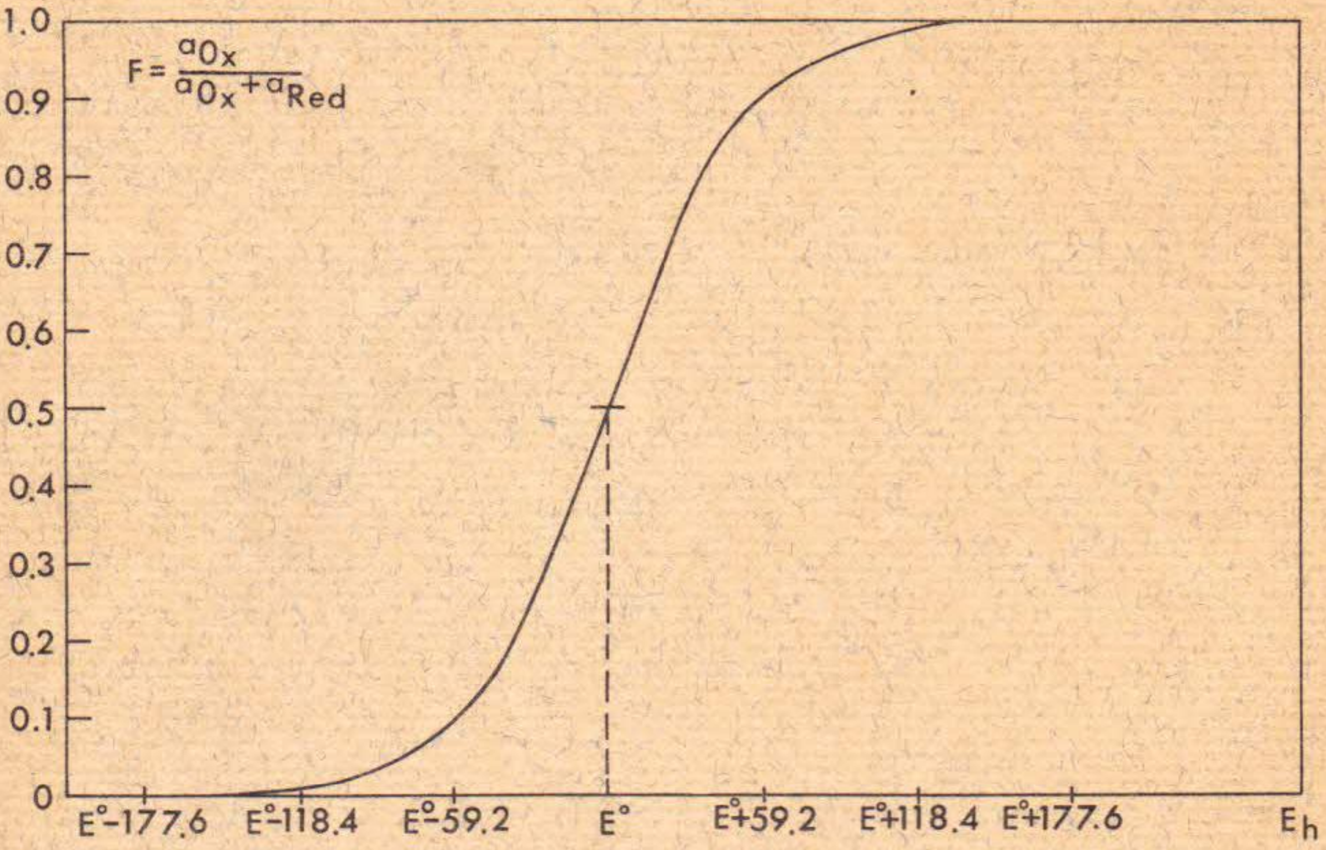


Fig. 2

DIAGRAM SHOWING THE RELATIONSHIP BETWEEN THE DEGREE OF OXIDATION F, AND THE REDOX-POTENTIAL, E_h.

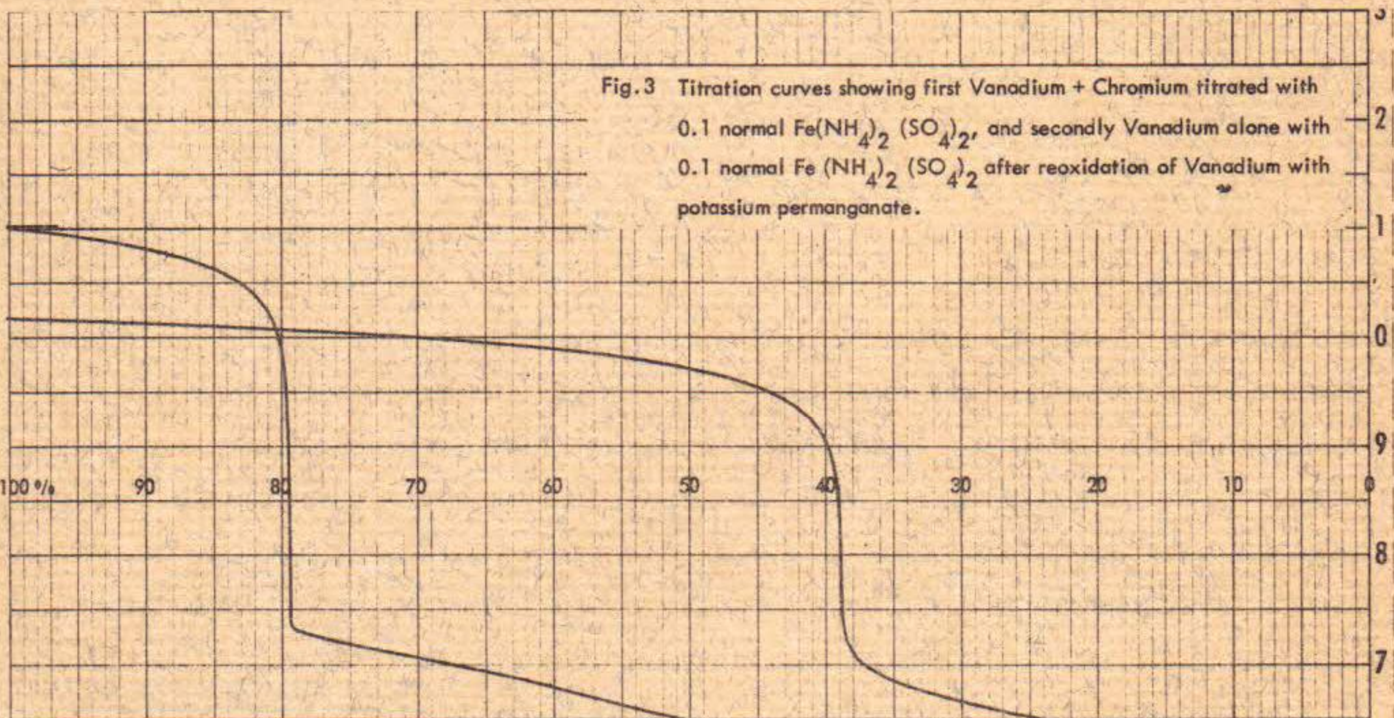


Fig. 3 Titration curves showing first Vanadium + Chromium titrated with 0.1 normal $Fe(NH_4)_2(SO_4)_2$, and secondly Vanadium alone with 0.1 normal $Fe(NH_4)_2(SO_4)_2$ after reoxidation of Vanadium with potassium permanganate.

r_{H_2} (rH) - vrednost CLARK 1926.

$$\underbrace{2H^+ + 2e}_{Ox} \rightleftharpoons 2H \rightleftharpoons \underset{Red}{H_2}$$ na Pt · elektrodi

$$E_H = \underset{0}{\cancel{E_0}} + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Red}} = \frac{0{,}06}{2} \log \frac{[H^+]^2}{p_{H_2}}$$

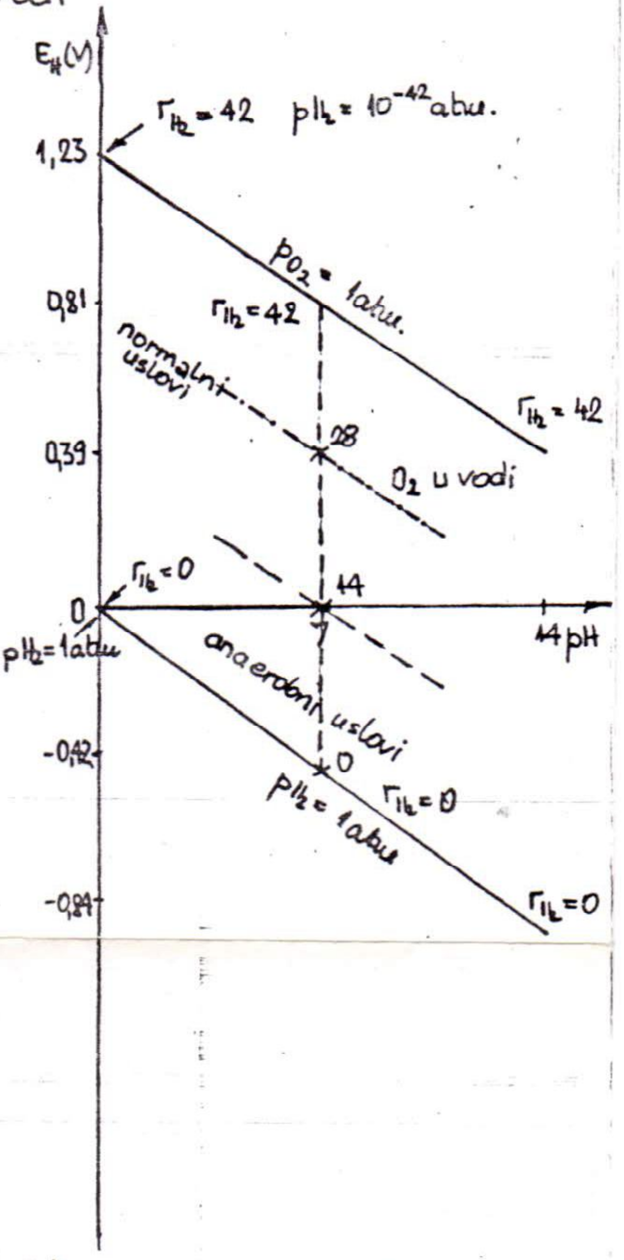
$$E_H = 0{,}03 \log [H^+]^2 - 0{,}03 \log p_{H_2} \quad /: 0{,}03$$

$$\frac{E_H}{0{,}03} = 2 \log [H^+] - \log p_{H_2} \quad /(-1)$$

$$-\log p_{H_2} = \frac{E_H}{0{,}03} - 2 \log [H^+]$$

$$r_{H_2} = \frac{E_H}{0{,}03} + 2pH \qquad r_{H_2} = \frac{EMS + \overset{E_{ZKE}}{250}}{29} + 2pH$$

(ako se meri Pt-ZKE)



r_{H_2} povezuje redox - potencijal i pH

$r_{H_2 \, min.} = 0$ $\qquad$ $r_{H_2 \, max.} = 42$

(pH_2 = 1atm.) $\qquad$ ($pH_2 = 10^{-42}$ atm.)

r_{H_2} vina : $EMS_{Pt^+/ZKE^-} = 100\,mV$ $\quad E_H^1 = 350\,mV$

$pH = 3{,}50 \qquad r_{H_2} = \frac{350}{30} + 2 \cdot 3{,}50 = 18{,}7$

Pri merenju $\Delta EMS \sim \pm 2mV$

U mereno vino ne sme da uđe vazduh!

Dobra vina imaju $r_{H_2} \sim 15$ (13,5 - 18,0)

- STANDARDNI REDOX - PUFER (Michaelis - Baylet) na 20°C $E_H = 406\,mV$ $r_{H_2} = 28$

$K_3[Fe(CN)_6]$	0,329 g
$K_4[Fe(CN)_6] \cdot 3H_2O$	0,422 g
KCl	0,149 g
H_2O destilovana	1000 cm^3

VAZDUH NE SMETA!

Po predavanjima prof.
Vilima Vajganda iz predmeta
„Instrumentalna analiticka
hemija"