Pourbaix, M. (1966): Atlas of Electrochemical Equilibria in Aqueous Solutions. – 644 p.; Oxford (Pergamon).

# FOREWORD

THE introduction into electrochemistry of potential–pH diagrams in the form originated by Pourbaix marks a new era in the study of electrochemical reactions occurring in an aqueous medium near an electrode. By means of them it is possible to predict, on a thermodynamic basis, for a given element, the equilibrium states of all the possible reactions between this element, its ions and its solid and gaseous compounds in the presence of water. Of course, application of the data contained in these diagrams is limited by the reactions which have been considered in establishing them as well as by the values assumed for the standard chemical potentials of the substances taking part in these reactions; in certain cases, for solid compounds, these chemical potentials may vary with the perfection of the crystalline state. Moreover, the diagrams are based on the activities of ions, and not on their real concentrations. However, even with these restrictions, it is evident that in a good many cases the diagrams provide data which lead to important conclusions concerning the possible reactions; these conclusions are particularly important in the study of corrosion in aqueous media.

It is only through the indomitable energy and perseverance of Pourbaix and his collaborators that this Treatise, the *Atlas of Electrochemical Equilibria*, comprising data for 90 elements, could have been produced.

Those who are acquainted with the history of these diagrams know that it goes back to Pourbaix's "doctorate thesis", presented at the Technical University of Delft in 1945 with the encouragement of my late colleague, F. E. C. Scheffer. However, this thesis was only a modest beginning compared with the "complete" *Atlas*. I sincerely hope that this *Atlas* will find a welcome appropriate to the enormous amount of work that has been necessary to produce it.

W. G. BURGERS

# PREFACE

### R. PIONTELLI

THE publication of the *Atlas of Electrochemical Equilibria* is a most rewarding culmination of all the efforts of Dr. M. Pourbaix since the appearance in 1945 of his doctorate thesis, which was presented in Delft with the encouragement of the late Professor F. E. C. Scheffer and of Professor W. G. Burgers, and which was translated into English in 1949 by J. N. Agar at the invitation of Dr. U. R. Evans.

Dr. Pourbaix, President-in-Charge of CITCE, has for many years been the driving-force of this organization, within which the activity of the "Potential–pH Diagrams" commission has been most intense and productive, counting also on the enlightened collaboration of its members, in particular Prof. Charlot, Prof. Delahay, Dr. Garrels, Dr. Hoar, Prof. Valensi and Prof. Van Rysselberghe.

Through the efforts of Dr. Pourbaix and his collaborators at CEBELCOR, and with the generous support of the Union Minière du Haut Katanga, the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et dans l'Agriculture (IRSIA), and CEBELCOR's Commission des Études Fondamentales et Applications CEFA, the gathering of data has made continual progress in volume and precision, thus enabling this *Atlas* to be produced.

Collected here in a condensed, logical and standardized form are the data which characterize the equilibrium conditions at 25°C of a very considerable number of processes. These processes involve water, hydrogen peroxide and 90 elements of the periodic system and are in direct relationship with the electrochemistry of aqueous solutions, both theoretical and applied: the extraction of metals, their finishing, corrosion and protection, analytical chemistry and other fields such as geology, whose connection with electrochemistry is not often very apparent.

Potential–pH equilibrium diagrams were originated for the theoretical prediction of oxidation-reduction catalysts (according to a method devised by Michaelis) and of the conditions under which oxidation and reduction reactions are possible or impossible in the presence of aqueous solutions (in a manner related to the experimental work of Travers and Thiesse). The method and technique used in establishing them are the same as those used previously by their originator in work on the prediction of catalysts in gas reactions; thus these potential–pH equilibrium diagrams result from the extrapolation to electrochemical systems involving an aqueous solution of work carried out on chemical systems involving a gaseous phase. Each of these two groups of work is based on the formulation of the equilibria of *all* the reactions possible in a given system as a function of *two* independent variables (the other possible variables being considered to be parameters). These two independent variables are chosen in such a way that the equilibrium formulae are linear (or practically linear): they are the logarithm of the oxygen partial pressure $\log p_{O_2}$ and the reciprocal of the absolute temperature $1/T$ in the case of chemical systems involving a gaseous phase, and the equilibrium electrode potential and the pH of the solution in the case of electrochemical systems involving an aqueous solution. By this method the equilibrium conditions of all the reactions possible in a given system are represented on a plane diagram by families of straight lines. An investigator who constructs such diagrams must have a certain appreciation both of science and art: the science is necessary in plotting the lines (i.e. above all in knowing the relevant thermodynamic data) and the art in using the lines to create pictures which are as simple and useful as possible, and which can, as U. R. Evans wrote in his Preface to the English translation of the Delft thesis, "diagrams embodying a vast amount of pertinent information in a small space".

The diagrams, which were originated for catalysis studies, have rapidly evolved towards problems of the electrochemistry of metals, and corrosion in particular. The productiveness of the method caused them to be applied to all the elements—metals and non-metals, and its applications have developed greatly, spreading to other branches of electrochemistry and related fields.

For each of the elements in turn, it is a question of characterizing the equilibrium conditions (both where there is a possibility of exchanging electrical work with the exterior and where there is not) for systems whose constituent species are: the element in question and its ions in aqueous solution, water and its constituents ($H^+$ and $OH^-$ ions, gaseous hydrogen and oxygen) and the products of the reactions of the element with these species (oxides and hydroxides, hydrides, etc.).

Corresponding to each reaction which is chemically possible there is a "free enthalpy of reaction" (referred by differentiation to unit variation in the degree of advancement of the reaction), whose value and sign determine the tendency of the system to react and the direction of the reaction. Under fixed physical conditions this free enthalpy of reaction can be expressed as the sum of a standard free enthalpy (which is constant for fixed physical conditions characteristic of a standard reference state) and a linear combination of logarithms of the activities of the substances taking part in the reaction. When the reaction is accompanied by the circulation of an electric current in a galvanic cell, the free enthalpy of reaction per unit electric charge gives us the value of the equilibrium potential difference at the terminals of the cell (or electromotive force) which corresponds to a state of equilibrium of the reaction considered.

An external source of electric current, such as that causing the circulation of "stray" currents in the ground, or the current supply of an electrolysis bath, can impose on a system the circulation of a current in a given direction and hence the production of a reaction in a given direction, subject to the condition (which is necessary but not sufficient) that the source is capable of maintaining a potential difference at the terminals which exceeds the equilibrium value, which is then called the "decomposition voltage". An "electrochemical" presentation of the free enthalpies of reaction is thus quite natural for reactions produced by an external current source. It is concerned with the very nature of the phenomena both in this case in which electrochemical reactions are caused by the external supply of electric current and also in the case of electrochemical reactions which produce electric current; spontaneous corrosion processes of the metallic elements are of the latter type.

Since 1792 (i.e. shortly after the discovery of galvanism) when Fabbroni clearly stated the hypothesis of the galavanic nature of corrosion processes together with his chemical theory of galvanic phenomena, throughout the studies of Davy, Thénard and De La Rive and up to the most recent ones, the electrochemical conception of corrosion has never ceased to be strengthened and confirmed. Systems in which spontaneous corrosion processes take place can thus be compared to galvanic systems which do not exchange electrical work with the outside world, for which the conditions necessary for the occurrence of modifications, or sufficient for their absence, can again be represented in an essentially electrochemical form.

Let us consider a galvanic couple in which one of the two electrodes is the standard hydrogen electrode, and for which one can represent the chemical modification as being the resultant of two complementary partial oxidation-reduction reactions, taking place respectively at each of the two electrodes with the participation of electrons in the phases having metallic conduction, the stoichiometric coefficients of the electrons having equal values and opposite signs for the two partial reactions.

The most common conventions concerning reference states for the thermodynamic properties of gaseous hydrogen and the hydrogen ion in aqueous solution automatically cancel out the contribution of the standard hydrogen electrode in the expression for the free enthalpy of reaction. One can thus consider the value of this free enthalpy as being inherent to the reaction taking place at the other electrode. The potential differences at the terminals of the galvanic couple are adopted, by definition, as values of the potentials (or "relative potentials") of this electrode with respect to the standard hydrogen electrode.(1) A series of such potentials will give us the scale of the "affinities" of the partial electrode

---

(1) With regard to the sign of these relative electrode potentials, the convention adopted by Dr. Pourbaix is in accordance with the IUPAC recommendations (Stockholm, 1953), and is the so-called "European Convention".

Using the notation of the writer of this Preface, the above choice is equivalent to using the values $E^{MH}$ to express the relative

*(Footnote continued opposite)*

reactions, referred to the reaction proceeding at the standard hydrogen electrode as a conventional reference level.

For the cell obtained by coupling *any* two electrodes, the equation of the overall reaction, the value of the free enthalpy of reaction and hence the value of the equilibrium potential difference can be deduced by simple algebraic addition of those corresponding to the cells formed by coupling each of these two electrodes in turn with the reference electrode; the exactitude of the result depends on the possible "liquid junction" contributions. In this way the study of redox reactions can be reduced to a study of partial electrode reactions (or "electrochemical" reactions involving free electrons or electrons in phases having metallic conduction); the other reactions will be studied in the way which is classical for purely chemical reactions not involving free electrons.

The equilibrium conditions can thus be represented in the general case of electrochemical reactions by a relation between the equilibrium potential, the standard free enthalpy of reaction (in the form of a standard equilibrium potential), and a linear combination of logarithms of activities. In the particular case of non-electrochemical reactions the equilibrium conditions assume a simpler form as no equilibrium potential is involved; these conditions are then expressed by a relation between the standard free enthalpy of reaction (in the form of an equilibrium constant) and a linear combination of logarithms of activities.

With a view to the graphical representation of the equilibrium conditions on a plane diagram, the choice of the relative electrode potential as one of the coordinates imposes itself in the more general case of reactions involving electrons.

In view of the exceptional place occupied by $H^+$ ions among the species whose activities appear in the equilibrium relations to be considered here, it was natural to choose a function of the activity of $H^+$ ions as the second coordinate; the pH was chosen in order to linearize the equilibrium relations, despite the difficulties inherent to the individual thermodynamic properties of ionic species.(¹)

The linear combination of the logarithms of the activities of the species different from $H^+$, whose thermodynamic level in the electrolytic medium is also variable, will be given the nature of a "parameter", which is variable from one curve to another in each family of equilibrium curves.

For electrochemical reactions which do not involve hydrogen ions the loci of points representing equilibrium conditions will be straight lines parallel to the pH axis; for "purely chemical" reactions involving hydrogen ions they will be straight lines parallel to the potential axis. When there is only one species of variable thermodynamic level, the parameter, which is then proportional to the logarithm of the activity of this species, characterizes the conditions of "practical existence" of this species in the medium, i.e. the domain of conditions under which the equilibrium can be realized in the presence of appreciable concentrations of the species. Let us consider a system consisting of a metal in contact with solution of its simple ions, these being the only ones which can exist; if the concentration of these ions which is compatible with the equilibrium conditions is lower than a fairly low conventional limit, one can then speak of a state of thermodynamic *immunity* of this metal. When the number of species of variable thermodynamic level is two, the parameter, which includes in general the ratio of their activities, gives these domains of relative predominance, which can become practically total for one to the exclusion of the other.

The diagrams thus give us a panoramic view of the "chemical configurations" of our systems, predicted on a thermodynamic basis. An examination of the properties of the potential–pH diagrams

---

potential of an electrode M with respect to the hydrogen electrode (the sign convention is indicated here by the order of the letters M and H). The "American" convention would correspond on the other hand, to using the value $E^{HM}$. There are arguments for considering the first choice as being the more "natural" one. It is, however, a question of adopting a simple convention, without touching on the scientific prestige of nations or schools, which at different periods and with numerous alternatives have preferred one or the other of the two conventions.

(¹) For the purposes envisaged by Pourbaix's diagrams one can assume that the pH gives us, in an indirect and approximate way the potential of an electrode, which, like the standard reference electrode is a hydrogen electrode and is saturated with gaseous hydrogen at 1 atm, but is immersed in the solution studied. One can also postulate that in this way one defines a quantity which has an operational significance and which is also capable of characterizing the thermodynamic level of the $H^+$ ions (and hence that of the $OH^-$ ions due to the dissociation equilibrium of water), with regard to their participation in any equilibrium.

suggests certain aspects which it is useful to know in order to apply them appropriately. It is evident that the electrochemical behaviour of a metallic phase, immersed in an electrolytic medium, depends on the composition of the layer of solution which is in immediate contact with this phase. This composition may differ considerably from the mean or initial composition of the medium on account of the absolute and relative rates of the possible processes of electrolysis and matter transport (by migration, diffusion and convection). This same observation is valid for the phases formed by the compounds of the metal, and must be considered carefully in using the diagrams.

When the metal forms soluble complexes of great stability with other substances (such as cyanides or ammonia), the equilibrium diagrams for the binary system metal–water must be modified: one must then take into account the equilibrium conditions of these complexes, for example by plotting equilibrium diagrams for a ternary system. This may modify appreciably the domains of relative predominance of the dissolved species and the domains of thermodynamic stability. In these cases one must therefore be very careful, particularly because only when a dissolved species is greatly predominant, in the case of dilute solutions at least, can one assume, as has been done in this *Atlas*, that the activities are virtually the same as the molarities.

Use of the diagrams therefore renders necessary corrections of activities with respect to molarities (or molalities); these corrections, which may be important for all the diagrams when one considers concentrated solutions, may also be important when one envisages the use of binary diagrams for studying ternary systems which involve stable complexes.

Amongst the reactions considered in establishing the diagrams a special place is held by those which involve a metal or its ions and oxygen or the ions derived from it, and which produce oxides or hydroxides. The equilibrium conditions concerning these phases have a fundamental interest, not only when they are the main subject of study but also when one considers the behaviour of the metal in electrochemical processes, such as those of corrosion. From this point of view the diagrams, in spite of their essentially thermodynamic nature, can give us information about one of the most important kinetic factors in the electrochemical behaviour of metals. Indeed, in the case of electrochemical reactions, amongst the factors which can be named "resistances to reaction" and which, in spite of the affinity available, determine the kinetics of the reaction, a most important place is occupied by those which depend on the formation of surface layers on the metallic phases. A fairly detailed study of these phenomena has suggested, quite recently, that one should distinguish between *passivation phenomena*, corresponding to an increase of resistance to ionic exchange reactions between a metal and a solution due to their separation by a surface layer, and *states of passivity* in which this resistance is sufficient to reduce the rates of these reactions below limits at which they are appreciable in spite of there being an affinity for the conversion of the metal into its corrosion products.

The solid compounds (oxides, hydroxides, basic salts) formed by the various metals with water represent the most common and important source of passivation of metals in an aqueous medium by a surface layer. Thus a knowledge of the conditions of thermodynamic stability of these oxides, hydroxides and basic salts can enable one to characterize the domains of passivation predicted by thermodynamics. The passivation may result in a state of passivity, which may be local or complete, depending on the structural properties of the phases involved. Indeed, in any branch of electrochemistry, theoretical and applied investigations can be carried out thoroughly only if one takes into account three types of factors: thermodynamic, kinetic and structural ones. It must be realized that thermodynamic studies are insufficient, even in conjunction with kinetic studies; structural studies are indispensable. This is the case first of all because they give us information on the deviation of the real phases from the ideal ones considered by theoretical thermodynamics and kinetics; moreover, they alone enable us to analyse, to control if possible, and sometimes to predict the properties of our galvanic deposits or passivating layers, the selectivity of the attack processes, and all those properties which determine to a large extent the success of the electrochemical processes of production, finishing and protection of metals, or the consequences of corrosion phenomena. While the scale of relative potentials gives us the degree of "thermodynamic nobility" of the various electrode processes, a knowledge of their "practical nobility" requires that one should also take into account kinetic laws and the influence of structural factors on these laws.

For those metals whose ionic exchanges at 25°C in aqueous media are rapid (metals which we have defined as being of "normal" electrochemical behaviour), the behaviour is in accordance with thermodynamic predictions, both when they are attacked anodically and when they are deposited cathodically, e.g. in a refining or electrodeposition bath, or in a displacement reaction, or in a corrosion process. For those metals whose ionic exchanges are slow, on the other hand, or even very slow (metals with "electrochemical inertia"), the divergence between the thermodynamic nobility and the practical nobility is sometimes very great, even when there is no passivation. For these metals a knowledge of these kinetic aspects of their behaviour is an indispensable complement to the information given by the equilibrium diagrams. One of the most important kinetic features in many branches of electrochemistry is the influence of the anions, as essential constituents of the metal solution double layers; as real catalysts of ionic exchanges (according to various mechanisms, such as competitive adsorption at the surface, excluding constituents which have an inhibiting action); or as destroyers of the surface layers, or as agents which can exploit their weak points, or as structural factors in cathodic deposition, or as selectivity factors in anodic attack. In all branches of the electrochemistry of metals the specific participation of anions, even independently of any complexing action and of their influence on the ionic activity values, can play an important part, which must often be considered to complete the information that one can obtain from the diagrams.

At present the potential–pH diagrams concern only pure metals and non-metals (there is also an attempt to apply them to sodium amalgams); these diagrams cannot therefore give us information about the behaviour of alloys, which often differs from that of the pure metals, with regard to all three factors mentioned above. It is fairly obvious that the corrosion behaviour of a bronze, or of a brass, is a fairly complex resultant of the properties of the constituent metals, and this is even more true of a stainless steel. On the other hand, a knowledge of the thermodynamic properties of the products of attack of the metals constituting an alloy can sometimes enable us to predict its passivation conditions too. The study of equilibrium conditions and kinetic conditions is fairly simple for galvanic systems consisting of two electrodes, each of which can be considered to be the site of a single well-determined reaction. In practice, systems in which corrosion phenomena occur are very often multiple electrode systems in which several reactions can occur simultaneously. Here, therefore, is a new source of complication, involving once again kinetic aspects of the phenomena in particular.

The considerations which I have just discussed help us to recognize the limits to the application of potential–pH equilibrium diagrams to concrete problems, either of theoretical or applied electrochemistry, or of some other nature, within the limits of accuracy of the available thermodynamic data. For anyone who might have claimed to find the answer in these diagrams to any theoretical or practical problem without exception, the above analysis may have brought some disillusionments.

The author of this *Atlas* himself has stated most explicitly the opinion that only a clear understanding of the limits of the diagrams, and hence a rational and appropriate use of them, can enable us to appreciate their great utility which justifies the generous, passionate and profitable efforts of Dr. Pourbaix and all those who have worked with him to realize this *Atlas*, whose success can easily be foreseen.

# INTRODUCTION

## REMARKS ON ELECTROCHEMICAL THERMODYNAMICS AND KINETICS

PIERRE VAN RYSSELBERGHE
*Stanford University, California, U.S.A.*

THE excellent Preface by Professor R. Piontelli provides a perfect basis for this Introduction which can thus be reduced to a few remarks concerning certain fundamental points, all the details of the calculation and of the construction of the tension–pH diagrams being presented by M. Pourbaix in the following chapters.

We shall begin by examining the meaning of the very name given to the diagrams in the present book. Let us recall that, for many years, their name has been both in French and in English, "potential–pH diagrams". Commission No. 2 of the International Committee for Electrochemical Thermodynamics and Kinetics (CITCE), "Electrochemical Nomenclature and Definitions", has presented in yearly reports since 1951 a critical study of electrochemical concepts and has made a number of recommendations concerning the exact significance of various terms currently used and, in some cases, it has found useful to insist on the adoption of certain new terms or of new and more precise definitions of old terms. In particular, Commission No. 2 of CITCE has presented in recent reports a systematic treatment of the various tensions—electrochemical, electric, chemical—which should be considered in the fundamental theory of electrochemical equilibria and of irreversible electrochemical phenomena. Up to now this vocabulary of tensions has received general approval among French-speaking electrochemists and, with the very precise translation *tension* = *Spannung*, that of their German-speaking colleagues. The situation seems to be the same in most of the other languages, but as far as English is concerned, certain resistances have been encountered, and some of these have been rather strong. On the other hand, encouragement has been forthcoming from some quarters in the United States, and statements of adoption of the new terms have been made, in Australia for instance.

Before entering into a brief discussion of the question it is advisable to note that the word "potential" has been used in thermodynamics, physics, etc., in so many different senses that the appellation "potential–pH diagram" appears to be really too vague, particularly in view of the fact that the potentials here involved are actually combinations of differences of inner electric potentials of the various phases or linear combinations of chemical potentials reduced to the unit of charge. The objection can, of course, immediately be made that the word "tension" has also been used in many different senses, but, when one has to distinguish between inner, outer and surface potentials; chemical potentials, electrochemical potentials; oxidation, reduction and redox potentials; thermodynamic potentials, etc., the three very precisely defined types of tensions, which are always differences or linear combinations (reduced to the unit of charge) of the corresponding potentials, certainly introduce a considerable amount of clarity.

In the general name "tension–pH diagrams" the word tension is used without adjective. We shall immediately see that it can be understood as referring to equilibrium electric tensions, but also, and, we submit, chiefly to reduction chemical tensions, which are also called in the CITCE reports reduction affinities per unit of charge and correspond to one of the possible types of the quantities which are rather currently called "electromotive forces".

As far as pH is concerned, the diagrams presented in this *Atlas* use it in the well-known operational sense. Commission No. 2 of CITCE has been examining for some time the possibility of establishing a rational definition of pH, but we shall not enter here into these theoretical considerations.

In order to define the various tensions as briefly and clearly as possible, let us first examine the typical example of the Daniell cell, which we shall represent by the following diagram:

$$\underset{1}{\mathrm{Cu}} \;/\; \underset{2}{\mathrm{Cu}^{++}} \;//\; \underset{3}{\mathrm{Zn}^{++}} \;/\; \underset{4}{\mathrm{Zn}} \;/\; \underset{1'}{\mathrm{Cu}}$$

followed by an external circuit $1' - 1$.

The inner electric potentials of the various phases are represented by $\varphi^1, \varphi^2, \ldots$ The electric tension U of the cell, considered from left to right in the direction of the numbering of the phases, is

$$\mathrm{U} = \varphi^1 - \varphi^{1'}, \tag{1}$$

whether a current passes through the cell (U is then an irreversible electric tension) or not (U is then the reversible electric tension, if one leaves out of consideration the electric tension $\varphi^2 - \varphi^3$ of the liquid junction between solutions 2 and 3, either by neglecting it or by estimating it numerically and subtracting it from the total electric tension). The terminals 1 and $1'$ being chemically identical, we may write

$$\mathrm{U} = \frac{\mu^1_{e-} - \mathrm{F}\varphi^1}{-\mathrm{F}} - \frac{\mu^{1'}_{e-} - \mathrm{F}\varphi^{1'}}{-\mathrm{F}}, \tag{2}$$

where $\mu^1_{e-} = \mu^{1'}_{e-}$ represent the chemical potential of the electron in copper and F represents the Faraday. Measuring instruments, potentiometers and voltmeters, always give us differences of electric potentials between chemically identical phases which should then always be associated to the phases of the electrochemist's galvanic and electrolytic cells. In general the copper wires used as connections will belong to the electrochemical systems under study.

Introducing the electrochemical potentials

$$\tilde{\mu}^1_{e-} = \mu^1_{e-} - \mathrm{F}\varphi^1, \qquad \tilde{\mu}^{1'}_{e-} = \mu^1_{e-} - \mathrm{F}\varphi^{1'}, \tag{3}$$

we have

$$\mathrm{U} + \frac{\tilde{\mu}^{1'}_{e-} - \tilde{\mu}^1_{e-}}{-\mathrm{F}} = 0, \tag{4}$$

where, in the denominator of the second term on the left-hand side, the charge $-\mathrm{F}$ is that transported by 1 mole of electrons passing from $1'$ to 1 through an external conductor. The difference of electrochemical potentials in the numerator is equal to the electrochemical affinity of the process

$$e^-(1') \rightarrow e^-(1), \qquad \tilde{\mathrm{A}} = \tilde{\mu}^{1'}_{e-} - \tilde{\mu}^1_{e-}. \tag{5}$$

If we reverse the mode of writing of the process, its electrochemical affinity changes sign:

$$e^-(1) \rightarrow e^-(1'), \qquad \tilde{\mathrm{A}} = \tilde{\mu}^1_{e-} - \tilde{\mu}^{1'}_{e-}. \tag{6}$$

The charge transported from $1'$ to 1 by the external circuit when the process occurs once is now $+\mathrm{F}$. We thus see that the quotient of the electrochemical affinity by the charge transported in the direction of the numbering of the phases is invarient in magnitude and in sign. It is called *electrochemical tension* of this process and we write, designating by E this electrochemical tension,

$$U + \frac{\tilde{\Lambda}}{zF} = U + \tilde{E} = 0, \tag{7}$$

where $z$ is the number of charges transported, expressed in Faradays. We have $z = -1$ for case (5) and $z = +1$ for case (6).

At the Zn/Cu contact between phases 4 and 1′ there is always electrochemical equilibrium for the transfer of electrons, intermetallic contacts being considered as unpolarizable. We then have, for the process

$$e^-(4) \rightarrow e^-(1'), \tag{8}$$

the electrochemical equilibrium condition

$$\tilde{\Lambda} = \tilde{\mu}^4_{e^-} - \tilde{\mu}^{1'}_{e^-} = 0 \tag{9}$$

and (4) can then be written

$$U + \frac{\tilde{\mu}^4_{e^-} - \tilde{\mu}^1_{e^-}}{-F} = 0 \tag{10}$$

whether there is, for the whole cell, equilibrium (zero current) or non-equilibrium (current passing either in the spontaneous direction, here from Zn, phase 4, to Cu, phase 1, in the cell, or in the non-spontaneous direction thanks to a suitable electric tension applied from the external current).

In the absence of current there is electrochemical equilibrium at the contact Cu (phase 1)/$Cu^{++}$ (phase 2) and at the contact $Zn^{++}$ (phase 3)/Zn (phase 4). We then have, for the processes

$$Cu(1) \rightarrow Cu^{++}(2) + 2e^-(1), \tag{11}$$

$$Zn^{++}(3) + 2e^-(4) \rightarrow Zn(4), \tag{12}$$

the respective electrochemical equilibrium conditions

$$2\tilde{\mu}^1_{e^-} = \mu^1_{Cu} - \tilde{\mu}^2_{Cu^{++}}, \tag{13}$$

$$2\tilde{\mu}^4_{e^-} = \mu^4_{Zn} - \tilde{\mu}^3_{Zn^{++}}. \tag{14}$$

From (10) we then obtain, but only for equilibrium (at all interfaces, 2/3 excepted) which we indicate by the subscript $I = 0$ (zero current):

$$U_{I=0} = -\frac{\tilde{\mu}^2_{Cu^{++}} + \mu^4_{Zn} - \mu^1_{Cu} - \tilde{\mu}^3_{Zn^{++}}}{-2F}. \tag{15}$$

Let us decompose the electrochemical potentials into their chemical and electric terms:

$$U_{I=0} = -\frac{\mu^2_{Cu^{++}} + \mu^4_{Zn} - \mu^1_{Cu} - \mu^3_{Zn^{++}}}{-2F} + (\varphi^2 - \varphi^3)_{I=0}, \tag{16}$$

the difference $(\varphi^2 - \varphi^3)_{I=0}$ being the electric tension of the liquid junction at zero current.

Let us introduce the *chemical tension* (or electromotive force) E of the cell reaction, equal to the chemical affinity of the reaction

$$Cu^{++}(2) + Zn(4) \rightarrow Cu(1) + Zn^{++}(3) \tag{17}$$

divided by its reaction charge $-2F$, or to the chemical affinity of the reaction

$$Cu(1) + Zn^{++}(3) \rightarrow Cu^{++}(2) + Zn(4) \tag{18}$$

divided by its reaction charge + 2F. We then have

$$U_{I=0} = -\frac{A}{zF} + (\varphi^2 - \varphi^3)_{I=0} \qquad \text{or} \qquad U_{I=0} + E = (\varphi^2 - \varphi^3)_{I=0}. \tag{19}$$

The difference between $U_{I=0}$ and U at I different from zero given by (10) can be written

$$U_{I=0} - U_I = \frac{\mu^2_{Cu^{++}} + 2\mu^1_{e^-} - \mu^1_{Cu}}{2F} + \frac{\mu^4_{Zn} - \mu^3_{Zn^{++}} - 2\mu^4_{e^-}}{2F} + (\varphi^2 - \varphi^3)_{I=0} - (\varphi^1 - \varphi^4)_I. \tag{20}$$

The first fraction on the right-hand side is equal to $(\varphi^1 - \varphi^2)_{I=0}$, the second fraction is equal to $(\varphi^3 - \varphi^4)_{I=0}$ and we have

$$U_{I=0} - U_I = (\varphi^1 - \varphi^2)_{I=0} - (\varphi^1 - \varphi^2)_I + (\varphi^3 - \varphi^4)_{I=0} - (\varphi^3 - \varphi^4)_I - (\varphi^2_I - \varphi^3_I), \tag{21}$$

in which the difference $\varphi^2_I - \varphi^3_I$ is equal to plus or minus the internal ohmic drop in the cell. The differences of differences appearing in (21) are the anodic and cathodic *overtensions* at the electrodes of the cell. When the current passes through the cell in the direction corresponding to that in which the cell reaction takes place spontaneously, hence from left to right according to (17), there is a displacement of positive charges from right to left in the cell diagram, copper being deposited on electrode 1 and zinc dissolving in solution 3. The cathodic overtension $\eta_c$ being always negative and the anodic overtension $\eta_a$ always positive, we have at the cathode 1/2:

$$(\varphi^1 - \varphi^2)_{I=0} - (\varphi^1 - \varphi^2)_I = -\eta_c > 0 \tag{22}$$

and at the anode 4/3:

$$(\varphi^3 - \varphi^4)_{I=0} - (\varphi^3 - \varphi^4)_I = +\eta_a > 0, \tag{23}$$

with

$$\varphi^3_I - \varphi^2_I = RI \tag{24}$$

and (21) can thus be written

$$U_{I=0} - U_I = |\eta_c| + \eta_a + RI > 0. \tag{25}$$

If the current passes through the cell from left to right, the cell reaction takes place from left to right according to (18), copper dissolving in solution 2 and zinc depositing on electrode 4. We have at the anode 1/2:

$$(\varphi^1 - \varphi^2)_{I=0} - (\varphi^1 - \varphi^2)_I = -\eta_a < 0 \tag{26}$$

and at the cathode 3/4:

$$(\varphi^3 - \varphi^4)_{I=0} - (\varphi^3 - \varphi^4)_I = +\eta_c < 0, \tag{27}$$

with

$$\varphi^2_I - \varphi^3_I = RI \tag{28}$$

and (21) is now written

$$U_I - U_{I=0} = \eta_a + |\eta_c| + RI > 0. \tag{29}$$

Let us now consider the *tensiometric cell*

$$\underset{A}{Cu} \;/\; \underset{1}{Zn} \;/\; \underset{2}{Zn^{++}} \;//\; \underset{3}{H^+}\left(a_{H^+} = 1\right) \;/\; \underset{4}{H_2}\left(p_{H_2} = 1 \text{ atm.}\right); \qquad Pt \;/\; \underset{B}{Cu}$$

in which the electrode on the right is a standard hydrogen electrode. The cell reaction is

$$Zn(1) + 2H^+(3) \rightarrow Zn^{++}(2) + H_2(4) \tag{30}$$

with the reaction charge +2F or

$$Zn^{++}(2) + H_2(4) \rightarrow Zn(1) + 2H^+(3) \tag{31}$$

with the reaction charge −2F. As in (19) we have, neglecting the electric tension of the liquid junction,

$$U_{I=0} = \varphi^A - \varphi^B = -\frac{A_{\text{oxid.}}}{+2F} = -\frac{A_{\text{red.}}}{-2F} = \frac{A_{\text{red.}}}{2F}, \tag{32}$$

where $A_{\text{oxid.}}$ represents the chemical affinity of reaction (30), which is the oxidation of Zn by $H^+$ at $a_{H^+} = 1$, and $A_{\text{red.}}$ represents the chemical affinity of reaction (31), which is the reduction of $Zn^{++}$ by $H_2$ at $p_{H_2} = 1$ atm. We also have

$$U_{I=0} = \frac{\mu^2_{Zn^{++}} - \mu^1_{Zn} - \left(2\mu^3_{H^+} - \mu^4_{H_2}\right)}{2F} = E_{\text{red.}} \tag{33}$$

Since Pourbaix represents by the symbol $E_0$ this electric tension at zero current or "equilibrium tension", our symbol $U_{I=0}$ corresponds to this symbol $E_0$ which is to be found in all the formulae and diagrams of the present *Atlas.*

The reversible electric tension of the tensiometric cell here considered is thus equal to the *reduction chemical tension*, which is identical with the reduction affinity per unit charge, as indicated in (32).

The chemical potentials $\mu^3_{H^+}$ and $\mu^4_{H_2}$ are the standard chemical potentials of $H^+$ and $H_2$, $\mu^{\bullet}_{H^+}$ and $\mu^{\bullet}_{H_2}$. The universal usage is to take the standard hydrogen electrode as reference electrode at all temperatures. Moreover one takes conventionally

$$2\mu^{\bullet}_{H^+} - \mu^{\bullet}_{H_2} = 0 \tag{34}$$

at all temperatures, with, specially, at 25°C:

$$\mu^0_{H^+} = 0 \quad \text{and} \quad \mu^0_{H_2} = 0. \tag{35}$$

Formula (33) is then written

$$U_{I=0} = E_{\text{red.}} = \frac{\mu^2_{Zn^{++}} - \mu^1_{Zn}}{2F}. \tag{36}$$

At the standard state of 25°C the $Zn/Zn^{++}$ electrode has a reversible electric tension of −0·76 V. We thus have

$$U^0_{I=0} = -0.76\ \text{V}, \qquad E^0_{\text{red.}} = -0.76\ \text{V},$$

with

$$E^0_{\text{oxid.}} = -E^0_{\text{red.}} = +0.76\ \text{V}. \tag{37}$$

If we take, still at 25°C, $\mu^0_{Zn} = 0$, we obtain $\mu^0_{Zn^{++}} = -0{\cdot}76 \times 2 \times 96\,500 = -146\,700$ J or $-0{\cdot}76 \times 2 \times 23 = -35$ kcal., a quantity which thus represents the standard free enthalpy of formation of the $Zn^{++}$ ion, equal to minus the standard chemical affinity of the reaction.

$$Zn + 2H^+\left(a_{H^+} = 1\right) \rightarrow Zn^{++}\left(a_{Zn^{++}} = 1\right) + H_2\left(p_{H_2} = 1\ \text{atm.}\right). \tag{38}$$

Let us now consider the general case of the electrode reaction

$$aA + mH^+ + ne^- \rightarrow bB + cH_2O, \tag{39}$$

in which A may represent a simple metallic ion and B the corresponding metal ($a = b = 1$, $m = c = 0$), but in which A and B may also both be dissolved species, for instance $Fe^{+++}$, $Fe^{++}$ and $FeO_2H^-$, or both oxides or hydroxides, etc. When the reagents and products do not include a metal, the electrons are furnished or liberated by an inert noble metal such as platinum. The reversible electric tension of a cell in which the electrode on the left is that at which reaction (39) can occur, the electrode on the right being always the standard hydrogen electrode is given by

$$(40) \qquad U_{I=0} = E_{red.} = \frac{a\mu_A + m\mu_{H^+} - b\mu_B - c\mu_{H_2O}}{nF},$$

an expression in which convention (34) has been taken into account.

The chemical potentials being of the form

$$(41) \qquad \mu_i = \mu_i^0(T, p) + RT \ln a_i$$

we have

$$(42) \qquad U_{I=0} = E_{red.} = E_0^{\bullet} + \frac{RT}{nF} \ln \frac{(a_A)^a \cdot (a_{H^+})^m}{(a_B)^b \cdot (a_{H_2O})^c},$$

with

$$(43) \qquad E_0^{\bullet} = \frac{a\mu_A^0 + m\mu_{H^+}^0 - b\mu_B^0 - c\mu_{H_2O}^0}{nF}.$$

The tension–pH diagrams presented in this *Atlas* apply to the temperature of 25°C. We then make $\mu_{H^+}^0 = 0$ in (43). The activity of water $a_{H_2O}$, exactly equal to the ratio of the vapor pressure of the solution to that of the pure solvent, is taken as practically equal to one. We then have, at 25°C and in terms of pH,

$$(44) \qquad U_{I=0} = E_{red.} = E_0^0 + \frac{0{,}059}{n} \log \frac{(a_A)^a}{(a_B)^b} - 0{,}059 \frac{m}{n}\, \text{pH}.$$

The systematic use of equations of this type in the construction of the tension–pH diagrams is discussed in detail in the chapters contributed by Pourbaix. The outline of theory presented in this Introduction has as main goal to bring out the fact that the tensions represented in the diagrams can be regarded as being either reversible or equilibrium electric tensions or reduction chemical tensions. In the majority of cases the experimentally accessible tensions are those derived from thermodynamic data, free enthalpies or affinities, obtainable themselves from thermochemical data (heats of formation and entropies), the electrically measurable tensions, at electrodes which must necessarily function reversibly, being definitely in a minority. In any case, the two types of tensions are immediately convertible into each other.

It can also be deduced from the above discussion, particularly from our brief mention of the overtensions, that, out of equilibrium, the reduction chemical tensions remain unchanged as long as the composition of the system, temperature and pressure remain unchanged, while the electric tensions vary on account of the overtensions and of the ohmic drops. It follows that the tension–pH diagrams continue to play a fundamental part out of equilibrium. They represent then, for an element and the ions, oxides and hydroxides resulting from its interaction with water, the various reduction chemical tensions to which one may compare, when they are experimentally obtained by means of polarization curves and plotted on the diagrams, the irreversible electric tensions corresponding to different values of the current or of the reaction velocity.

It is the role of electrochemical kinetics to unravel the mechanisms of irreversible oxidation and reduction processes and to furnish theoretical foundations for the interpretation of the empirical relations between overtensions and currents. In spite of the considerable progress in this field during the last few years and of the abundant experimental and theoretical literature appearing at a constantly accelerated rate, it must be recognized that electrochemical kinetics is still far from having reached a satisfactory degree of logic and coherence.

When the concentration and resistance polarizations have been separated from the total polarization and the activation polarization remains alone to be considered, it is generally found that a law of the

Tafel type applies at sufficiently large overtensions and currents. For a cathodic process, for instance, we have

$$|\eta_c| = a + b \ln \mathrm{I} \tag{45}$$

or

$$|\eta_c| = \frac{\mathrm{RT}}{\alpha z \mathrm{F}} \ln \frac{\mathrm{I}}{\mathrm{I}_0}, \tag{46}$$

the transfer coefficient $\alpha$ and the exchange current $\mathrm{I}_0$ being empirically obtained from the slope and the extrapolation of the "Tafel straight line". In the range of overtensions and currents for which the velocity of the reverse process, here an oxidation, is not negligible, one writes

$$\mathrm{I} = \mathrm{I}_0 \left[ \exp\left( \frac{\alpha z \mathrm{F} |\eta_c|}{\mathrm{RT}} \right) - \exp\left( - \frac{\beta z \mathrm{F} |\eta_c|}{\mathrm{RT}} \right) \right], \tag{47}$$

the transfer coefficient $\beta$ of the reverse process being generally taken equal to $1 - \alpha$. Finally, in the range of very small overtensions, it is possible to retain only the first two terms of the developments in series of the two exponentials and we have

$$\mathrm{I} = \mathrm{I}_0 \frac{(\alpha + \beta) z \mathrm{F}}{\mathrm{RT}} |\eta_c|, \tag{48}$$

a formula which expresses the proportionality in the vicinity of equilibrium between current or reaction velocity and electrochemical affinity. It is thus a typical formula of the thermodynamics of irreversible processes.

A complete theoretical deduction of these formulae explaining the exact significance of the transfer coefficient and determining the influence of the composition of the system on the exchange current remains to be established. At the eleventh yearly meeting of CITCE held in Vienna around 1st October 1959, we have suggested, on the basis of earlier communications and of a preliminary study presented in our *Electrochemical Affinity* (Hermann, Paris, 1955), that the use in electrochemistry, for each elementary step of a reaction mechanism, of the Marcelin–De Donder formula (see our article "Reaction rates and affinities", *J. Chem. Phys.* **29**, 640 (1958)), could lead to considerable clarification. This is of the form

$$v = \vec{v}_e \left( \exp \frac{\vec{\mathrm{A}} - \vec{\mathrm{A}}_e}{\mathrm{RT}} - \exp \frac{\overleftarrow{\mathrm{A}} - \overleftarrow{\mathrm{A}}_e}{\mathrm{RT}} \right), \tag{49}$$

in which $v$ is the reaction velocity, $\vec{\mathrm{V}}_e = \overleftarrow{\mathrm{V}}_e$ is the exchange velocity at equilibrium, $\vec{\mathrm{A}}$ and $\overleftarrow{\mathrm{A}}$ are the opposed partial affinities equal to the sums of chemical potentials of reagents and products (we have $\vec{\mathrm{A}} - \overleftarrow{\mathrm{A}} = \mathrm{A}$). $\vec{\mathrm{A}}_e = \overleftarrow{\mathrm{A}}_e$ is the common value of these affinities at equilibrium. In the case of electrochemical reactions these various affinities become sums of electrochemical potentials. We had already insisted in 1949 (*J. Chem. Phys.* **17**, 1226 (1949)) on the advisability of using systematically the electrochemical potentials in the typical case of hydrogen overtensions. Current theoretical studies in the field of electrochemical kinetics combine in general the principles of purely chemical kinetics with empirical considerations intended to describe the role of the electric field in the transition layer from metal to solution. It is, however, clear that the total influence, chemical and electric, of a charge constituent on the velocity of a reaction in which it participates results from the value of its electrochemical potential at the spot where the reaction act takes place. This influence cannot then result from separate and functionally different contributions of the local chemical and electric potentials.

Among the numerous current and future applications of the tension–pH diagrams assembled in this *Atlas* it appears certain that they will serve as foundations for numerous investigations in the field of electrochemical kinetics to the great benefit of this discipline.

# METHOD OF ESTABLISHING POTENTIAL–pH EQUILIBRIUM DIAGRAMS(1)

M. POURBAIX

SUMMARY

## 1. INTRODUCTION

WHEN iron corrodes in the presence of air in tap water from a town water supply (Fig. 1), a large number of reactions take place simultaneously: the iron corrodes with evolution of hydrogen and the water becomes alkaline according to the reaction $Fe + 2H_2O \rightarrow Fe^{++} + H_2 \nearrow + 2OH^-$; in strongly aerated regions the ferrous ions thus formed are oxidized to ferric ions by dissolved oxygen according to the reaction $4Fe^{++} + O_2 + 2H_2O \rightarrow 4Fe^{+++} + 4OH^-$, and these ferric ions react with the hydroxyl ions according to the reaction $4Fe^{+++} + 12OH^- \rightarrow 4Fe(OH)_3 \downarrow$ to form a brown deposit of ferric hydroxide; in less aerated regions the action of oxygen leads to the separation, not of ferric hydroxide, but of magnetite $Fe_3O_4$. In general these oxides are deposited in the form of rust at a certain distance from the place where the iron dissolves, in which case the corrosion of the metal proceeds

---

(1) Detailed accounts of this have been given in the following publications:

[1] M. POURBAIX, *Thermodynamique des solutions aqueuses diluées. Représentation graphique du rôle du pH et du potentiel* (*Thesis*, Delft, 1945; Béranger, Paris and Liège). 3rd Edition, Cebelcor 1963. *Thermodynamics of Dilute Aqueous Solutions, with Applications to Electrochemistry and Corrosion* (foreword by U. R. EVANS), Arnold, London, 1950.

[2] M. POURBAIX, *Leçons sur la Corrosion électrochimique* (2e fascicule) (Rapport technique RT.30 of CEBELCOR, 1956).

[3] M. POURBAIX, *Leçons sur la Corrosion électrochimique* (3e fascicule) (Rapport technique RT.49 of CEBELCOR, 1957).

The author expresses his gratitude to P. Van Rysselberghe and R. Defay for numerous discussions relating to the present text.

in a permanent manner; sometimes these oxides are deposited in an adherent form at the actual place where the iron dissolves, in which case they can cover the metal with a more or less protective coating. Other changes can occur simultaneously with these reactions: the local alkalinization of the water due to the evolution of hydrogen or the reduction of oxygen causes the conversion of bicarbonate ions, according to the reaction $HCO_3^- + OH^- \rightarrow CO_3^{--} + H_2O$, into carbonate ions, which react with the dissolved calcium ions to form calcium carbonate according to the reaction $CO_3^{--} + Ca^{++} \rightarrow CaCO_3 \downarrow$. If this calcium carbonate is deposited on the metal, which frequently happens with tap water, it can form on the surface, in combination with ferric oxide or hydroxide, an adherent coating which effectively protects the metal against further corrosion.

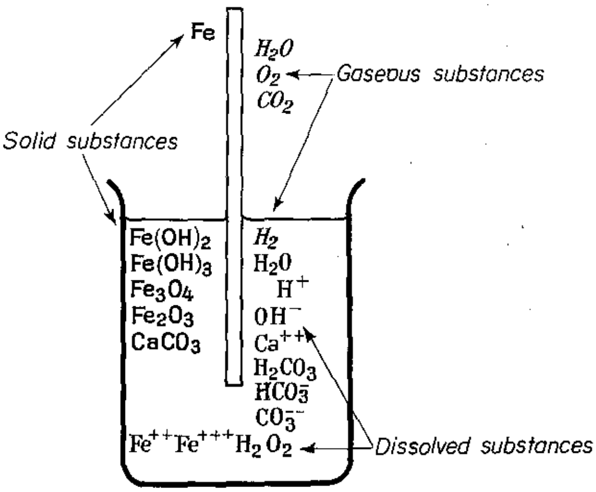


FIG. 1. Iron in the presence of tap water from a town water supply.

Finally, in the course of this corrosion of iron, other reactions can lead to the formation of small quantities of hydrogen peroxide.

Under these conditions, therefore, the corrosion of iron gives rise to the formation of a large number of substances in the dissolved, solid and gaseous states; these substances react chemically and electrochemically among themselves, and we are faced with an inextricable problem if we try to study these reactions separately. For the study of these complex phenomena it is best to employ graphical methods which enable us to study simultaneously the equilibria of *all* the entangled reactions,(2) both chemical and electrochemical, that may occur.

It is for the study of such problems that the electrochemical equilibrium diagrams discussed here are intended.

## 2. CONVENTIONS FOR WRITING THE REACTIONS. CHEMICAL REACTIONS AND ELECTROCHEMICAL REACTIONS

### 2.1. GENERAL

Throughout this *Atlas* we shall concern ourselves in particular with the study of equilibrium states of reactions, which are the same in whichever direction one considers the reactions. We shall therefore

---

(2) The idea of "entangled equilibria" was introduced by P. Montagne in his treatise *Calcul numérique des équilibres chimiques en phase gazeuse homogène; applications à l'étude théorique des combustions*, Gauthier-Villars, Paris, 1934.

write these reactions in a manner that does not necessarily imply that the reaction takes place in a definite direction (for instance from left to right, a convention which the majority of authors use at present) rather than in the other direction (from right to left).

For example, the equation $2H_2O = 2H_2 + O_2$ will not necessarily be taken to represent the dissociation of water $2H_2O \rightarrow 2H_2 + O_2$; it will represent equally well the synthesis of water $2H_2O \leftarrow 2H_2 + O_2$. The equation $H_2 = 2H^+ + 2e^-$ will not necessarily be taken to represent the oxidation $H_2 \rightarrow 2H^+ + 2e^-$; it will also represent the reduction $H_2 \leftarrow 2H^+ + 2e^-$.

## 2.2. CHEMICAL REACTIONS

A *chemical reaction* is a reaction in which only neutral molecules and positively or negatively charged ions take part, with the exclusion of electrons (see later on the definition of an electrochemical reaction).

The following reactions are examples:

| | |
|---|---|
| Dissociation of water vapour | $2H_2O_{(g)} \rightarrow 2H_{2(g)} + O_{2(g)}$ |
| Electrolytic dissociation of liquid water | $H_2O_{(l)} \rightarrow H^+_{(aq.)} + OH^-_{(aq.)}$ |
| Precipitation of ferrous hydroxide | $Fe^{++}_{(aq.)} + 2OH^-_{(aq.)} \rightarrow Fe(OH)_{2(s)}$ |
| Dissolution of gaseous $CO_2$ | $CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq.)}$ |
| Corrosion of iron with evolution of hydrogen | $Fe_{(s)} + 2H^+_{(aq.)} \rightarrow Fe^{++}_{(aq.)} + H_{2(g)}$ |
| Oxidation of ferrous ions by permanganate | $MnO^-_{4(aq.)} + 8H^+_{(aq.)} + 5Fe^{++}_{(aq.)} \rightarrow Mn^{++}_{(aq.)} + 4H_2O_{(l)} + 5Fe^{+++}_{(aq.)}$. |

These reactions can be written in the general form

$$\nu'_1 M'_1 + \nu'_2 M'_2 + \ldots = \nu''_1 M''_1 + \nu''_2 M''_2 + \ldots, \qquad (1)$$

in which the "stoichiometric coefficients" $\nu'_1$, $\nu'_2$, ... and $\nu''_1$, $\nu''_2$ ... are positive numbers.

By bringing all the terms to one side of the equation, we can write the reaction equation (1) in a shortened form

$$\boxed{\Sigma \nu M = 0,} \qquad (2)$$

in which the stoichiometric coefficients $\nu$ have the same numerical values as in (1) but bear either a + or a − sign; *as a sign convention* we say that the coefficients $\nu$ are positive for the reacting substances M on the right-hand side of the reaction equation (1), and negative for the reacting substances on the left-hand side.

For example, the following reaction written in form (1)

$$MnO_4^- + 8H^+ + 5Fe^{++} \rightarrow Mn^{++} + 4H_2O + 5Fe^{+++}$$

will be written in form (2)

$$Mn^{++} + 4H_2O + 5Fe^{+++} - MnO_4^- - 8H^+ - 5Fe^{++} = 0.$$

By writing the reaction in form (1) or form (2) we do not assume that we know the direction in which the reaction is really proceeding. Depending on the circumstances, reaction (1) can take place from left to right, using up certain quantities of substances M′ to produce substances M″, or conversely from right to left, producing substances M′ at the expense of substances M″. When the reaction takes place from left to right we say in general that it takes place in the positive direction; when it takes place from right to left, we say in general that it retrogresses, or takes place in the negative direction.

In short, by choosing the direction in which to write a reaction, we do not assert that it will proceed in this direction; we merely choose the direction which will be taken as positive; when a reaction takes place from left to right, we say moreover, that it takes place in the direction in which it is written.

The rule for the signs of the stoichiometric coefficients in the reaction equation (2) can be stated very simply as follows: when reaction (1) takes place in the direction in which it is written, the constituents which appear have positive stoichiometric coefficients in (2) and those which disappear have negative stoichiometric coefficients.

## 2.3. ELECTROCHEMICAL REACTIONS

We shall define *an electrochemical reaction* (or electrode reaction) as being a reaction involving, besides molecules and ions, negative electrons $e^-$ arising from a metal or other substance by metallic conduction. Such reactions will be *oxidations* if they proceed in the direction corresponding to the liberation of electrons; they will be *reductions* if they proceed in the direction corresponding to the absorption of electrons.

Some examples of electrochemical reactions are:

| | |
|---|---|
| Reduction of hydrogen ions to gaseous hydrogen | $2H^+_{(aq.)} + 2e^- \rightarrow H_{2(g)}$ |
| Reduction of gaseous oxygen to hydroxyl ions | $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq.)}$ |
| Reduction of permanganate to manganous ions | $MnO^-_{4(aq.)} + 8H^+_{(aq.)} + 5e^- \rightarrow Mn^{++}_{(aq.)} + 4H_2O_{(l)}$ |
| Oxidation of iron to ferrous ions | $Fe_{(s)} \rightarrow Fe^{++}_{(aq.)} + 2e^-$ |
| Oxidation of ferrous ions to ferric ions | $Fe^{++}_{(aq.)} \rightarrow Fe^{+++}_{(aq.)} + e^-.$ |

These reactions can be written in the general form

$$\nu'_1 M'_1 + \nu'_2 M'_2 + \ldots + n\, e^- = \nu''_1 M''_1 + \nu''_2 M''_2 + \ldots \tag{3}$$

or

$$\boxed{\Sigma \nu M + n\, e^- = 0.} \tag{4}$$

## 2.4. METHOD OF WRITING THE REACTIONS

It is well known that, *for every chemical reaction* involving, among other substances, gases and/or dissolved substances, there exists an *equilibrium constant* whose value for a given temperature and total pressure is a certain function of the *partial pressures* (or the *fugacities*) of the gaseous reacting substances and of the *concentrations* (or the *activities*) of the dissolved reacting substances. Some examples of such equilibrium constants are:

dissociation in the gaseous phase (Guldberg and Waage's constant, mass action constant):

$$2H_2O_{(g)} = 2H_{2(g)} + O_{2(g)}, \qquad K = \frac{(p_{H_2})^2 \cdot p_{O_2}}{(p_{H_2O})^2};$$

dissociation in solution (Ostwald's constant, dissociation constant, ionic product of water):

$$H_2O_{(l)} = H^+_{(aq.)} + OH^-_{(aq.)}, \qquad K = C_{H^+} \cdot C_{OH^-};$$

dissolution of sparingly soluble solid substances (solubility product):

$$Fe(OH)_{2(s)} = Fe^{++}_{(aq.)} + 2OH^-_{(aq.)}, \qquad K = C_{Fe^{++}} \cdot C^2_{OH^-};$$

$$As_2O_{3(s)} + H_2O_{(l)} = 2HAsO_{2(aq.)}, \qquad K = C_{HAsO_2};$$

dissolution of gaseous substances:

$$CO_{2(g)} + H_2O_{(l)} = H_2CO_{3(aq.)}, \qquad K = \frac{C_{H_2CO_3}}{p_{CO_2}}.$$

It is possible to show(³) that, *for every electrochemical reaction* involving gases and/or dissolved substances, there also exists an *equilibrium constant* whose value, for a given temperature and total pressure, is a function, not only of the partial pressures (or fugacities) of the gaseous reacting substances and of the concentrations (or activities) of the dissolved reacting substances, but also of a *difference of electric potential* (or *electrode tension*).

Consequently, if, in order to establish equilibrium diagrams as a function of pH and electrode potential, we concern ourselves with investigating the influence of the *pH* and the *electrode potential* on the equilibrium characteristics of the different reactions that we are interested in, it is as well to write these reactions in a certain specified manner which makes clearly apparent in the reaction equation any $H^+$ ions and electric charges $e^-$ that may take part in the reaction.

For this purpose we shall in general use the *following convention for writing the reactions*: for example in writing the reaction for the conversion of permanganate ions $MnO_4^-$ into manganous ions $Mn^{++}$ (reduction of permanganate in acid solution) we proceed as follows: we write the symbols for these two substances on either side of the = sign.

$$MnO_4^- = Mn^{++}$$

We balance the O's with $H_2O$: $MnO_4^- = Mn^{++} + 4H_2O$

We balance the H's with $H^+$: $MnO_4^- + 8H^+ = Mn^{++} + 4H_2O$

We balance the electric charges with $e^-$: $MnO_4^- + 8H^+ + 5e^- = Mn^{++} + 4H_2O.$

Below are some other examples (reduction of permanganate in non-acid solution, and reduction of dichromate):

$$\begin{array}{llll} MnO_4^- & = MnO_2 & Cr_2O_7^{--} & = 2Cr^{+++} \\ MnO_4^- & = MnO_2 + 2H_2O & Cr_2O_7^{--} & = 2Cr^{+++} + 7H_2O \\ MnO_4^- + 4H^+ & = MnO_2 + 2H_2O & Cr_2O_7^{--} + 14H^+ & = 2Cr^{+++} + 7H_2O \\ MnO_4^- + 4H^+ + 3e^- & = MnO_2 + 2H_2O & Cr_2O_7^{--} + 14H^+ + 6e^- & = 2Cr^{+++} + 7H_2O; \end{array}$$

Also for the precipitation of ferrous hydroxide, for example, we shall not write:

$$Fe^{++} + 2OH^- = Fe(OH)_2,$$

but we shall write instead

$$Fe^{++} + 2H_2O = Fe(OH)_2 + 2H^+.$$

In general, the reaction for the conversion of an oxidized substance A into a reduced substance B, for instance, will be written:

$$aA + cH_2O + n\,e^- = bB + mH^+.$$

By applying the general equilibrium formulae that we are about to deduce to reactions written in this way, we shall obtain equilibrium relations which will automatically be expressed as a function of the pH and the electrode potential;

the pH measures the effect of the $H^+$ ions;

the electrode potential measures the effect of the charges $e^-$.

## 3. GENERAL FORMULA FOR CHEMICAL EQUILIBRIA

Let us consider a *chemical reaction*

$$\Sigma \nu M = 0, \tag{2}$$

which involves gaseous substances and/or substances dissolved in aqueous solution.

---

(³) See *loc. cit.* [1].

The affinity A of this reaction can be expressed by the equation

$$(5) \qquad A = -\Sigma \nu \mu,$$

in which $\mu$ represents the "chemical potentials" of the various reacting substances M.

If we use the common symbol (M) to represent the fugacity or "corrected" partial pressure of the gaseous substances (expressed in atmospheres), and the activity or "corrected" concentration of the dissolved substances (expressed as a molality, i.e. in gram-molecules or gram-ions per kilogram of solvent), the values of the chemical potentials $\mu$ of each of the reacting substances M can be expressed by the following equation:[4]

$$(6) \qquad \mu = \mu^{\circ} + RT \ln(M),$$

in which

$\mu^{\circ}$ is the "standard chemical potential" of the substance considered;
R is the ideal gas constant (1·985 cal.-deg. mole);
T is the absolute temperature;
ln represents a Napierian logarithm.

In the case of a gaseous constituent, the standard chemical potential $\mu^{\circ}$ depends solely on the temperature; it is the chemical potential of the substance when it is by itself at the temperature considered and under such a pressure that its fugacity is 1 atm. (760 mm Hg).

In the case of a condensed constituent, $\mu^{\circ}$ is the chemical potential of the pure substance in this condensed state; it depends on the temperature T and the pressure *p*.

In the case of a solution, the standard chemical potential of the solvent is the chemical potential of the pure solvent at the temperature and pressure considered; the standard chemical potential of a dissolved substance is the chemical potential of this substance at the pressure and temperature considered, in a reference state chosen according to certain conventions in which the substance is attributed an activity of unity.

Now the chemical potential $\mu$ of a constituent can be expressed by the equation

$$(7) \qquad \mu = h - Ts,$$

in which *h* is the specific molar enthalpy of this constituent and *s* is its specific molar entropy, under the conditions of medium, pressure, temperature and concentration experienced by the constituent.

For the chemical reaction $\Sigma\nu M = 0$ we can write, on the basis of equations (5) and (7):

$$(8) \qquad -A = \Sigma \nu \mu = \Sigma \nu h - T \Sigma \nu s$$

or, representing the summation $\Sigma \nu x$ by the notation $\Delta X$:

$$(9) \qquad -A = \Delta G = \Delta H - T \Delta S,$$

in which G represents the free enthalpy $G = H - TS$; we point out, however, that although the X corresponding to $x = \mu$ is being represented more and more widely by the symbol G, it is still often represented by the symbol F used by G. N. Lewis and his collaborators.

Equation (9) can be written in particular for reagents and reaction products considered separately in the pure state and under the same conditions of temperature and pressure. For example, if we consider the reaction

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$$

representing the formation of liquid $H_2O$ starting from the substances $H_2$ and $O_2$ in the gaseous state, we have

$$\Delta G = \mu_{H_2O_{(l)}} - \mu_{H_{2(g)}} - \frac{1}{2} \mu_{O_{2(g)}}$$

---

(4) See *loc. cit.* [2], p. 9.

A very widely adopted convention consists of assigning the value zero to the chemical potentials of elements in their normal molecular state at 25°C and 1 atm. pressure. If $H_2$ and $O_2$ are both considered at 1 atm. pressure we have therefore,

$$\Delta G = \mu_{H_2O_{(l)}},$$

which shows that the free enthalpy of formation of liquid $H_2O$ starting from its elements at 25°C and 1 atm. is the same as the chemical potential of liquid $H_2O$, a substance which is then in its standard state.

In view of this, and taking into account equation (5), the condition for thermodynamic equilibrium of a chemical reaction, i.e. the condition which expresses that the affinity of such a reaction is zero, can be written

$$\Sigma \nu\mu = 0 \tag{10}$$

or, substituting into this equation the values of the chemical potentials $\mu$ shown in equation (6),

$$\Sigma \nu\mu^\circ + RT\,\Sigma \nu \ln(M) = 0 \tag{11}$$

or further, by replacing the ideal gas constant R by its numerical value, and changing from Napierian logarithms to decimal logarithms:

$$\Sigma \nu\mu^\circ + 4.575\,T\,\Sigma \nu \log(M) = 0 \tag{12}$$

that is

$$\boxed{\Sigma \nu \log(M) = -\frac{\Sigma \nu\mu^\circ}{4.575\,T}} \tag{13}$$

which can be written

$$\begin{array}{l}(14)\\ (15)\end{array}\qquad \boxed{\begin{aligned}\Sigma \nu \log(M) &= \log K,\\ \log K &= -\frac{\Sigma \nu\mu^\circ}{4.575\,T}\end{aligned}}\qquad \text{(5)}$$

Now the formulation

$$\Sigma \nu M = 0 \tag{2}$$

of a reaction equation is equivalent to the usual formulation

$$\nu'_1 M'_1 + \nu'_2 M'_2 + \ldots = \nu''_1 M''_1 + \nu''_2 M''_2 + \ldots. \tag{1}$$

The stoichiometric coefficients $\nu$ of the formulation (2) are usually considered as being positive for the substances M″ on the right-hand side of the usual formulation; they are considered as being negative for the substances M′ on the left-hand side. Equation (13) can therefore be expressed in the form

$$\log \frac{(M''_1)^{\nu''_1}.(M''_2)^{\nu''_2}\ldots}{(M'_1)^{\nu'_1}.(M'_2)^{\nu'_2}\ldots} = -\frac{\Sigma \nu\mu^\circ}{4.575\,T} \tag{16}$$

or

$$\frac{(M''_1)^{\nu''_1}.(M''_2)^{\nu''_2}\ldots}{(M'_1)^{\nu'_1}.(M'_2)^{\nu'_2}\ldots} = 10^{-\frac{\Sigma \nu\mu^\circ}{4.575\,T}} \tag{17}$$

---

(5) It would be as well to point out that the formulation (15) of the value of the equilibrium constant K is equivalent to the usual equation

$$\ln K = -\frac{\Sigma \nu\mu^\circ}{RT}$$

and to the equation

$$K = e^{\frac{A^\circ}{RT}},$$

in which $A^\circ$ is the standard affinity of the reaction, i.e. the affinity of the reaction in the particular case when all the reacting substances are in the standard state.

or

$$\boxed{\begin{aligned} &\frac{(M''_1)^{\nu''_1}.(M''_2)^{\nu''_2}\ldots}{(M'_1)^{\nu'_1}.(M'_2)^{\nu'_2}\ldots} = K, && (18)\\ &\log K = -\frac{\Sigma\nu\mu^{\circ}}{4.575T}. && (19)\end{aligned}}$$

Consequently for every chemical reaction $\Sigma\nu M = 0$, the equilibrium condition at a temperature T can be expressed by the equation

$$\Sigma\nu\log(M) = \log K, \tag{14}$$

i.e. the algebraic sum $\Sigma\nu\log(M)$ of the logarithms of the fugacities, and activities (M) of the gaseous and dissolved reacting substances is a constant which is the logarithm of an "equilibrium constant" K. The value of this equilibrium constant is connected with the values of the standard chemical potentials $\mu^{\circ}$ of the reacting substances and with the absolute temperature by the equation

$$\log K = -\frac{\Sigma\nu\mu^{\circ}}{4.575T}. \tag{15}$$

When the temperature is $t = 25{\cdot}0$°C, i.e. $T = 298{\cdot}1$°K, as is considered throughout this *Atlas*, equilibrium conditions (13), (14) and (15) become respectively

$$\boxed{\Sigma\nu\log(M) = -\frac{\Sigma\nu\mu^{0}}{1363},} \tag{20}$$

$$\boxed{\begin{aligned} \Sigma\nu\log(M) &= \log K, && (14)\\ \log K &= -\frac{\Sigma\nu\mu^{0}}{1363}, && (21)\end{aligned}}$$

in which $\mu^{\circ}$ represents the standard chemical potentials at 25°C of the reacting substances M.

Relation (20) [and relations (14) and (21) which are derived from it] is the *general formula for chemical equilibria* (or physicochemical ones) at 25°C.

This relation expresses that, when the equilibrium state of a chemical or physicochemical change is obtained at a given temperature and pressure, the algebraic sum $\Sigma\nu\log(M)$ of the logarithms of the fugacities and activities (M) of the gaseous and dissolved reacting substances is equal to a constant log K, whose value depends only on the temperature and pressure, and can be calculated from relation (21) if the values of the standard chemical potentials $\mu^{\circ}$ of all the reacting substances are known for the standard reference state, which is:

for condensed substances (solid or liquid), the pure state;
for gaseous substances, the state having a fugacity (or "corrected" partial pressure) of 1 atm.;
for dissolved substances, the state having an activity (or "corrected" molality) of 1 g-mol (or 1 g-ion) per kilogram of solvent.

Given below are some examples of the calculation of the equilibrium constant, for the four types of chemical reactions considered in paragraph 2.4, and also for the vaporization of water, based on the following standard chemical potentials $\mu^{\circ}$ at 25°C; (6)

| | | | |
|---|---|---|---|
| $H_2O$ (gaseous) | − 54 635 cal | $Fe(OH)_2$ (solid) | − 115 570 cal |
| $H_2$ (gaseous) | 0 „ | $Fe^{++}$ (dissolved) | − 20 300 „ |
| $O_2$ (gaseous) | 0 „ | $As_2O_3$ (solid) | − 137 680 „ |
| $H_2O$ (liquid) | − 56 690 „ | $HAsO_2$ (dissolved) | − 96 250 „ |
| $H^+$ (dissolved) | 0 „ | $CO_2$ (gaseous) | − 94 260 „ |
| $OH^-$ (dissolved) | − 37 595 „ | $H_2CO_3$ (dissolved) | − 149 000 „ |

---

(6) *Enthalpies libres de formation standard* (Rapport technique RT. 87 of CEBELCOR, 1960).

*Homogeneous reaction in the gaseous phase:*

$2H_2O_{(g)} = 2H_{2(g)} + O_{2(g)}$ :

$$\log \frac{(p_{H_2})^2 \cdot p_{O_2}}{(p_{H_2O})^2} = -\frac{2\mu^0_{H_2} + \mu^0_{O_2} - 2\mu^0_{H_2O}}{1\,363} = -\frac{0 + 0 + 109\,270}{1\,363}$$

$$= -80.16$$

[Guldberg and Waage's law of dissociation in the gaseous phase (mass-action law)].

*Homogeneous reaction in aqueous solution:*

$H_2O_{(l)} = H^+_{(aq.)} + OH^-_{(aq.)}$ :

$$\log C_{H^+} \cdot C_{OH^-} = -\frac{\mu^0_{H^+} + \mu^0_{OH^-} - \mu^0_{H_2O}}{1\,363} = -\frac{0 - 37\,595 + 56\,690}{1\,363}$$

$$= -14.00$$

(Oswald's law of electrolytic dissociation).

*Heterogeneous reactions—solid/solution type:*

$Fe(OH)_{2(s)} = Fe^{++}_{(aq.)} + 2\,OH^-_{(aq.)}$:

$$\log C_{Fe^{++}} \cdot (C_{OH^-})^2 = -\frac{\mu^0_{Fe^{++}} + 2\mu^0_{OH^-} - \mu^0_{Fe(OH)_2}}{1\,363} = -\frac{-20\,300 + 75\,190 + 115\,570}{1\,363}$$

$$= -14.73$$

(solubility product law);

$As_2O_{3(s)} + H_2O_{(l)} = 2HAsO_{2(aq.)}$ :

$$\log C_{HAsO_2} = -\frac{1}{2}\,\frac{2\mu^0_{HAsO_2} - \mu^0_{As_2O_3} - \mu^0_{H_2O}}{1\,363}$$

$$= -\frac{-192\,500 + 137\,680 + 56\,690}{2\,726} = -0.68$$

(solubility).

*Heterogeneous reaction—gas/solution type:*

$CO_{2(g)} + H_2O_{(l)} = H_2CO_{3(aq.)}$:

$$\log \frac{C_{H_2CO_3}}{p_{CO_2}} = -\frac{\mu^0_{H_2CO_3} - \mu^0_{CO_2} - \mu^0_{H_2O}}{1\,363}$$

$$= -\frac{-149\,000 + 94\,260 + 56\,690}{1\,363} = -1.43$$

(Henry's gas solubility law).

*Conversion from condensed phase (solid or liquid) to gaseous phase:*

$H_2O_{(l)} = H_2O_{(g)}$ :

$$\log p_{H_2O} = -\frac{\mu^0_{H_2O_{(g)}} - \mu^0_{H_2O_{(l)}}}{1\,363} = -\frac{-54\,635 + 56\,690}{1\,363} = -1.505.$$

that is

$$p_{H_2O} = 10^{-1.505}\ \text{atm.} = 0.0313\ \text{atm.} = 23.7\ \text{mm Hg}.$$

(vapour pressure law).

It is important that we should be well aware of the fact that *the different equilibrium laws which these equations express are only particular cases of a single law of physico-chemical equilibrium*

(14) $$\boxed{\Sigma \nu \log (M) = \log K,}$$

or

(21) $$\boxed{\log K = -\frac{\Sigma \nu \mu^0}{1\,363},}$$

in which the constant K is known by different names, according to the nature of the change that is being studied: Guldberg and Waage's constant (mass–action constant), Ostwald's constant (dissociation constant, ionic product of water), solubility product, solubility, Henry constant, vapour pressure. *The value of each of these equilibrium constants* K *is connected with the values of the standard free enthalpies formation (or standard chemical potentials)* $\mu^\circ$ *of the substances taking part in the change, by the same relation, which is at* 25°C:

$$\log K = -\frac{\Sigma \nu \mu^0}{1363}. \tag{21}$$

## 4. GENERAL FORMULA FOR ELECTROCHEMICAL EQUILIBRIA (7)

### 4.1. GALVANIC CELLS

We have defined an electrochemical reaction (or electrode reaction) as being a reaction involving both chemical substances M (neutral molecules and/or positively or negatively charged ions) and free electric charges (for instance negative electrons $e^-$ arising from a metal or other substance with metallic conduction):

$$\Sigma \nu M + n e^- = 0 \quad (^7) \qquad \text{for example} \quad Zn_{(s)} = Zn^{++}_{(aq.)} + 2e^-.$$

Such reactions can be brought about by the coupling of two electrodes at which take place respectively absorption and liberation of electrons, for instance according to the reactions

$$\begin{array}{l} \Sigma \nu_1 M_1 + n_1 e^- = 0, \\ \Sigma \nu_2 M_2 - n_1 e^- = 0, \end{array}$$

leading to the overall chemical reaction

$$\overline{\Sigma \nu_1 M_1 + \Sigma \nu_2 M_2 = 0.} \tag{22}$$

These galvanic cells may operate either without the external addition of electrical energy (in which case the overall chemical reaction takes place in the direction suggested by its affinity), or with the external addition of electrical energy (in which case the overall chemical reaction takes place in the opposite direction to that suggested by its affinity alone). In the first case, which is obtained in the discharge of batteries and accumulators and in the spontaneous corrosion of metals, there is oxidation at the negative electrode of the cell and reduction at the positive electrode(8); in the second case, which is obtained in electrolysis and in the charging of accumulators, there is reduction at the negative electrode and oxidation at the positive electrode; in the two cases we call the electrode where there is oxidation the *anode*, and the electrode where there is reduction the *cathode.*

For example (Figs. 2 and 3), the synthesis of water in a hydrogen/oxygen gas cell and the discharge of a zinc/copper Daniell cell take place according to the following reactions:

| | | |
|---|---|---|
| – ve Electrode (oxidation) | $2H_2 \rightarrow 4H^+ + 4e^-$ | $Zn \rightarrow Zn^{++} + 2e^-$ |
| + ve Electrode (reduction) | $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ | $Cu^{++} + 2e^- \rightarrow Cu$ |
| Overall reaction | $2H_2 + O_2 \rightarrow 2H_2O$ | $Zn + Cu^{++} \rightarrow Zn^{++} + Cu$ . |

---

(7) See *loc. cit.* [3], pp. 5–14.

(8) Here we call the electrode attached to the negative terminal of the cell the negative electrode, and the electrode attached to the positive terminal of the cell the positive electrode.

Conversely, the electrolysis of water and the charging of a Daniell cell take place as follows:

| | | |
|---|---|---|
| − ve Electrode (reduction) | $4H^+ + 4e^- \rightarrow 2H_2$ | $Zn^{++} + 2e^- \rightarrow Zn$ |
| + ve Electrode (oxidation) | $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ | $Cu \rightarrow Cu^{++} + 2e^-$ |
| Overall reaction | $2H_2O \rightarrow 2H_2 + O_2$ | $Zn^{++} + Cu \rightarrow Zn + Cu^{++}$. |

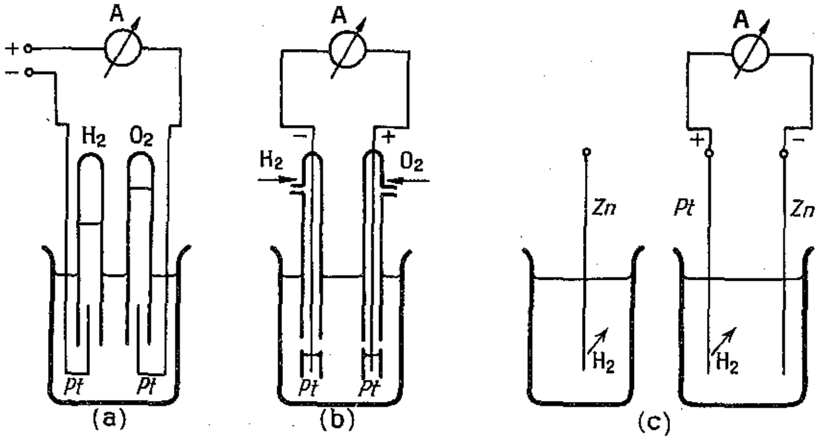


FIG. 2. Electrochemical realization of chemical reactions.

(*a*) Decomposition of water (electrolysis): $2H_2O \rightarrow 2H_2 + O_2$.
(*b*) Synthesis of water (gas cell): $2H_2 + O_2 \rightarrow 2H_2O$.
(*c*) Corrosion of zinc with the evolution of hydrogen: $Zn + 2H^+ \rightarrow Zn^{++} + H_2$.

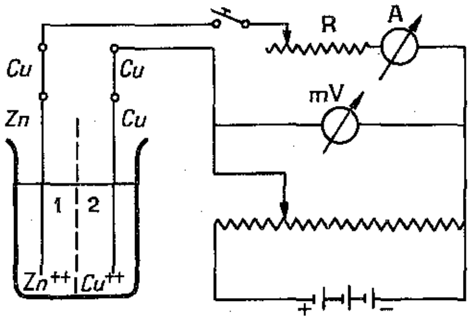


FIG. 3. Daniell cell.

### 4.2. EQUILIBRIUM POTENTIAL DIFFERENCE OF A GALVANIC CELL

The electromotive force of such galvanic cells is the potential difference $\varphi_1 - \varphi_2$ (⁹) (or tension at the terminals of the cell) when the cell is "on open circuit", and *when the whole system is in electrochemical equilibrium.* The value of this potential difference is connected with the value of the affinity $A_{1.2}$ of the overall chemical reaction (22) by the relation

$$\varphi_1 - \varphi_2 = -\frac{A_{1.2}}{n_1 F} \tag{23}$$

---

(⁹) $\varphi_1$ and $\varphi_2$ represent respectively the internal electric potentials of chemically identical terminals (both made of copper for instance) attached to the two electrodes of the cell. The electromotive force (or chemical tension) of the cell is $A_{1.2}/nF$.

or, since

$$A_{1,2} = -(\Sigma\nu_1\mu_1 + \Sigma\nu_2\mu_2), \tag{24}$$

$$\varphi_1 - \varphi_2 = \frac{\Sigma\nu_1\mu_1 + \Sigma\nu_2\mu_2}{n_1 F}. \tag{25}$$

This difference of electric potentials, or electric "tension", is the *equilibrium potential difference* of the galvanic cell.

If we express the electric potentials in volts and the chemical potentials $\mu$ in calories per mole, equation (25) becomes

$$\varphi_1 - \varphi_2 = \frac{\Sigma\nu_1\mu_1 + \Sigma\nu_2\mu_2}{23\,060\, n_1}. \tag{26}$$

Let us consider, for example, a Daniell cell in which the $Zn^{++}$ and $Cu^{++}$ ions are in the standard state (activities: 1 g-ion/l at 25°C), and for which the chemical potentials have the following values (according to Latimer):

$$\mu^0_{Zn} = 0 \text{ cal.,} \qquad \mu^0_{Cu} = 0 \text{ cal.,}$$
$$\mu^0_{Zn^{++}} = -35\,184 \text{ »} \qquad \mu^0_{Cu^{++}} = +15\,530 \text{ »}$$

Equation (22) gives

$$\varphi_{Zn} - \varphi_{Cu} = \frac{-35\,184 - 0 + 0 - 15\,530}{46\,120} = -\frac{50\,714}{46\,120} = -1.099 \text{ V}.$$

The potential at the terminals of this Daniell cell in the equilibrium state is 1·099 V; the zinc is the negative electrode, i.e. the copper wire which is attached to it is negative with respect to the other terminal of the cell.

### 4.3. ELECTRODE POTENTIAL. EQUILIBRIUM POTENTIAL OF AN ELECTROCHEMICAL REACTION

With a view to studying any electrochemical reaction $\Sigma\nu_1 M_1 + n_1 e^- = 0$, let us consider a galvanic cell of a special type (Fig. 4) made up of an electrode 1 on which is taking place the reaction that we wish to study, and a *reversible reference electrode* (hydrogen electrode, calomel electrode, silver chloride electrode) *on which the state of thermodynamic equilibrium of the electrochemical reference reaction is obtained.* It must be understood that this reference electrode is connected to the reaction solution by means of a siphon to avoid the existence of a diffusion potential between the two solutions (for instance

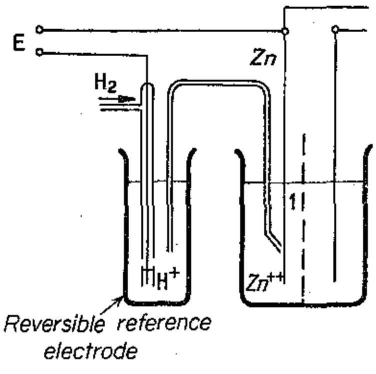


FIG. 4. Measurement of electrode potential. (Haber and Luggin's method.)

a siphon of agar-agar jelly saturated with KCl) and which, when an electric current flows in the reaction solution, *emerges in this solution in the immediate neighbourhood of the metallic surface on which the reaction to be studied is taking place* (Haber and Luggin's siphon or Piontelli's siphon). The equation

$$\varphi_1 - \varphi_{\text{ref}} = \frac{\Sigma \nu_1 \mu_1 + \Sigma \nu_{\text{ref}} \mu_{\text{ref}}}{23\,060\, n_1} \tag{27}$$

which is deduced from equation (24) gives the value of the equilibrium potential difference of the cell formed by coupling the electrode studied and the reference electrode, i.e. the value of the potential difference when the whole of the system is in electrochemical equilibrium. Now the reference electrode is, by definition, in a state of equilibrium. *Equation* (27) *therefore expresses the equilibrium condition of the electrochemical reaction studied.*

Consequently a general electrochemical reaction $r$, i.e. $\Sigma \nu_r \mathrm{M}_r + n_r e^- = 0$, will be in a state of equilibrium if the difference between the potential $\varphi$ of the electrode on which this reaction is taking place and the potential $\varphi_{\text{ref}}$ of a given (10) reversible reference electrode has a fixed value, given in

$$\varphi_r - \varphi_{\text{ref}} = \frac{\Sigma \nu_r \mu_r - \Sigma \nu_{\text{ref}} \mu_{\text{ref}}}{23\,060\, n_r}. \tag{28}$$

We shall call the difference of potential thus measured between an electrode and a reversible reference electrode the "potential" of this electrode, or *electrode potential* E, and we shall call this electrode potential the *equilibrium potential of a reaction* in the particular case when it corresponds to the state of equilibrium of an electrochemical reaction taking place on this electrode. If we use the symbol $\mathrm{E}_{0r}$ to denote the equilibrium potential of a reaction $r$ written in the form $\Sigma \nu_r \mathrm{M}_r + n_r e^- = 0$, equation (28) can be written

$$\mathrm{E}_{0r} = \frac{\Sigma \nu_r \mu_r - \Sigma \nu_{\text{ref}} \mu_{\text{ref}}}{23\,060\, n_r}. \tag{29}$$

If we use as a reference electrode the standard hydrogen electrode for which the chemical potentials of the constituents $\mathrm{H}^+$ (at pH = 0) and $\mathrm{H}_2$ (at 1 atm. pressure) are taken to be zero, the equilibrium condition (27) takes the simpler form

$$\boxed{\mathrm{E}_{0r} = \frac{\Sigma \nu_r \mu_r}{23\,060\, n_r}.} \tag{30}$$

Consequently, *for any given electrochemical reaction taking place under fixed physico-chemical conditions* (to which correspond fixed values of the chemical potentials $\mu_r$) *there exists a fixed value of the electrode potential at which the equilibrium state of the reaction is obtained.*

If we consider a metal–solution system at the interface of which an electrochemical reaction can occur (for example zinc in a zinc sulphate solution, in which the reaction $\mathrm{Zn} = \mathrm{Zn}^{++} + 2e^-$ can take place; or platinum in a solution of ferrous and ferric ions, in which the reaction $\mathrm{Fe}^{++} = \mathrm{Fe}^{+++} + e^-$ can take place; or any metal in a solution saturated with gaseous hydrogen, in which the reaction $\mathrm{H}_2 = 2\mathrm{H}^+ + 2e^-$ can take place), there exists a value of the electrode potential of the metal for which the equilibrium state of the reaction is obtained. When the potential of the metal has this value, the reaction cannot take place either in the oxidation direction or in the reduction direction: for example there can be neither corrosion nor electrodeposition of zinc, neither oxidation of ferrous ions nor reduction of ferric ions, neither evolution nor oxidation of hydrogen. For any other value of the electrode

---

(10) It is understood that this difference of potential is measured by Haber and Luggin's method mentioned above (Fig. 4). The electric potentials in question here are those of chemically identical terminals (e.g. copper) attached to the electrodes of the cell.

potential, the state of thermodynamic equilibrium will not be obtained, and it is possible, from the energetic point of view, for the reaction to take place, either in the oxidation direction (if the electrode potential is above the equilibrium potential of the reaction), or in the reduction direction (if the electrode potential is below this equilibrium potential).

As P. Van Rysselberghe has shown in his excellent *Introduction* to this *Atlas*, the *equilibrium potential* $E_0$ of an electrochemical reaction is equal to the *reduction affinity* per unit charge, i.e. the affinity of the chemical reaction obtained by combining, in the reduction direction, the electrochemical reaction studied with the electrochemical reference reaction.

For example, in the case of the reaction $Fe_{(s)} = Fe^{++}_{(aq.)} + 2e^-$ for which the standard equilibrium potential at 25°C, measured with respect to the standard hydrogen electrode, is $E^0_0 = -0{\cdot}440$ V, the reduction affinity, relating to the reaction $Fe^{++}_{(aq.)} + H_{2(g)} \rightarrow Fe_{(s)} + 2H^+_{(aq.)}$ taking place under standard conditions, is $-0{\cdot}440$ V; the oxidation affinity, relating to the reaction $Fe_{(s)} + 2H^+_{(aq.)} \rightarrow Fe^{++}_{(aq.)} + H_{2(g)}$ is $+0{\cdot}440$ V.

### 4.4. FORMULATION OF ELECTROCHEMICAL EQUILIBRIA

The equation

$$\boxed{E_0 = \frac{\Sigma \nu\mu}{23\,060\,n}} \tag{31}$$ (11)

(which gives in magnitude and sign the value of the equilibrium potential of a given electrochemical reaction $\Sigma \nu M + ne^- = 0$) expresses in short the condition of thermodynamic equilibrium of this reaction. Indeed, the affinity A of an electrochemical reaction can be expressed by the equation

$$A = -\Sigma \nu\mu + 23\,060\,n\,E \tag{32}$$

and the equation

$$\Sigma \nu\mu - 23\,060\,n\,E_0 = 0 \tag{33}$$

which is equivalent to equation (29) expresses that the affinity of the electrochemical reaction is zero at the equilibrium.

Equation (33) enables us to compare the equilibrium condition for chemical reactions and the equilibrium condition for electrochemical reactions:

| | Reactions | |
|---|---|---|
| | Chemical | Electrochemical |
| Reaction equation | $\Sigma \nu M = 0$ | $\Sigma \nu M + ne^- = 0$ |
| Equilibrium condition | $\Sigma \nu\mu = 0$ | $\Sigma \nu\mu - 23\,060\,nE = 0$ |

We see that in the same way that the equation of an electrochemical reaction differs from that of a chemical one only by the presence of a term which indicates the presence of free electrons $e^-$, the equilibrium condition of an electrochemical reaction differs from that of a chemical one only by the presence of a term which expresses the energetic influence of these electrons, in the form of an electrode potential E.

By manipulating equation (33) as we manipulated equation (8) relating to chemical equilibria, in paragraph 3, we obtain successively, by substituting fugacities and activities (M) and standard chemical potentials $\mu^{\circ}$:

$$\Sigma \nu\mu^{\circ} + 4.575\,T\,\Sigma \nu \log(M) - 23\,060\,n\,E = 0. \tag{34}$$

---

(11) Equation (31) is equation (30) in which the indices *r* have been omitted to simplify the discussion. However, all the symbols arising in this equation concern a definite electrochemical reaction.

which becomes at 25°C

$$\Sigma \nu \mu^0 + 1\,363\,\Sigma \nu \log(\mathrm{M}) - 23\,060\,n\mathrm{E} = 0 \tag{35}$$

or

$$\boxed{\begin{aligned} &\mathrm{E}_0 = \mathrm{E}_0^0 + \frac{0,0591}{n}\,\Sigma \nu \log(\mathrm{M}), && (36)\\ &\mathrm{E}_0^0 = \frac{\Sigma \nu \mu^0}{23\,060\,n}, && (37)\end{aligned}}$$

in which

$\mathrm{E}_0$ is the *equilibrium potential* of the electrochemical reaction;
$\mathrm{E}_0^0$ is the *standard equilibrium potential* of the reaction at 25°C, i.e. its equilibrium potential for the particular case in which all the reacting substances are in the standard state at 25°C: fugacity, 1 atm. for gaseous substances; activity, 1 g-mol/l (or 1 g-ion/kg of water) for dissolved substances.

The value of the standard equilibrium potential $\mathrm{E}_0^0$ can easily be calculated from equation (37) if we know the standard chemical potentials $\mu^\circ$ of all the substances taking part in the reaction.

Given below are some examples of standard equilibrium potentials and the corresponding equilibrium formulae, based on the following values of standard chemical potentials $\mu^\circ$ (6):

| | | | |
|---|---|---|---|
| $Fe^{++}$ (dissolved) | – 20 300 cal | $H_2O$ (liquid) | – 56 690 cal |
| $Fe^{+++}$ (dissolved) | – 2 530 „ | $O_2$ (gaseous) | 0 „ |
| $Fe$ (solid) | 0 „ | $H^+$ (dissolved) | 0 „ |

*Homogeneous reaction in aqueous solution:*

$\mathrm{Fe}^{++}_{(\mathrm{aq.})} = \mathrm{Fe}^{+++}_{(\mathrm{aq.})} + e^-$ :

$$\mathrm{E}_0^0 = \frac{\mu^0_{\mathrm{Fe}^{+++}} - \mu^0_{\mathrm{Fe}^{++}}}{23\,060} = \frac{-2\,530 + 20\,300}{23\,060} = +0.771 \text{ V}.$$

$$\mathrm{E}_0 = +0.771 + 0.0591 \log \frac{(\mathrm{Fe}^{+++})}{(\mathrm{Fe}^{++})} \quad (\text{volt}) \qquad \text{(redox tension)}$$

*Solid/solution reaction:*

$\mathrm{Fe}_{(\mathrm{s})} = \mathrm{Fe}^{++}_{(\mathrm{aq.})} + 2e^-$ :

$$\mathrm{E}_0^0 = \frac{\mu^0_{\mathrm{Fe}^{++}} - \mu^0_{\mathrm{Fe}}}{23\,060 \times 2} = \frac{-20\,300 - 0}{46120} = -0.440 \text{ V},$$

$$\mathrm{E}_0 = -0.440 + 0.0295 \log(\mathrm{Fe}^{++}) \quad (\text{volt}) \qquad \text{(metal solution tension)}$$

*Gas/solution reaction:*

$2\mathrm{H_2O}_{(l)} = \mathrm{O}_{2(g)} + 4\mathrm{H}^+_{(\mathrm{aq.})} + 4e^-$ :

$$\mathrm{E}_0^0 = \frac{\mu^0_{\mathrm{O}_2} + 4\mu^0_{\mathrm{H}^+} - 2\mu^0_{\mathrm{H_2O}}}{23\,060 \times 4} = \frac{0 + 0 + 113\,380}{92\,240} = +1.228 \text{ V}.$$

$$\mathrm{E}_0 = +1.228 - 0.0591\,\mathrm{pH} + 0.0148 \log p_{\mathrm{O}_2} \quad (\text{volt}) \qquad \text{(gas electrode tension)}$$

It follows from the above that the *redox tensions* (or "redox potentials"), the *metal solution tensions* (or "metal solution potentials") and the *gas electrode tensions* (or "gas electrode potentials") are only three particular cases of the *equilibrium tension of an electrochemical reaction.*

## 5. CONSTRUCTION OF POTENTIAL–pH EQUILIBRIUM DIAGRAMS(¹²)

In view of the above we shall now show how to proceed with the construction of potential–pH equilibrium diagrams. We shall consider, by way of an example, the particular case of the system iron–water at 25°C, which is treated in detail in Section 12.1 of Chapter IV.

### 5.1. STANDARD CHEMICAL POTENTIALS

We draw up a list of all the substances that we propose to consider and find out from chemical literature the values of the standard chemical potentials $\mu^\circ$ of all these substances. Except where indicated, these values have been taken from Latimer.(*) We make a table of these values (in small calories) grouping separately the condensed substances (solid substances and liquid substances other than water), the solvent (water) and the dissolved substances, and the gaseous substances. In each of these groups we classify the derivatives of the element considered in order of increasing oxidation number Z. In the case of hydroxides or other hydrated oxides, the chemical potentials are preferably calculated for the anhydrous oxide which would have the same stability(¹³); when the same oxide exists in different forms (allotropic modifications, or differently hydrated oxides) we classify these forms in order of decreasing stability, i.e. in order of increasing value of chemical potential calculated for the same chemical formula (which is the anhydrous form here), and we label these forms by the indices *a*, *b*, *c*, . . .

Concerning the values accepted for the standard chemical potentials, we indicate their degree of accuracy by writing in italics the figures which cannot reasonably be considered exact, the last of the figures not in italics nevertheless being subject to caution.

For example, here are the values of the standard chemical potentials $\mu^\circ$ which we have taken in the case of iron:

| Oxidation Number (Z). | Solid Substances | | Solvent and dissolved Substances | |
|---|---|---|---|---|
| – | – | – | $H_2O$ | — 56 690 cal. |
| – | – | – | $H^+$ | 0 » |
| 0 | Fe | 0 cal. | – | – |
| +2 | FeO hydr. ($Fe(OH)_2$) | — 58 88*0* » | $Fe^{++}$ | — 20 3*00* » |
| » | – | – | $HFeO_2^-$ | — 90 627 » |
| +2.67 | $Fe_3O_4$ | —242 *400* » | – | – |
| +3 | *a*. $Fe_2O_3$ | —177 *100* » | $Fe^{+++}$ | — 2 *530* » |
| » | *b*. $Fe_2O_3$ hydr. ($Fe(OH)_3$) | —161 *930* » | $FeOH^{++}$ | — 55 9*10* » |
| » | – | – | $Fe(OH)_2^+$ | —106 *200* » |
| +6 | – | – | $FeO_4^{--}$? | —11*1 685* » |

### 5.2. REACTIONS

We write the equations of the various reactions in which these substances can take part two by two in the manner shown in paragraph 2 above, i.e. possibly introducing, apart from these two substances A and B, water $H_2O$, the $H^+$ ion, and the free electric charge $e^-$.

---

(¹²) A similar account giving in detail the method of construction of the potential–pH equilibrium diagram relating to the system copper–water, has been published elsewhere (*Leçons sur la corrosion électrochimique* (3ᵉ fascicule), pp. 28–34, Rapport technique RT.49 of CEBELCOR, 1957).

(¹³) The chemical potential of this anhydrous oxide is calculated by adding to the chemical potential of the hydrated oxide as many times 56 690 cal. (i.e. $-\mu^0_{H_2O\,(\mathrm{liquid})}$) as there are water molecules in the chemical formula of the hydrated oxide. For example $\mu^0_{Fe(OH)_2} = -115\,570$ cal. corresponds to $\mu^0_{FeO} = -115\,570 + 56\,690 = -58\,880$ cal.

(*) W. M. LATIMER, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd. ed., Prentice-Hall, New York, 1952; *Recent References to Thermodynamic Data*, University of California, 1954.

These reaction equations will therefore have the following general form:

$$a\mathrm{A} + c\mathrm{H_2O} + n\,e^- = b\mathrm{B} + m\mathrm{H^+}\ \ (^{14}).$$

We group these reactions as follows according to the physical state of the substances A and B, indicating, for each reaction, the oxidation numbers Z of the element in each of these two forms:

*a.* homogeneous reactions (two dissolved forms);
*b.* heterogeneous reactions involving two condensed substances (generally two solid forms);
*c.* heterogeneous reactions involving one condensed substance (generally solid) and one dissolved substance.

When the system considered includes substances in the gaseous state, we also consider all or some of the groups of reactions below (group *d* will not be considered when there is only one substance in the gaseous state):

*d.* heterogeneous reactions involving two gaseous substances;
*e.* heterogeneous reactions involving one gaseous substance and one dissolved substance;
*f.* heterogeneous reactions involving one gaseous substance and one condensed substance (generally solid).

In each of these groups, we consider separately the chemical reactions, in which the forms A and B have the same oxidation number Z and in which electrons $e^-$ do not appear (the coefficient *n* of the electron is then equal to zero), and the electrochemical reactions in which the forms A and B have different oxidation numbers, and in which electrons appear (the coefficient *n* is then not equal to zero).

In each of these groups the chemical reactions are classified in order of increasing oxidation number; the electrochemical reactions are classified in increasing oxidation number of the least oxidized form, and following this successively in increasing oxidation number of each of the more oxidized forms in turn.

Each reaction is given an identification number, with the intention that we reject those reactions which, at a later stage of the work, appear to present no practical interest.

Thus we have below the reactions that we considered in the case of iron(15):

(*a*) *Homogeneous reactions* (two dissolved forms):

| Z | n° | |
|---|---|---|
| $+2$ | 1. | $\mathrm{Fe^{++}} + 2\mathrm{H_2O} = \mathrm{HFeO_2^-} + 3\mathrm{H^+}$ |
| $+3$ | 2. | $\mathrm{Fe^{+++}} + \mathrm{H_2O} = \mathrm{FeOH^{++}} + \mathrm{H^+}$ |
| » | 3. | $\mathrm{FeOH^{++}} + \mathrm{H_2O} = \mathrm{Fe(OH)_2^+} + \mathrm{H^+}$ |
| $+2 \rightarrow +3$ | 4. | $\mathrm{Fe^{++}} = \mathrm{Fe^{+++}} + e^-$ |
| » | 5. | $\mathrm{Fe^{++}} + \mathrm{H_2O} = \mathrm{FeOH^{++}} + \mathrm{H^+} + e^-$ |
| » | 6. | $\mathrm{Fe^{++}} + 2\mathrm{H_2O} = \mathrm{Fe(OH)_2^+} + 2\mathrm{H^+} + e^-$ |
| » | 7. | $\mathrm{HFeO_2^-} + \mathrm{H^+} = \mathrm{Fe(OH)_2^+} + e^-$ |
| $+2 \rightarrow +6$ | 8. | $\mathrm{HFeO_2^-} + 2\mathrm{H_2O} = \mathrm{FeO_4^{--}} + 5\mathrm{H^+} + 4e^-$ |
| $+3 \rightarrow +6$ | 9. | $\mathrm{Fe^{+++}} + 4\mathrm{H_2O} = \mathrm{FeO_4^{--}} + 8\mathrm{H^+} + 3e^-$ |
| » | 10. | $\mathrm{FeOH^{++}} + 3\mathrm{H_2O} = \mathrm{FeO_4^{--}} + 7\mathrm{H^+} + 3e^-$ |
| » | 11. | $\mathrm{Fe(OH)_2^+} + 2\mathrm{H_2O} = \mathrm{FeO_4^{--}} + 6\mathrm{H^+} + 3e^-$ |

---

(14) By the convention discussed in paragraph 2, this equation can represent equally well the oxidation

$$a\mathrm{A} + c\mathrm{H_2O} + n\,e^- \leftarrow b\mathrm{B} + m\mathrm{H^+}$$

and the reduction

$$a\mathrm{A} + c\mathrm{H_2O} + n\,e^- \rightarrow b\mathrm{B} + m\mathrm{H^+}$$

(15) In the equations below, the chemical symbols in heavy type represent solid substances; the symbols in normal type represent water and substances dissolved in aqueous solution.

(*b*) *Heterogeneous reactions involving two solid substances:*

| | | |
|---|---|---|
| $0 \rightarrow +2$ | 12. | $\mathbf{Fe} + H_2O = \mathbf{FeO} + 2H^+ + 2e^-$ |
| $0 \rightarrow +2.67$ | 13. | $3\mathbf{Fe} + 4H_2O = \mathbf{Fe_3O_4} + 8H^+ + 8e^-$ |
| $0 \rightarrow +3$ | 14. | $2\mathbf{Fe} + 3H_2O = \mathbf{Fe_2O_3} + 6H^+ + 6e^-$ |
| $+2 \rightarrow +2.67$ | 15. | $3\mathbf{FeO} + H_2O = \mathbf{Fe_3O_4} + 2H^+ + 2e^-$ |
| $+2 \rightarrow +3$ | 16. | $2\mathbf{FeO} + H_2O = \mathbf{Fe_2O_3} + 2H^+ + 2e^-$ |
| $+2.67 \rightarrow +3$ | 17. | $2\mathbf{Fe_3O_4} + H_2O = 3\mathbf{Fe_2O_3} + 2H^+ + 2e^-$ |

(*c*) *Heterogeneous reactions involving one solid substance and one dissolved substance:*

| | | |
|---|---|---|
| $+2$ | 18. | $Fe^{++} + H_2O = \mathbf{FeO} + 2H^+$ |
| » | 19. | $\mathbf{FeO} + H_2O = HFeO_2^- + H^+$ |
| $+3$ | 20. | $2Fe^{+++} + 3H_2O = \mathbf{Fe_2O_3} + 6H^+$ |
| » | 21. | $2FeOH^{++} + H_2O = \mathbf{Fe_2O_3} + 4H^+$ |
| » | 22. | $2Fe(OH)_2^+ = \mathbf{Fe_2O_3} + H_2O + 2H^+$ |
| $0 \rightarrow +2$ | 23. | $\mathbf{Fe} = Fe^{++} + 2e^-$ |
| » | 24. | $\mathbf{Fe} + 2H_2O = HFeO_2^- + 3H^+ + 2e^-$ |
| $0 \rightarrow +3$ | 25. | $\mathbf{Fe} = Fe^{+++} + 3e^-$ |
| $+2 \rightarrow +2.67$ | 26. | $3Fe^{++} + 4H_2O = \mathbf{Fe_3O_4} + 8H^+ + 2e^-$ |
| » | 27. | $3HFeO_2^- + H^+ = \mathbf{Fe_3O_4} + 2H_2O + 2e^-$ |
| $+2 \rightarrow +3$ | 28. | $2Fe^{++} + 3H_2O = \mathbf{Fe_2O_3} + 6H^+ + 2e^-$ |
| » | 29. | $2HFeO_2^- = \mathbf{Fe_2O_3} + H_2O + 2e^-$ |

### 5.3. EQUILIBRIUM CONDITIONS FOR THE REACTIONS

For each of these reactions we evaluate the equilibrium condition, by applying the following equations, established in paragraph 3 and 4.4:

for *chemical reactions:*

$$\boxed{\Sigma \nu \log(M) = \log K, \quad \text{where} \quad \log K = -\frac{\Sigma \nu \mu^0}{1363},}$$

for *electrochemical reactions:*

$$\boxed{E_0 = E_0^0 + \frac{0.0591}{n} \Sigma \nu \log(M), \quad \text{where} \quad E_0^0 = \frac{\Sigma \nu \mu^0}{23\,060 n}}$$

and we write these equations in such a way as to make explicit the influence of pH, which occurs implicitly in the term $\Sigma \nu \log(M)$.

In the case of *chemical reactions* written in the form

$$aA + cH_2O = bB + mH^+, \tag{38}$$

in which B is the alkaline form and A is the acid form of the element in question, the condition for equilibrium will be of the form

$$\log \frac{(B)^b}{(A)^a} = \log K + m\,pH \tag{39}$$

and, in the most common case when $a = b = 1$, and the reaction is $A + cH_2O = B + mH^+$

$$\log \frac{(B)}{(A)} = \log K + m\,pH. \tag{40}$$

This equation shows that the ratio of the fugacity (or activity) of the alkaline form to the fugacity (or activity) of the acid form increases linearly with the pH.

In the case of *electrochemical reactions* written in the form

$$a\,\mathrm{A} + c\,\mathrm{H_2O} + n\,e^- = b\,\mathrm{B} + m\,\mathrm{H^+}, \tag{41}$$

in which A is the oxidized form and B the reduced form of the element in question, the condition for equilibrium will be of the form

$$\mathrm{E_0} = \mathrm{E_0^0} - \frac{0.0591\,m}{n}\,\mathrm{pH} + \frac{0.0591}{n}\log\frac{(\mathrm{A})^a}{(\mathrm{B})^b} \tag{42}$$

and in the most common case when $a = b = 1$, and the reaction is $\mathrm{A} + c\mathrm{H_2O} + ne^- = \mathrm{B} + m\mathrm{H^+}$

$$\mathrm{E_0} = \mathrm{E_0^0} - \frac{0.0591\,m}{n}\,\mathrm{pH} + \frac{0.0591}{n}\log\frac{(\mathrm{A})}{(\mathrm{B})}. \tag{43}$$

It is as well to note that the fugacity (or activity) of the oxidized form A occurs *in the numerator* of the term log (A)/(B): the equilibrium tension $\mathrm{E_0}$, increases when the percentage of the oxidized form increases.

The equilibrium formulae for the twenty-nine reactions quoted in paragraph 5.2 can be found in paragraph 2 of section 12.1 of Chapter IV (p. 308).

In the particular case of solid substances existing in different varieties having different free formation enthalpies (labelled in 5.1 by the indices *a*, *b*, *c*, ...) we label the corresponding equilibrium constants and standard tensions with these same indices [see, for example, equations (17) and (20) concerning anhydrous $\mathrm{Fe_2O_3}$ and hydrated $\mathrm{Fe_2O_3}$ (or $\mathrm{Fe(OH)_3}$)].

Finally, if we put (A) = (B) in equilibrium relations of the type (40) or (42), we obtain the following equations which express the conditions of pH and electrode potential for which the activities (or the fugacities) of these two forms are equal(16), being valid for the case when the forms A and B of the element in question are either both in the dissolved state or both in the gaseous state:

$$\mathrm{pH} = \frac{1}{m}\log\mathrm{K}, \tag{44}$$

$$\mathrm{E_0} = \mathrm{E_0^0} - \frac{0.0591\,m}{n}\,\mathrm{pH}. \tag{45}$$

Such equations, concerning the reactions between the dissolved forms of iron according to reactions (1)–(11) are given under numbers 1′–11′ of paragraph 2 of section 12.1 of Chapter IV (p. 309).

### 5.4. CONSTRUCTION OF THE EQUILIBRIUM DIAGRAMS

Considering the electrode potential and the pH as independent variables and the logarithmic function of the concentrations and/or pressures of the substances A and B as a parameter, we can now proceed to establish potential-pH equilibrium diagrams on millimetre paper on which we have previously drawn the lines *a* and *b*:

$$\mathrm{E_{0\it a}} = 0.000 - 0.0591\ \mathrm{pH}\quad(\text{volt})\qquad(\text{line } a)$$
$$\mathrm{E_{0\it b}} = 1.228 - 0.0591\ \mathrm{pH}\quad(\text{volt})\qquad(\text{line } b)$$

which express respectively the reduction equilibrium of water according to the reaction $\mathrm{H_2} = 2\mathrm{H^+} + 2e^-$ (*a*) and its oxidation equilibrium according to the reaction $2\mathrm{H_2O} = \mathrm{O_2} + 4\mathrm{H^+} + 4e^-$ (*b*) at a hydrogen or oxygen pressure of 1 atm.

---

(16) These simple relationships can only be applied when the formulae of the two substances A and B refer to the same number of atoms of the substance under consideration, e.g. $\mathrm{Fe^{++}/Fe^{+++}}$. For example this is not the case for the systems $\mathrm{Cr_2O_7/Cr^{+++}}$ or $\mathrm{N_2/NO}$; relationships have to be modified by allowing for the total concentration C (or activity) of the element in the two forms in solution $\mathrm{Cr_2O_7^{--} + Cr^{+++}}$) or the total pressure P (or fugacity) of the two gaseous forms ($\mathrm{N_2 + NO}$).

The drawing of lines expressing the conditions under which the concentrations (or activities) of the two dissolved substances are equal [equations (1′)–(11′) relating to iron] enables us to represent in Fig. 1 (section 12.1 of Chapter IV) the *domains of relative predominance of the dissolved forms in question:* $Fe^{++}$, $HFeO_2^-$, $FeOH^{++}$, $Fe(OH)_2^+$ and $FeO_4^{--}$.

The drawing of lines which express the equilibrium conditions for two solid substances [equations (12)–(17)] enables us to represent the *domains of relative stability of the solid substances in question.* Such a representation can be made, not only for stable equilibria ($Fe/Fe_3O_4/Fe_2O_3$), but also for unstable equilibria [$Fe/Fe(OH)_2/Fe(OH)_3$].

By superimposing these two diagrams, we can easily pick out the conditions of potential and pH under which a given solid substance and a given dissolved substance can be simultaneously stable. By giving a definite value (for instance zero) to the logarithmic term which, in the equilibrium equation for this solid substance and this dissolved substance [relations (18)–(29)], expresses the value of the concentration (or activity) of the dissolved substance (for instance $10^0 = 1$ g-ion/l), we define a line which represents the conditions under which the *solubility* of the solid substance considered, in the dissolved form considered, has this value. In this way it is easy to draw, step by step, a line which represents the locus of the points of the diagram for which the *solubility of the different solid substances in all the different dissolved forms* has the same value. It is often useful to establish such "equisolubility" lines for different solubility values (for example, $10^0$, $10^{-2}$, $10^{-4}$ and $10^{-6}$ g-atm. of the element considered per kilogram of water([17])). We thus obtain, after omitting those lines or parts of lines which have no practical interest, figures such as Figs. 4 and 5 which are two electrochemical equilibrium diagrams for the systems $Fe–H_2O$; Fig. 4 represents only stable equilibria; Fig. 5 represents, with regard to $Fe(OH)_2$ and $Fe(OH)_3$, unstable equilibria.

It is as well to note that each of the lines indicating the solubility of the different condensed substances in all the different dissolved forms changes direction abruptly at the places where the composition of the system changes abruptly (for example in Fig. 4, when we pass from the domain of relative stability of Fe to the domain of relative stability of $Fe_3O_4$); these lines change direction progressively when the composition of the system changes progressively, that is in the neighbourhood of the lines which separate the domains of relative predominance of the dissolved substances (for example $Fe^{++}$ and $Fe^{+++}$). The drawing of these curved portions of the equisolubility lines can be done by a graphical method that we have described elsewhere([18]). These equal solubility lines therefore have sharp points at the limits of the domains of stability of the condensed substances, they have gradual curves near the limits of the domains of predominance of the dissolved substances.

Such diagrams are valid only for solutions in the presence of which the metal or metalloid considered can exist only in the forms that have been considered in establishing the diagram. When the solutions contain substances capable of forming soluble complexes with the metal or metalloid (for instance cyanides forming ferro- and ferricyanides) or insoluble salts (for instance phosphates forming ferrous and ferric phosphates), it is necessary to modify the diagram by adding to it a representation of the stability conditions of these dissolved or solid substances. It is then necessary to establish diagrams for systems which are not binary such as $Fe—H_2O$, but ternary such as $Fe—CN^-—H_2O$ or $Fe—PO_4^{---}—H_2O$.

---

([17]) We shall often use, from the point of view of simplification, the fact that solubilities expressed per litre of aqueous solution are almost the same as solubilities expressed per kilogram of water.

([18]) *Leçons sur la corrosion électrochimique*, 2^e^ fascicule (Rapport technique RT. 30 of CEBELCOR, 1956, pp. 22 and 23).

## CHAPTER III

# USE OF POTENTIAL–pH EQUILIBRIUM DIAGRAMS

## SECTION 1

# GENERALITIES

M. Pourbaix

In the important preface that R. Piontelli has kindly written for this *Atlas*, he has brought out the practical significance of potential–pH equilibrium diagrams and has pointed out the limitations which we must be aware of when using them. In the accounts which follow, the reader will find some examples of the application of these diagrams to the study of concrete problems of inorganic chemistry, analytical chemistry, corrosion, electrodeposition and geology. Elsewhere can be found some examples of their application to catalysis(1) and the study of batteries and accumulators(2).

We shall therefore be very brief here, and content ourselves with reviewing a few particularly important fundamental ideas.

We know well the tremendous scope given to chemistry by *chemical thermodynamics*, which is the science of the application of energetics to chemistry and is based on the concept of chemical equilibrium. Chemical thermodynamics, whose fundamental basis was established around 1876 by J. Willard Gibbs, and whose applications have greatly developed since the beginning of this century, has enabled us to understand a large number of formerly mysterious chemical phenomena; it has allowed us to predict certain facts prior to experiment; and it has greatly helped in the perfection of numerous processes of chemistry and metallurgy.

*Electrochemical thermodynamics* can, within limits, provide for electrochemistry a help analogous to that provided for chemistry by chemical thermodynamics. The potential–pH equilibrium diagrams have the essential purpose of supplying a thermodynamic framework for electrochemical reactions involving an aqueous solution.

In electrochemistry as in chemistry, the fact that a reaction is thermodynamically possible does not entail that this reaction actually takes place. Such a conformity between theoretical possibility and reality exists only for reactions which are practically reversible; the world of electrochemical reactions is full of irreversible changes which, like many chemical reactions can take place only on the condition that there is an appreciable affinity, and their speed is influenced by the presence of catalysts; the chemical synthesis of water, although thermodynamically possible between 25° and 100°C, generally takes place only extremely slowly under these conditions, and can be accelerated by the presence of catalysts such as platinum; similarly, the electrochemical synthesis of water, which occurs in a hydrogen/oxygen gas cell, takes place only in a very irreversible manner at these temperatures and is affected by the catalytic action of the metals constituting the electrodes.

Electrochemical reactions (or electrode reactions) differ from chemical reactions in that they involve, apart from chemical reagents, an electric reagent (the negative electron) which acts at the

---

(1) M. Pourbaix, *Sur l'interpretation thermodynamique des courbes de polarisation* (Rapport technique RT.1 of CEBELCOR, 1952). The utility of thermodynamic Interpretation of Polarization Curves—J. Electrochem. Soc. *101*, 217–221c (1954).

(2) See the work of Commission No. 6 of CITCE, *Batteries and Accumulators*, presided over by J. P. Brenet.

interface between a metal (or another phase with metallic conduction) and a solution of electrolytes. This fact has a fundamental consequence from the experimental point of view: the affinity of the reaction can be measured in magnitude and sign by an *electrode potential*, or rather by the difference E—$E_0$ between the electrode potential E of the metallic surface and the equilibrium potential $E_0$ of the reaction; if these two potentials are *equal*, the affinity is zero and the state of *thermodynamic equilibrium* of the reaction is obtained; if the electrode potential is *above the equilibrium potential*, the affinity is positive and the reaction can take place only in the *oxidation* direction; if the electrode potential is *below the equilibrium potential*, the affinity is negative and the reaction can take place only in the *reduction* direction. If we denote the speed of the electrochemical reaction by the magnitude $i$ of the electric current which corresponds to it by Faraday's Law, considering this reaction current to be positive in the case of oxidation and negative in the case of reduction, the relations above between the sign of the difference in potentials E—$E_0$ (which we can define to be the *overpotential* of the reaction on the electrode studied) and the direction of the reaction can be expressed by the inequality

$$\boxed{(E - E_0)\, i \geqq 0}$$

according to which the reaction current $i$ is always either zero, or of the same sign as the overpotential E—$E_0$.(³)

Consequently, if we wish to know in which direction a certain electrochemical reaction of known equilibrium potential will proceed on a metallic surface in contact with an aqueous solution, it is sufficient to measure the electrode potential of this surface and compare the value of this electrode potential with the value of the equilibrium potential of this reaction. This is true, not only in the particular case in which a single reaction is possible, but also in the general case in which several reactions can occur. If we know the potential–pH equilibrium diagrams for such a set of reactions, we can pick out the point on these diagrams which represents the conditions of potential and pH of the interface studied; all those reactions whose equilibrium potentials are below the potential of this point can take place only in the oxidation direction; all those reactions whose equilibrium potentials are above the potential of this point can take place only in the reduction direction.

If, for example, we consider a surface of iron and ferric oxide $Fe_2O_3$ immersed in an aerated aqueous solution of pH = 4 containing $10^{-4}$ g-at Fe/l (6·0 mg/l), and if this iron surface has an electrode potential of $-0{\cdot}20$ V, the electrochemical equilibrium diagram for iron (Fig. 4 of section 12.1, Chapter IV) leads to the following conclusions: the iron tends to corrode according to the reaction $Fe \rightarrow Fe^{++} + 2e^-$ (23) without evolution of hydrogen, but with reduction of oxygen according to the reaction $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (*b*) and with reduction of ferric oxide according to the reaction $Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{++} + 3H_2O$ (28).(⁴)

If, for this same pH and potential the solution contains hydrogen peroxide, the latter will tend to be reduced to water according to the reaction $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (2) (see Section 1.2, Chapter IV); if the solution contains cupric ions, a cement of copper can be formed by the reduction $Cu^{++} + 2e^- \rightarrow Cu$ (15) (see section 14.1, Chapter IV); if it contains a chromate, a deposit of $Cr_2O_3$ capable of passivating the metal can be formed by the reduction $2CrO_4^{--} + 10H^+ + 6e^- \rightarrow Cr_2O_3 + 5H_2O$ (54) (see section 10.1, Chapter IV).

It must be understood that the electrode potentials and pH considered here are the characteristics of a metal/solution interface, and not of some other part of the metal or solution. In the very frequent

---

(³) A detailed account of this is outside the scope of the present Treatise; see principally M. Pourbaix, Thesis, Delft, 1945 (*loc. cit.*), and *Vue d'ensemble sur le comportement électrochimique des métaux* (2ᵉ partie) (Recueils de Mémoires RM. 5 of CEBELCOR, 1953).

The relation $(E - E_0)i \geqslant 0$ results from the adaptation to electrochemical reactions of De Donder's relation $Av \geqslant 0$ which connects the direction of a chemical reaction (fixed by the sign of its speed $v$) with the sign of its affinity A.

(⁴) The numbers in brackets are those under which these reactions have been classified in Chapter IV in section 12.1 for iron, section 1.2 for hydrogen peroxide, section 14.1 for copper, and section 10.1 for chromium.

case in which the metal or solution is the site of electric currents or chemical changes, it is necessary to make sure that the chemical composition assumed for the solution (and consequently its pH) is that of the fraction of the solution in direct contact with the metal, since this composition can differ greatly from the mean composition of the solution; careful note must also be taken that the electrode potential of the metal is measured in such a way as to avoid any effects of ohmic fall or diffusion potential; for this purpose, it is best to use Haber and Luggin's capillary siphon method or Piontelli's method.

Finally, we cannot insist too much on the fact that the equilibrium diagrams discussed here can only, by themselves, solve a very limited number of problems, as Piontelli has made very clear in the final part of his preface. They are only tools at the disposal of the electrochemist and they must always be used in conjunction with other means of investigation. Among these means, a particularly important place is held by studies of electrochemical kinetics, which are based on the experimental determination of potential–current curves (for example by intensiostatic or potentiostatic methods) and which enable us to establish the laws connecting the speed *i* of an electrochemical reaction and its affinity $E—E_0$.(5) A bright future can be predicted for groups of investigators who are competent at the same time in thermodynamics, kinetics, and physics and physical chemistry of metals.

---

(5) See *loc. cit.* (1).

## SECTION 2

# GENERAL CHEMISTRY

G. VALENSI

### SUMMARY

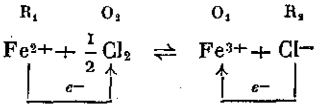
## 1. INTRODUCTION

*The electrochemical diagram* of an element summarizes in an extremely condensed form the most salient features of its solution chemistry. To cover such a vast domain necessarily requires a certain complexity of the diagrams, the basic features of which may thus escape a first examination.

It is perhaps not superfluous, therefore, before considering some concrete examples, to remind the reader of certain concepts introduced in the preceding articles, but at the same time relating them more directly to chemical considerations.

## 2. REDOX COUPLES

Solution reactions, in particular those of inorganic chemistry, very often involve a transfer of electrons $e^-$ from a reducing agent $R_1$ to an oxidizing agent $O_2$. The possibility of the reverse process under different conditions implies that $R_1$ is converted into a conjugate oxidizing agent $O_1$ while $O_2$ is converted into a conjugate reducing agent $R_2$. Thus the action of chlorine on ferrous salts can be represented by the scheme:



$$\overset{R_1}{Fe^{2+}} + \overset{O_2}{\tfrac{1}{2}Cl_2} \rightleftharpoons \overset{O_1}{Fe^{3+}} + \overset{R_2}{Cl^-}$$

In general, if the stoichiometric coefficients are chosen so that the reaction involves only one electron (for the sake of convenience), the free enthalpy of a so-called *redox* reaction:

$$(1) \qquad a_1 R_1 + b_2 O_2 \rightleftharpoons b_1 O_1 + a_2 R_2$$

is given by the expression

$$(2) \qquad \Delta G = \Delta G^0 + RT \operatorname{Log} \frac{(O_1)^{b_1}(R_2)^{a_2}}{(R_1)^{a_1}(O_2)^{b_2}} = \Delta G^0 + 2.3\,RT \log \frac{(O_1)^{b_1}(R_2)^{a_2}}{(R_1)^{a_1}(O_2)^{b_2}}.$$

R denotes the gas constant; T, the absolute temperature; Log, a natural logarithmic; log, a decimal logarithm; the symbols in brackets denote the fugacities or activities of the corresponding constituents, i.e. to a first approximation, the pressure for all gaseous substances, the molality (number of moles per kilogram of solvent) for all dissolved substances; the mole fraction for each liquid or solid solvent; in particular, the activity is unity for a pure condensed substance, and almost unity for the water in an aqueous solution when sufficiently dilute. The first term $\Delta G^0$ represents the standard free enthalpy of reaction, i.e. the free enthalpy of reaction, $\Delta G$, when all the fugacities and activities involved are unity.

By choosing a reference couple under specific conditions at the temperature considered, generally the couple $\underset{(1\text{ atm.})}{H_2} \Big| \underset{(\text{act. }1)}{H^+}$, it is possible to decompose (1) into two half-reactions:

$$a_1 R_1 + \underset{(\text{act. }1)}{H^+} \rightleftharpoons b_1 O_1 + \frac{1}{2}\underset{(1\text{ atm.})}{H_2},$$

and

$$\frac{1}{2}\underset{(1\text{ atm.})}{H_2} + b_2 O_2 \rightleftharpoons \underset{(\text{act. }1)}{H^+} + a_2 R_2,$$

whose free enthalpies are respectively

$$\Delta G_1 = \Delta G_1^0 + RT \operatorname{Log} \frac{(O_1)^{b_1}}{(R_1)^{a_1}},$$

and

$$-\Delta G_2 = -\Delta G_2^0 - RT \operatorname{Log} \frac{(O_2)^{b_2}}{(R_2)^{a_2}}.$$

At the temperature considered (usually 25°C) and at a given pressure (usually 1 atm.), reaction (1) is thermodynamically possible only if

$$\Delta G = \Delta G_1 - \Delta G_2 < 0 \qquad \text{i.e.} \qquad \Delta G_1 < \Delta G_2.$$

Now, the half-reaction corresponding to a redox couple $i$ can theoretically be brought about reversibly by means of the electrochemical cell

$$\text{Pt} \left| \begin{matrix} O_i,\ R_i \\ \text{aq.} \end{matrix} \right| . \left| \begin{matrix} H^+ \\ (\text{act. }1) \\ \text{aq.} \end{matrix} \right| \text{Pt},\ \underset{(1\text{ atm.})}{H_2},$$

of which the *reversible potential difference* (electric potential of the first pole less that of the second when there is a perfect potentiometric compensation) is

$$(3) \qquad E_i = \frac{\Delta G_i}{F} = \frac{\Delta G_i^0}{F} + \frac{2.3\,RT}{F} \log \frac{(O_i)^{b_i}}{(R_i)^{a_i}} = E_i^0 + \frac{2.3\,RT}{F} \log \frac{(O_i)^{b_i}}{(R_i)^{a_i}}.$$

$E_i^0 = \Delta G_i^0/F$ may be termed the *standard potential* associated with the couple $i$; F represents one Faraday in the system of units employed. The M.K.S. system implies that $E_i$ and $E_i^0$ should be expressed in volts; R in joules $\text{mol}^{-1}\ \text{deg}^{-1}$; F in coulombs.$\text{equivalent}^{-1}$. At 25°C, 2·3RT/F is therefore equal to 0·0591 V, as seen in Chapter II.

Tables such as those of W. M. Latimer(¹) list numerical values of $E_i^0$ for $x$ couples, enabling us to predict the thermodynamic possibility of $2x(x - 1)$ redox reactions under the most varied conditions: the reducing agent $R_1$ of a couple 1 reacts with the oxidizing agent $O_2$ of a couple 2 when $E_1 < E_2$.

It should be noted that in tables of this kind the half-reactions are written:

$$a_i R_i \rightleftharpoons b_i O_i + ne^-, \tag{4}$$

(as is done systematically in this *Atlas*), instead of

$$a_i R_i + \underset{(\text{act.}\,1)}{H^+} \rightleftharpoons b_i O_i + \frac{1}{2}\underset{(1\ \text{atm.})}{H_2}. \tag{5}$$

With regard to calculating the free enthalpy, and on account of the standard potential given in (3), the result is the same, it being understood that the state of the electrons considered is their aqueous dissolution equilibrium (producing an unknown electron concentration) in the reference couple. Let us suppose first of all that $n = 1$: the free enthalpy of the reaction

$$e^-_{\text{aq.}} + \underset{(\text{act.}\,1)}{H^+} \rightleftharpoons \frac{1}{2}\underset{(1\ \text{atm.})}{H_2} \tag{6}$$

is zero. Now reaction (5), whose free enthalpy is given by formula (3), is the sum of reactions (4) and (6). Since their free enthalpies are also additive, it follows that (4) and (5) have the same free enthalpy. When $n \neq 1$, one can divide both sides of equation (4) by $n$ to replace (3) by the more general equation

$$E_i = E_i^0 + \frac{2.3\,RT}{F}\log\frac{(O_i)^{\frac{b_i}{n}}}{(R_i)^{\frac{a_i}{n}}} = E_i^0 + \frac{2.3\,RT}{nF}\log\frac{(O_i)^{b_i}}{(R_i)^{a_i}}. \tag{3'}$$

### 3. COEXISTENCE POTENTIALS

In the initial absence of $O_1$ and $R_2$, $\Delta G = -\infty$ from (2). This means that a redox reaction can always begin, but the question is to know how far it can continue. One may consider it to be practically significant when more than 50 per cent of the reducing agent $R_i$ put into the system can disappear. Thus it is useful to consider for each couple $i$ a coexistence potential $i$ for equal parts of $R_i$ and $O_i$. We will provisionally denote this potential by $E_i^{(0.5)}$. Let $\alpha_i$, $\beta_i$ be the atomicities of the element involved in its respective forms $R_i$, $O_i$ (e.g. $\alpha_i = 1$ for $Cl^-$; $\beta_i = 2$ for $Cl_2$) and let $C_i$ be the overall concentration of the system (which may consist of one or several phases) in gram-atoms of this element per kilogram of water present: $C_i$ remains constant throughout any reaction which produces only a small amount of additional water, e.g. when the reagent employed is solid or gaseous or when it is in a very concentrated solution. Let us denote by $x_i$ the fraction of the active element of couple $i$ present in the oxidized state $O_i$. There are three principal cases to be considered.

3.1. $O_i$ and $R_i$ are two constituents dissolved in the aqueous phase. One then has

$$\beta_i(O_i) = x_i C_i; \qquad \alpha_i(R_i) = (1 - x_i)C_i.$$

Substituting in (3′) we obtain

$$E_i = E_i^0 + \frac{0.0591}{n}\log\frac{\alpha_i^{a_i}}{\beta_i^{b_i}} + \frac{0.0591\,(b_i - a_i)}{n}\log C_i + \frac{0.0591}{n}\,b_i\log x_i - \frac{0.0591}{n}\,a_i\log(1 - x_i),$$

---

(¹) *Oxidation Potentials*, 2nd ed., Prentice-Hall, New York, 1952.

$E_i$, which varies in the same sense as $x_i$ is thus a real measure of the fraction oxidized. In order to obtain the coexistence potential $E_i^{(0\cdot5)}$, one merely puts $x_i = 0\cdot5$. Hence

$$E_i^{(0.5)} = E_i^0 + \frac{0.0591}{n}\log\frac{(2\alpha_i)^{a_i}}{(2\beta_i)^{b_i}} + \frac{0.0591\,(b_i - a_i)}{n}\log C_i. \tag{7}$$

3.2. $O_i$ is a pure substance at 1 atm. pressure (gas, solid or liquid); $R_i$ is a dissolved constituent of the aqueous phase. One then has

$$(O_i) = 1\,; \qquad \alpha_i(R_i) = (1 - x_i)\,C_i.$$

Hence

$$E_i = E_i^0 + \frac{0.0591}{n}\log\alpha_i^{a_i} - \frac{0.0591}{n}\,a_i\log C_i - \frac{0.0591}{n}\,a_i\log(1 - x_i),$$

$E_i$ again varies in the same sense as $x_i$ and thus remains a measure of the fraction oxidized. Putting $x_i = 0\cdot5$ we obtain

$$E_i^{(0.5)} = E_i^0 + \frac{0.0591}{n}\log(2\alpha_i)^{a_i} - \frac{0.0591}{n}\,a_i\log C_i. \tag{8}$$

3.3. $O_i$ is a dissolved constituent of the aqueous phase; $R_i$ is a pure substance at 1 atm. pressure. One then has

$$\beta_i(O_i) = x_i C_i\,; \qquad (R_i) = 1.$$

Hence

$$E_i = E_i^0 - \frac{0.0591}{n}\log\beta_i^{b_i} + \frac{0.0591}{n}\,b_i\log C_i + \frac{0.0591}{n}\,b_i\log x_i,$$

Once again $E_i$ varies in the same sense as $x_i$ and is thus still a measure of the fraction oxidized. Putting $x_i = 0\cdot5$ we obtain

$$E_i^{(0.5)} = E_i^0 - \frac{0.0591}{n}\log(2\beta_i)^{b_i} + \frac{0.0591}{n}\,b_i\log C_i \quad (^2). \tag{9}$$

Suppose, therefore, that we add an oxidizing agent $O_2$ to a couple 1 which can act as an effective reducing agent $R_1$; $x_1$ increases, and $E_1$ correspondingly, but the coexistence potential $E_1^{(0\cdot5)}$ can be exceeded, i.e. the reaction can be considered to be practically significant ($x_1 > 0\cdot5$) when $O_2$ is introduced in the stoichiometric proportion, only if $E_2^{(0\cdot5)} > E_1^{(0\cdot5)}$. This is due to the fact that in the final equilibrium state, $\Delta G = 0$, i.e. $E_2 = E_1$. Now $x_1 > 0\cdot5$ implies that $E_1 > E_1^{(0\cdot5)}$, but also implies that $x_2 < 0\cdot5$, i.e. $E_2 < E_2^{(0\cdot5)}$. Hence

$$0 = E_1 - E_2 > E_1^{(0.5)} - E_2^{(0.5)}.$$

Since the order of addition of reagents to the system does not influence the equilibrium state obtained, the same relation $E_1^{(0\cdot5)} < E_2^{(0\cdot5)}$ is evidently appropriate for predicting a significant reaction when one adds a reducing agent $R_1$ to a medium containing a certain oxidizing agent $O_2$.

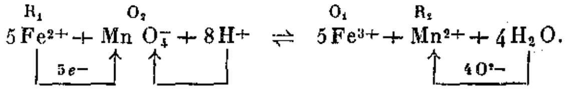
## 4. MIXED COUPLES

In most cases a complication arises: when the active element does not exist as a simple substance in one or the other of its two forms $R_i$, $O_i$ (as in the couples $Fe^{2+}|Fe^{3+}$ and $Cl^-|Cl_2$), the couple under consideration does not involve only an ability to transfer electrons, but can involve simultaneously the release or capture of other particles. The most important case is when the only elements linked to the active element are those of the aqueous solvent, i.e. hydrogen and oxygen. Thus, the action of potassium permanganate on ferrous salts in acid solution can be interpreted as a transfer of electrons

---

(²) Between $\alpha_i$, $\beta_i$, $a_i$, $b_i$, there exists the relation $\alpha_i a_i = \beta_i b_i$, but to introduce this into the preceding formulae would simplify them only in certain special cases.

on to manganese, accompanied by a capture of protons by the oxygen combined with it, while the reverse reaction can be interpreted as a transfer of electrons on to iron, accompanied by a release of protons by the solvent, which supplies the oxygen then necessary for the stability of the manganese atom deprived of electrons



$$\overset{R_1}{5\,Fe^{2+}} + \overset{O_2}{Mn\,O_4^-} + 8\,H^+ \rightleftharpoons \overset{O_1}{5\,Fe^{3+}} + \overset{R_2}{Mn^{2+}} + 4\,H_2O.$$

In most cases, therefore, we shall be considering half-reactions which can be represented by

$$a_i R_i + q H_2O \rightleftharpoons b_i O_i + m H^+ + n e^- \quad \text{(3)} \tag{10}$$

of which the free enthalpy is

$$\Delta G_i = \Delta G_i^0 + 2.3\,RT \log \frac{(O_i)^{b_i}(H^+)^m}{(R_i)^{a_i}},$$

the activity of the water being practically unity. The reversible potential which can be associated with the couple $i$ is here

$$E_i = \frac{\Delta G_i}{nF} = \frac{\Delta G_i^0}{nF} + \frac{2.3\,RT\,m \log(H^+)}{nF} + \frac{2.3\,RT}{nF} \log \frac{(O_i)^{b_i}}{(R_i)^{a_i}}.$$

Introducing the symbol $pH = -\log(H^+)$:

$$E_i = E_i^0 - \frac{0.0591\,m}{n}\,pH + \frac{0.0591}{n} \log \frac{(O_i)^{b_i}}{(R_i)^{a_i}}. \tag{3''}$$

In fact, (3″) differs from (3′) only in the term $E_i' = E_i^0 - 0{\cdot}0591 m/n\,pH$, linear in pH, which replaces the constant term $E_i^0$. The prediction of redox reactions must therefore take into account the pH of the medium. In general it varies throughout such reactions, unless the medium is suitably buffered. Let us suppose that this condition is fulfilled: formulae (7), (8) and (9), which are expressions for the coexistence potentials of $R_i$ and $O_i$, remain valid, provided that $E_i^0$ is replaced by E′. For the principal cases considered in 3.1, 3.2 and 3.3, we have the following coexistence potentials:

4.1. $O_i$ and $R_i$ in the aqueous phase:

$$E_i^{(0.5)} = \left[E_i^0 + \frac{0.0591}{n} \log \frac{(2\alpha_i)^{a_i}}{(2\beta_i)^{b_i}} + \frac{0.0591}{n}(b_i - a_i) \log C_i\right] - \frac{0.0591\,m}{n}\,pH. \tag{7'}$$

4.2. $O_i$ a pure substance at 1 atm. pressure; $R_i$ in the aqueous phase:

$$E_i^{(0.5)} = \left[E_i^0 + \frac{0.0591}{n} \log (2\alpha_i)^{a_i} - \frac{0.0591}{n} a_i \log C_i\right] - \frac{0.0591\,m}{n}\,pH. \tag{8'}$$

4.3. $O_i$ in the aqueous phase; $R_i$ a pure substance at 1 atm. pressure:

$$E_i^{(0.5)} = \left[E_i^0 - \frac{0.0591}{n} \log (2\beta_i)^{b_i} + \frac{0.0591}{n} b_i \log C_i\right] - \frac{0.0591\,m}{n}\,pH. \tag{9'}$$

For each pH, the calculation of $E_1^{(0{\cdot}5)}$ and $E_2^{(0{\cdot}5)}$ by means of these formulae will once again enable us to predict the possibility (when $E_1^{(0{\cdot}5)} < E_2^{(0{\cdot}5)}$) of a practically significant reaction between a reducing agent $R_1$ and an oxidizing agent $O_2$.

---

(3) *m* and *q* are positive or zero in most cases; sometimes they are negative, however, as in the case for the couple $NiO_2H^- | Ni_3O_4$, for which the half-reaction is: $3NiO_2H^- + H^+ \rightleftharpoons Ni_3O_4 + 2H_2O + 2e^-$, where $q = -2$; $m = -1$ (*see* IV. 12).

### 5. GRAPHICAL REPRESENTATION

Instead of carrying out a fresh calculation for each application, it is more convenient to make a graphical representation, once and for all, of the $E_i^{(0\cdot5)}$ values for each couple $(R_i, O_i)$. They depend on two variables, $C_i$ and pH, and one can therefore plot a family of iso-$C_i$ straight lines using E and pH as co-ordinates.

In general there will be several such families of lines corresponding to a given element, since its chemical properties generally involve the existence of various redox couples in which it takes part. For example, chlorine is the active element of the various couples:

$$Cl^- | Cl_2. \quad Cl_2 | ClO^-. \quad ClO^- | ClO_2^-. \quad ClO_2^- | ClO_3^-. \quad ClO_3^- | ClO_4^-.$$

The collection of families of iso-$C_i$ lines for a given element, in terms of (E, pH) co-ordinates, constitutes the electrochemical equilibrium diagram for this element.

For a certain value of $C_i$, each $(R_i, O_i)$ line of such a diagram separates the plane into two regions: below it one has $x_i < 0{\cdot}5$, i.e. the reduced form $R_i$ predominates; above it one has $x_i > 0{\cdot}5$, i.e. the oxidized form predominates. Thus $E_i$ has a meaning at each point of the plane; the straight lines $E = A - B\text{pH}$ represent the particular values $E_i^{(0\cdot5)}$, which one need no longer denote differently.

In order to predict the possibility of a reaction between an oxidizing agent $O_2$ and a reducing agent $R_1$, one can superimpose the corresponding two diagrams: after selecting the appropriate iso-$C_i$ lines, it follows that, depending on whether the line $(R_2, O_2)$ lies above or below the line $(R_1, O_1)$ on the pH vertical considered, $R_1$ can be oxidized, or is practically unoxidized. In the second case, it is the reverse reaction, i.e. the reaction between the oxidizing agent $O_1$ and the reducing agent $R_2$, which becomes possible. The case of two lines intersecting at a point P (Fig. 1) is by no means exceptional: it reveals the marked influence of pH on the direction of certain reactions. For example, the coexistence potential corresponding to the reference couple $H_2 | H^+ (E_1^0 = 0)$ at 1 atm. pressure, is $E_1 = -0{\cdot}0591$ pH. The coexistence potential corresponding to the couple $MoO_2(\text{solid}) | Mo^{3+}$ is $E_2 = 0{\cdot}311 - 0{\cdot}2364$ pH $-0{\cdot}0591 \log(Mo^{3+})$, where $(Mo^{3+})$ represents $C_2/2$. Let us suppose that $C_2 = 0{\cdot}2$, i.e. $(Mo^{3+}) = 0{\cdot}1$. Then $E_2 = 0{\cdot}311 - 0{\cdot}2364$ pH. In an acid solution, will hydrogen at a pressure of 1 atm. reduce $MoO_2$ to dissolved $Mo^{3+}$? The condition necessary for this is

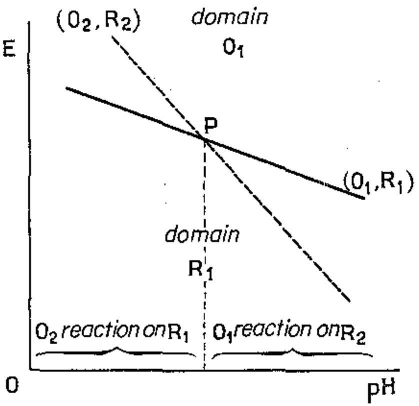


FIG. 1.

$$-0.0591\,\text{pH} < 0.370 - 0.2364\,\text{pH},$$

i.e. the reduction is possible at pH's below

$$\text{pH} = \frac{0.370}{0.1773} = 2.1,$$

whilst at higher pH's, $Mo^{3+}$ can on the other hand decompose water with the evolution of hydrogen and the precipitation of $MoO_2$. These conclusions are apparent, without the necessity for calculation, on looking at the electrochemical diagram for molybdenum (IV. 10).

We call attention here to the particular importance of two couples which are involved in any aqueous system, due to the presence of the solvent: the couple $H_2|H^+$, of which the coexistence potential is $E_a = -0{\cdot}0591\ \mathrm{pH}$, and the couple $H_2O|O_2$, of which the coexistence potential is $E_b = 1{\cdot}230 - 0{\cdot}0591\ \mathrm{pH}$. The straight lines (a) and (b) representing these couples are indicated in broken lines on all the diagrams in the *Atlas.*

## 6. DISPROPORTIONATION

A redox *amphoter* is a state X of an element which is at the same time the reducing agent $R_1$ of a certain couple $R_1|O_1$ and the oxidizing agent $O_2$ of another couple $R_2|O_2$. Thus, the $Fe^{2+}$ ion is an amphoter, being the reducing agent of the couple $Fe^{2+}|Fe^{3+}$ and the oxidizing agent of the couple $Fe|Fe^{2+}$. To a given amphoter therefore correspond (at a fixed concentration) two coexistence lines: $E_1 = A_1 - B_1\,\mathrm{pH}$; $E_2 = A_2 - B_2\,\mathrm{pH}$. Now, in order for the amphoter to be stable, it must not be able to react with itself according to the equation

$$\underset{R_1}{a_1 X} + q_1 H_2O + \underset{O_2}{b_2 X_2} + m_2 H^+ \rightleftharpoons \underset{O_1}{b_1 O_1} + m_1 H^+ + \underset{R_2}{b_2 R_2} + q_2 H_2O.$$

It is thus necessary that

$$E_1^{(0.5)} > E_2^{(0.5)} \qquad \text{or} \qquad A_1 - B_1\,\mathrm{pH} > A_2 - B_2\,\mathrm{pH}\ :$$

the line representing its reducing function must lie above the line representing its oxidizing function. The three predominance domains involved are situated in the right-hand part of Fig. 2.

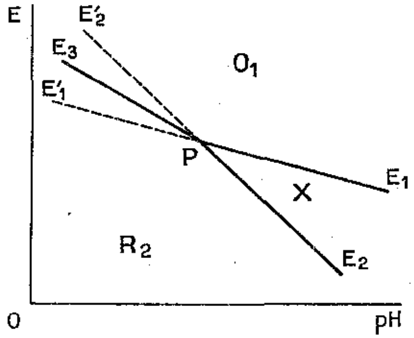


FIG. 2.

Three cases may arise:

6.1. The line $E_2$ lies below the line $E_1$ over the whole range of pH considered. The amphoter is then stable over the whole of this range. For example, the aqueous solvent is an amphoter since it is involved in the two couples $H_2O|O_2$ (couple 1) and $H_2|H^+$ (couple 2), represented by the two lines (*b*) and (*a*) mentioned above: these two lines are parallel and the first lies above the second, which explains the great stability of water at all pH's.

6.2. The line $E_2$ lies above the line $E_1$ over the whole range of pH considered. The amphoter (if it is known experimentally) is then always metastable. This is the case, for example, for the oxygen-containing compounds of sulphur, apart from those corresponding to sulphuric acid ($HSO_4^-$, $SO_4^{2-}$) and dipersulphuric acid ($S_2O_8^{2-}$), as will be seen in IV. 19. The less oxygenated compounds owe their isolation solely to the manifestly slow rate at which they *disproportionate*, which is probably a consequence of the activation energies necessary for breaking the covalent bonds. Thus, complete metastability is encountered only exceptionally amongst metal compounds, since electrovalent bonds predominate in these compounds. Each of them can be denoted on an electrochemical equilibrium diagram, but such a possibility of existence is incompatible with reality for many non-metal compounds. This difficulty can be avoided by disregarding certain very stable states (such as sulphates in the case of sulphur), for the purpose of certain narrowly defined practical applications, but this means that the number of diagrams corresponding to a given non-metal must be increased, as has been done for chlorine (IV. 20); these diagrams then correspond to different degrees of stability.

6.3. The line $E_1$ cuts the line $E_2$ in a point P. In this case, which is shown in Fig. 2, the state X is stable only in the region of pH situated to that side of P on which $E_1$ lies above $E_2$. In the opposite region X must disappear by disproportionation. The extension $E'_1$, $E'_2$ of the lines $E_1$, $E_2$ into this region do not therefore appear to have any meaning: the only couple to be considered in this region is $R_2 | O_1$, spanning in a way the metastable amphoter X. A new coexistence line $E_3$, starting from P, separates the domains $O_1$ and $R_2$ which have become contiguous. Reasoning step by step in this way, one understands why the predominance domains of most amphoters (but not those of the extreme states, i.e. those which are richest or poorest in electrons) appear on the diagrams as closed domains. Their limits in a horizontal direction are often due to the disappearance of a state simply on account of a variation in pH, without there being oxidation or reduction of the active element. The acid function of certain hydrogen-containing compounds involves an equilibrium between the protons released and the rest of the molecule. Thus for dissolved hypochlorous acid: $HClO \rightleftharpoons ClO^- + H^+$. If, at a given temperature, $k$ is the equilibrium constant for such a dissociation, and $pk = -\log k$, one has

$$\mathrm{pH} = pk + \log \frac{(\mathrm{ClO^-})}{(\mathrm{HClO})}.$$

Now the above definition of coexistence requires a *vertical* boundary, of abscissa pH = $pk$, separating the domains HClO (*on the left*) and $ClO^-$ (*on the right*). In this example, $pk = 7{\cdot}49$ at 25°C. The generalization of this idea to other schemes of proton release in the absence of redox reactions, e.g.

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\,CrO_4^{2-} + 2\,H^+$$

creates no difficulties.

The existence of triple points P not involving a vertical boundary, as in Fig. 2, implies however the possibility of the *reversible disproportionation* of an amphoter X on change of pH of the medium. For all pH's at which X is stable, the point representing the equilibrium of its disproportionation into $O_1$ and $R_2$ lies in fact inside its predominance domain; it remains there if one changes the pH in the sense which brings it nearer to the abscissa of P. The trajectory of the equilibrium point always lies between the lines $PE_1$ and $PE_2$ and finishes up at the triple point. If one continued to change the pH in the same sense, X would cease to be stable and would be converted into $O_1 + R_2$; the active element would divide itself between these states in proportions of the same order; the trajectory would then continue in the immediate neighbourhood of $PE_3$, the boundary between the domains $R_2 | O_1$. By way of an example, we shall discuss a diagram showing metastable states of sulphur. This diagram, which has been previously published(4), is not incorporated among the plates of the *Atlas*, but is reproduced on a small scale in Fig. 3. It disregards the existence of thionates, which would exclude certain predominance domains, and sulphates, which would allow only the domains of sulphur and hydrogen sulphide and its ions to subsist beside their own domains (*see* IV. 19). In order not to make the representation too complicated, only one overall concentration, corresponding to 1 g-at of sulphur per kilogram of solvent, has been considered. The hydrogen sulphide is then in the gaseous state at 1 atm. pressure. Ten domains are then apparent, i.e. those for: dissolved $H_2SO_3$, $HSO_3^-$, $SO_3^{2-}$, $HS_2O_3^-$, $S_2O_3^{2-}$, $S_{oct.}$, $S_5^{2-}$, $H_2S_{gas.}$, $HS^-$, $S^{2-}$. The boundaries of the domains are numbered; each one corresponds to a half-reaction which can easily be identified; the triple points can conveniently be referred to by the numbers of the three lines which meet at them. Several reversible disproportionations, which do in fact characterize the experimental chemistry of sulphur, can be interpreted by this diagram:

---

(4) G. VALENSI, *C.R. CITCE*, 2, 1950, p. 51, Tamburini, Milan, 1951.

(a) *Action of acids on thiosulphate solutions.* The representative point traverses in a north-west direction the interior of the $S_2O_3^{2-}$ domain (15–16–17–24–22–20–19) and crosses line (15), the $S_2O_3^{2-}|HS_2O_3^-$ boundary, where first of all the reaction

$$S_2O_3^{2-} + H^+ \rightleftharpoons HS_2O_3^-.$$

takes place.

It then crosses, in the same direction, the $HS_2O_3^-$ domain (13–14–15–18), going as far as the vertex (12–13–18), where the well-known disproportionation:

$$HS_2O_3^- + H^+ \rightleftharpoons S + H_2SO_3$$

takes place.

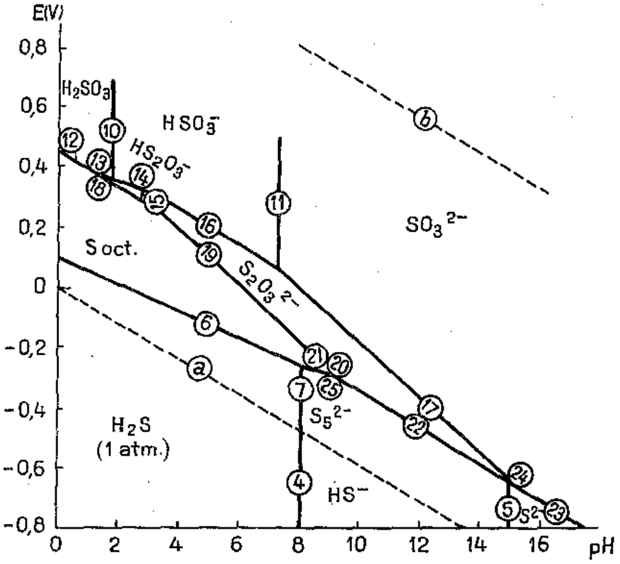


FIG. 3.

(b) *Disproportionation of sulphur in alkaline solution.* The representative point traverses in a south-east direction the interior of the $S_{oct.}$ domain (12–18–19–21–6) finishing up at the vertex (19–20–21) where the following disproportionation occurs:

$$12S + 3H_2O \rightleftharpoons S_2O_3^{2-} + 2S_5^{2-} + 6H^+,$$

Taking into account the alkalinity then acquired by the medium, whose pH reaches about 10, this can be represented as

$$12S + 6OH^- \rightleftharpoons S_2O_3^{2-} + 2S_5^{2-} + 3H_2O.$$

One can interpret in this way the industrial manufacture of polysulphides destined for agricultural uses; they are always mixed with thiosulphates. To increase the rate of reaction, one is however compelled to work at a temperature considerably greater than 25°C.

(c) *Disproportionation of polysulphides by alkalization.* The polysulphidation index of such solutions, which is 5 at the equilibrium, in the presence of an excess of solid sulphur, decreases when the final alkalinity increases, i.e. when one increases the initial proportion of alkali with respect to the sulphur used. Now, the polysulphides of index $y$ intermediate between 5 and 1 are amphoters and can therefore disproportionate according to the equation $2S_y^{2-} \rightleftharpoons S_{y+1}^{2-} + S_{y-1}^{2-}$. The coexistence potentials of the various couples involved are very close and it would thus be somewhat arbitrary to define a separate domain for each of the intermediate polysulphides. If, starting from the pentasulphide, i.e. from the domain (21–20–25), one continues to increase the pH, one arrives finally at the vertex (20–25–7), where the ultimate disproportionation of the polysulphide sulphur takes place, giving $S_2O_3^{2-} + HS^-$, thus producing the minimum index $y = 1$. In actual fact, all the indices intermediate between 5 and 1 can be obtained by increasing the initial proportion of alkali with respect to sulphur, providing that one works at a sufficiently high temperature.

(d) *Disproportionation of polysulphides by acidification.* Under conditions in which the rate is sufficiently great, i.e. at a fairly high temperature, the disproportionations (c) and (b) are reversed if one re-acidifies the solutions obtained. This is due to the fact that in the mixtures of polysulphides and thiosulphate corresponding to such solutions, the representative point lies on line (20) and moves along it up to the vertex (19–21–20) on addition of acid; one can then move into the sulphur region, by means of the reaction of $S_2O_3^{2-}$ with $S_5^{2-}$, the reverse of the disproportionation (b) considered above.

This is no longer true if one starts with a polysulphide solution free from thiosulphate, which can be prepared as indicated below: its representative point then lies inside the domain (21–20–25); it moves towards the vertex (7–21–25) on acidification. At this vertex there occurs the disproportionation $S_5^{2-} + H^+ \rightleftharpoons HS^- + 4S$; line (7) is then followed as far as the vertex (6–7–4), which lies on the vertical line corresponding to the acid couple $H_2S|HS^-$; hydrogen sulphide is then produced according to the equation

$$HS^- + H^+ \rightleftharpoons H_2S.$$

It is in fact well known that the acidification of polysulphide solutions, even at ordinary temperatures, liberates hydrogen sulphide, with the deposition of sulphur. The two successive reactions involved have moreover been separated experimentally(⁵).

Nevertheless, at ordinary temperatures, the disproportionation of sulphur by alkalinization is a slow reaction, as is the reverse reaction, i.e. the action of acids on disproportionated solutions. Under these conditions, a different diagram for the metastable states of sulphur, neglecting all oxygen-containing sulphur compounds(⁶) would give a better description of certain phenomena which can be observed only at room temperature. On such an auxiliary diagram, the polysulphide domain is naturally considerably enlarged. The representative point for alkaline solutions of disproportionated sulphur no longer lies on a boundary and, at room temperature, acidification of such solutions has the same effect as if one were dealing with polysulphide solutions free from thiosulphate. Nevertheless, the thiosulphate present would no longer be inert at low pH's and would show its presence by the disproportionation (a), which produces additional sulphur $+ SO_2$ below a pH of about 2.

## 7. AMPHOTERIZATION

One may call the reverse reaction of a disproportionation an *amphoterization*. Returning to Fig. 2, one may imagine that, at a pH compatible with the stability of X, one causes the oxidizing agent $O_1$ to react with the reducing agent $R_2$: the reaction is possible, since the line $PE_1$ then lies above the line $PE_2$; it will give rise to the amphoter X. Hence one can derive a rule that when two states lie on either side of a given domain, they can react together to produce the state proper to this domain; this is an amphoterization. Let us return now to Fig. 3 for some examples of this:

(a) *Action of hydrogen sulphide on sulphurous acid.* The $H_2SO_3$ and $H_2S$ domains, (12–13–10) and (6–4), lie on either side of the $S_{oct.}$ domain, (18–19–21–6). One can therefore have the reaction

$$SO_2 + 2H_2S \rightleftharpoons 3S + 2H_2O.$$

which does in fact constitute the second phase of the process for extracting sulphur from Lacq gases. At room temperature it is complicated by the formation of thionic compounds, which we have neglected in plotting the metastable diagram in Fig. 3.

(b) *Dissolution of sulphur in sulphite solutions.* The domains of the dissolved ions $HSO_3^-$, $SO_3^{2-}$ and that of $S_{oct.}$ lie on either side of the $S_2O_3^{2-}$ domain. Sulphur can therefore react with sulphite

---

(⁵) G. Valensi, *C.R. Acad. Sc.*, 221, 1945, p. 352.

(⁶) G. Valensi, *C.R. CITCE*, 2, 1950, p. 51, Tamburini, Milan, 1951.

solutions according to the equation

$$S + SO_3^{2-} \rightleftharpoons S_2O_3^{2-}.$$

This is indeed one of the methods used for preparing alkali metal thiosulphates.

(c) *Dissolution of sulphur in sulphide solutions.* On account of the small second dissociation constant of hydrogen sulphide, an alkali metal sulphide dissolved in aqueous solution is converted largely into hydrosulphide according to the equation

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^-.$$

Now the $S_{oct.}$ and $HS^-$ domains lie on either side of the $S_5^{2-}$ domain (21–20–25); sulphur can therefore react with a solution of sulphide ($HS^-$ + $OH^-$) according to the equation

$$4S + HS^- + OH^- \rightleftharpoons S_5^{2-} + H_2O.$$

This is a method for preparing polysulphide solutions free from thiosulphate, and it can be used even at room temperature. At this temperature it is not interfered with by the disproportionation of sulphur to give polysulphide + thiosulphate, which is still very slow, as we have already seen.

## 8. RATES OF REACTIONS WHICH ARE THERMODYNAMICALLY POSSIBLE

The preceding paragraphs show how much care is required in making use of the thermodynamic predictions embodied in the electrochemical equilibrium diagrams. For this reason they should be considered as a means of interpreting known experimental facts rather than discovering new ones. Thermodynamics cannot give information about the rates—which are often almost zero—of reactions which are compatible with the state of a given medium. If this were not the case, many substances, such as sulphites, thiosulphates, etc. would have remained unknown. In practice it is as if a double barrier were associated with each redox co-existence line, at a certain distance above it (for the reducing function) and below it (for the oxidizing function). As explained in III. 1, such divergences may be characterized by *overpotentials*, which depend on catalytic conditions. Their values (anodic or cathodic) for reactions which can be brought about by electrolysis, vary from case to case. For example the generally slow couples, whose co-existence potentials are represented by the lines (a) and (b) for water, are most often protected by overpotentials of the order of a volt. This means that gaseous oxygen does in fact oxidize only those reducing agents whose coexistence line is more than 1 V below line (*b*). Returning to Fig. 3, one can see that a stream of oxygen can oxidize a dissolved thiosulphate only with difficulty to sulphite. On the other hand it can easily oxidize dissolved hydrogen sulphide to sulphur, and likewise it can easily oxidize an alkali metal hydrosulphide to pentasulphide at pH's between 8 and 10, or to thiosulphate at pH's above 10. This explains the well known difference between the ageing of a solution of ammonium hydrosulphide used for qualitative analysis, buffered at a pH of about 9 on account of its nature, and that of a solution of potassium hydrosulphide, whose pH is nearer 14. In the same way one can interpret another industrial process for the manufacture of thiosulphates, which consists of disproportionating the sulphur first of all in an alkaline solution, thus bringing its representative point on to the boundary (20), then passing a stream of air through the solution, thus bringing the representative point inside the domain (15–16–17–22–20).

## 9. CONCLUSION

The few examples discussed above are sufficient to point out the usefulness of electrochemical diagrams as a means of linking up the respective features of the various compounds of a given element.

The systematic introduction of these diagrams into a text-book of descriptive inorganic chemistry would, in view of their recourse to logical arguments, help to make it more attractive than an enumeration of apparently unrelated facts. This would also enable certain chapters to be condensed, and would thus compensate to some extent the alarming increase in subject matter to be taught.(7)

---

(7) G. VALENSI, *Bull. Union Physiciens* (France), 45, 1950, p. 61.

Apart from their educational applications, electrochemical diagrams are of use in research, where they can enable one to dispense with a good deal of the preliminary calculation connected with determining the thermodynamic possibility of a new reaction, before tackling an experimental investigation, which would be completely futile under conditions excluded by the diagrams.

But this is all that one can ask of these electrochemical diagrams. They do not enable one to predict the kinetics of a phenomenon, although this is the decisive factor for the yield. A certain latitude must moreover be allowed with regard to the position of the domain boundaries: on the one hand, the replacement of activities by concentrations is only a rough approximation; on the other hand, the accelerating influence of a rise in temperature, which is often taken advantage of in practice, naturally modifies the boundaries valid at 25°C.

## SECTION 3

# ANALYTICAL CHEMISTRY

G. CHARLOT

AMONG the reactions employed by analytical chemistry, oxidation-reduction reactions, whether they be chemical or electrochemical, are the most useful. It is therefore important to the chemist to be able to predict these reactions and be able to bring them about or prevent them in order to achieve a desired result.

Among the factors that enable us to influence the properties of the majority of oxidation-reduction systems, pH is one of the most important, and undoubtedly the easiest to control. The knowledge of oxidation-reduction potentials, which enable us to predict the reactions for each pH, is also one of the primary concerns of the analyst. Potential–pH diagrams present these properties in their most useful form.

By comparing various diagrams it is possible to predict oxidation-reduction reactions; to predict the possibility of these reactions we should say, because, unlike most other reactions, oxidation-reduction reactions sometimes have very small reaction rates, and the equilibria can not therefore be attained. Now, for practical reasons, the analyst uses only fast reactions. In some cases the equilibria are reached so slowly that prediction of the reactions by means of equilibrium diagrams is of no interest. In other cases the diagrams are valuable for a first approximation. Finally, in many cases they enable quantitative predictions to be made. In these cases the diagrams summarize a large number of properties, and they do it in a manner which is more precise than previous methods.

We can quote some examples which are particularly striking, especially as far as the understanding and teaching of chemical properties is concerned. For example, the potential–pH diagram for manganese: Mn (II), Mn (II–III), Mn (III), Mn (IV), Mn (VI), Mn (VII). Starting from potential determinations in alkaline media and the solubility product of manganese (II) hydroxide, the whole of the diagram can be constructed. This diagram shows, better than calculations or descriptions, the domains of existence of the various chemical species, the various substances that can be obtained, and the various reactions that can be predicted for each pH. Making use of this diagram we can not only predict reactions, but we can also see under what conditions they can be avoided. For instance, by comparing this diagram with those of the halogens, we see that in a mixture of chloride and bromide, the bromide will be oxidized by the permanganate at $pH = 3$; the chloride can then be oxidized at $pH = 0$. We can predict those substances which will reduce permanganate to Mn (II) and also the smaller number of substances which will reduce it to manganese dioxide at $pH = 0$, and the very large number of substances which will reduce it to Mn (II–III), (III) and (IV) in alkaline media, etc.

The diagram for cerium, for instance, shows us that salts of Ce (IV) are very powerful oxidizing agents at $pH = 0$, and that salts of Ce (III), on the other hand, are very powerful reducing agents in slightly acid media.

Reduction by metals, titration of oxidizing or reducing agents using oxidation-reduction indicators, separations, etc., can be predicted and perfected by means of these diagrams.

These properties are no less important for the electrochemical reactions used in analysis. Electrochemical reactions can be dealt with in a manner analogous to chemical oxidation-reduction reactions. The knowledge of equilibrium potentials as a function of the pH is the basic piece of information in the case of so-called rapid electrochemical reactions (oxidations and reductions involving certain metals, the antimony electrode, the hydroquinone electrode, etc.). In other cases kinetic factors must be introduced, but, as in the case of chemical reactions, the knowledge of the equilibrium potential for each pH is still often a good enough first approximation to predict or distinguish between a certain number of possibilities. Electrochemical reactions are, of course, the basis of numerous electrochemical methods used in analysis: potentiometric, amperometric, coulometric methods, separation by electrolysis, etc.

To conclude: the knowledge of potential–pH equilibrium diagrams provides an important instrument for analytical chemistry, which very often involves chemical or electrochemical reactions in solution.

It seems likely that this systematic method will be used more and more widely in the future.

## BIBLIOGRAPHY

G. Charlot, *Sur l'utilisation des diagrammes potentiel–pH en chimie analytique: l'analyse qualitative et les réactions en solution,* Masson, Paris, 1957; Methuen, London, 1954; Aquilar, Madrid, 1954; Kijoritsu Syuppan, Tokyo, 1958.

## SECTION 4

# CORROSION

M. Pourbaix

### SUMMARY

1. *Theoretical corrosion, immunity and passivation conditions.*
2. *Resistance of metal to pure water.*
3. *Metals which can be passivated and activated.*
4. *Oxidizing corrosion inhibitors.*
5. *Degree of nobility of metals.*
   *Thermodynamic nobility and immunity.*
   *Practical nobility, immunity and passivation.*
6. *Experimental applications.*
7. *Note on the significance and practical implications of the potential–pH electrochemical equilibrium diagrams.*

## 1. THEORETICAL CORROSION, IMMUNITY AND PASSIVATION CONDITIONS

Let us assume, as a first approximation, that a metal is corrodible in the presence of an aqueous solution initially containing none of this metal according as the quantity of this metal which can be dissolved thermodynamically by the solution is lower or higher than a very small quantity which, for the sake of argument, we shall set arbitrarily at $10^{-6}$ g-at.wt./l; this content corresponds to 0·06 mg/l in the case of iron, copper and zinc; it corresponds to 0·03 mg/l for aluminium and to 0·2 mg/l for lead. If this hypothesis is at all correct, the lines on the potential–pH equilibrium diagrams which correspond to a solubility of $10^{-6}$ g-at.wt. of metal per litre (i.e. the $^{-6}$ equi-solubility lines) make a clear distinction between the domain where corrosion is possible (corrosion domain) and a domain where corrosion is impossible (non-corrosion domain). In the non-corrosion domain, two regions (or groups of regions) can be distinguished: in one of these regions, the solid stable form is the metal itself (domain of *immunity*, or *cathodic protection*), in which case, although presenting a genuine metal surface, the metal is quite incorrodible because the corrosion reaction is energetically impossible: in the other region (or regions), the solid stable form is not the metal but an oxide, a hydroxide, a hydride or a salt (*passivation* domain); the metal then tends to become coated with this oxide, hydroxide, hydride or salt which can, according to the circumstances, form on the metal either a non-porous film practically preventing all direct contact between the metal itself and the solution (in which case protection against corrosion is perfect), or a porous deposit which only partially prevents contact between the metal and the solution (in which case the protection is only imperfect). Understood in this way, *passivation thus does not necessarily imply the absence of corrosion.* Experience shows that, in the case of non-chlorinated solutions at least, the oxide films are generally perfect protectors for numerous metals, among which are aluminium, chromium, iron and tin.

In some relatively rare cases, a degradation of the metal may come about through the action, not of *dissolution*, but of gasification accompanied by the formation of a volatile hydride or oxide. If, as a rough guide, we assume that metal corrosion can take place in this way if the partial equilibrium pressure of the hydride or the oxide is equivalent to at least $10^{-6}$ atm., the lines of the potential–pH equilibrium diagrams which correspond to a hydride or oxide pressure equivalent to $10^{-6}$ atm. will enable us to establish a domain of corrosion by gasification.

It goes without saying that the concentration ($10^{-6}$ g-at.wt./l) and pressure ($10^{-6}$ atm.) values adopted here for the definition of the corrosion thresholds are arbitrary and that, in practice, there are good reasons for modifying these critical values. With this reservation, however, this theory can be regarded as exact as far as protection by immunity (or cathodic protection) is concerned.

As for protection by passivation, on the other hand, this theory is rather an over-simplification; although, thanks to U. R. Evans, the part played by oxides in protection by passivation received formal sanction in 1927, this role is not proved in all cases of passivation; for example, absorption phenomena can play a predominant part. On the other hand, there is a great scarcity of sufficiently precise data concerning the composition and the thermodynamic properties of protective oxide films, and such data are indispensible for an exact knowledge of their stability conditions. However this may be, in spite of these imperfections which it is well to take into account, the conclusions provided by the theoretical "corrosion, immunity and passivation" diagrams frequently coincide appreciably, quantitatively speaking, with the facts.

For further details, the reader is referred to the exposés which will be made in Chapter IV. We point particularly to three such cases of agreement concerning respectively the resistance of metals to pure water, metals which can be activated and passivated and oxidizing inhibitors of corrosion. We proceed to use these diagrams for the purpose of building up an overall picture of the degree of nobility of metals and of some non-metallic elements.

## 2. RESISTANCE OF METALS TO PURE WATER (See Fig. 1)

Generally speaking, the metals showing perfect resistance to pure water at a temperature in the region of 25°C will be those having an equilibrium diagram on which the perpendicular from $pH = 7$ crosses only the immunity or passivation domains (outside all corrosion domains) at potentials between $-0{\cdot}8$ and $+0{\cdot}7$ V, which are possible only in the normal conditions of use for construction metals.

With some reservations which will be pointed out later, and apart from the six metals in the platinum group, the following thirteen metals fall into this category: beryllium, aluminium, gallium, indium, tin, silver, gold, titanium, zirconium, hafnium, niobium, tantalum and chromium.

As for those of the above-mentioned metals for which a corrosion possibility exists at very low electrode potentials (tin, titanium), it will be particularly important to avoid all reducing action and to see that the surface has a good polish. As for chromium and silver, and also possibly gold and titanium, metals for which a corrosion possibility exists at high electrode potential, slight dissolution will be observed in the presence of a highly oxidizing action.

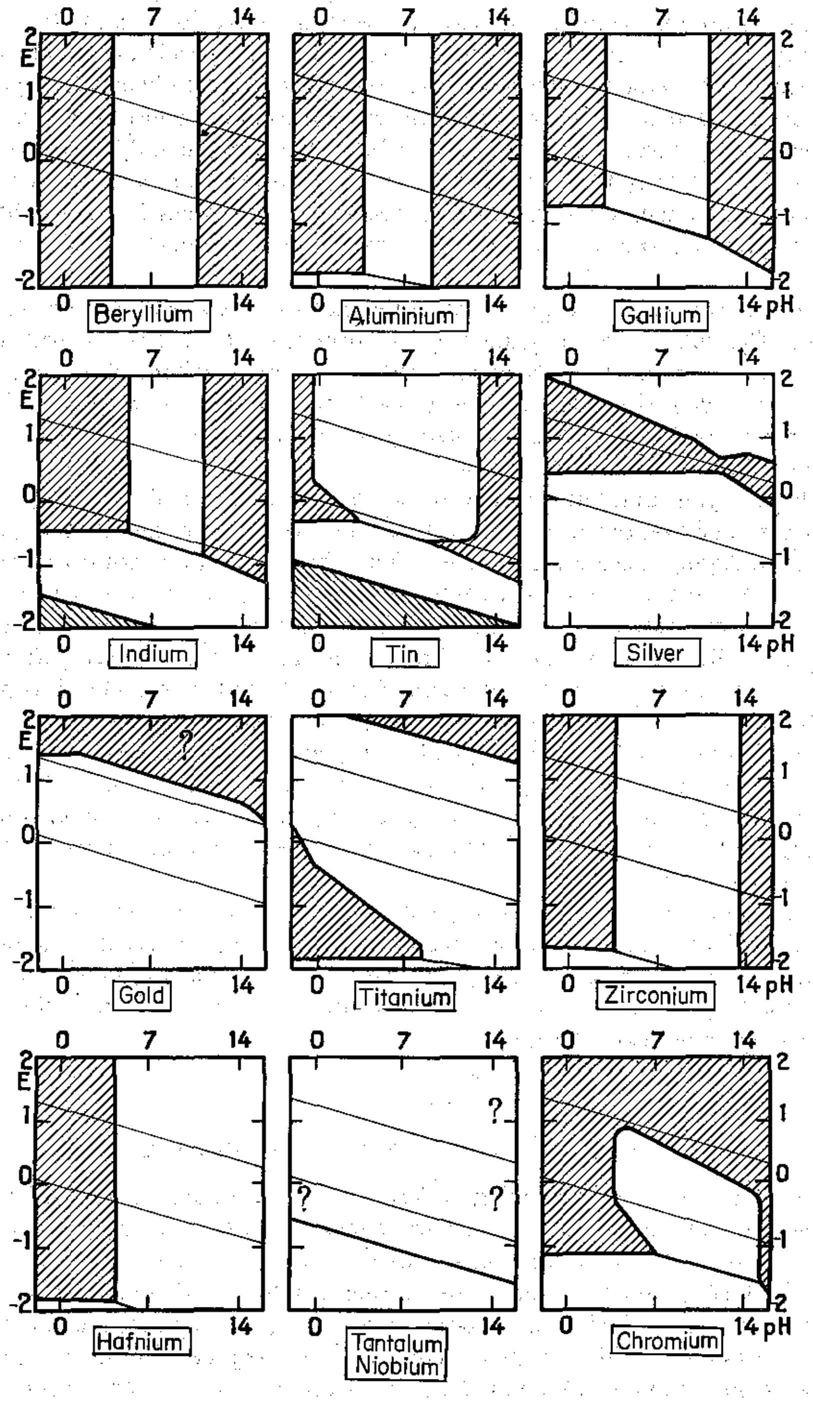


FIG. 1. Metals resistant to pure water. The hatched regions indicate theoretical corrosion domains. The non-hatched regions indicate theoretical immunity and passivation domains.

### 3. METALS WHICH CAN BE PASSIVATED AND ACTIVATED (See Fig. 2)

Generally speaking, the metals which can be passivated by oxidation and activated by reduction are those which have a higher oxide less soluble than a lower oxide and will thus present a triangular corrosion domain; the lower the apex of this triangle in the diagram, the easier it will be to passivate the metal by oxidation. This applies to the following metals, in descending order of passivability: titanium, chromium, tin, iron, manganese, lead, silver, nickel and cobalt.(¹)

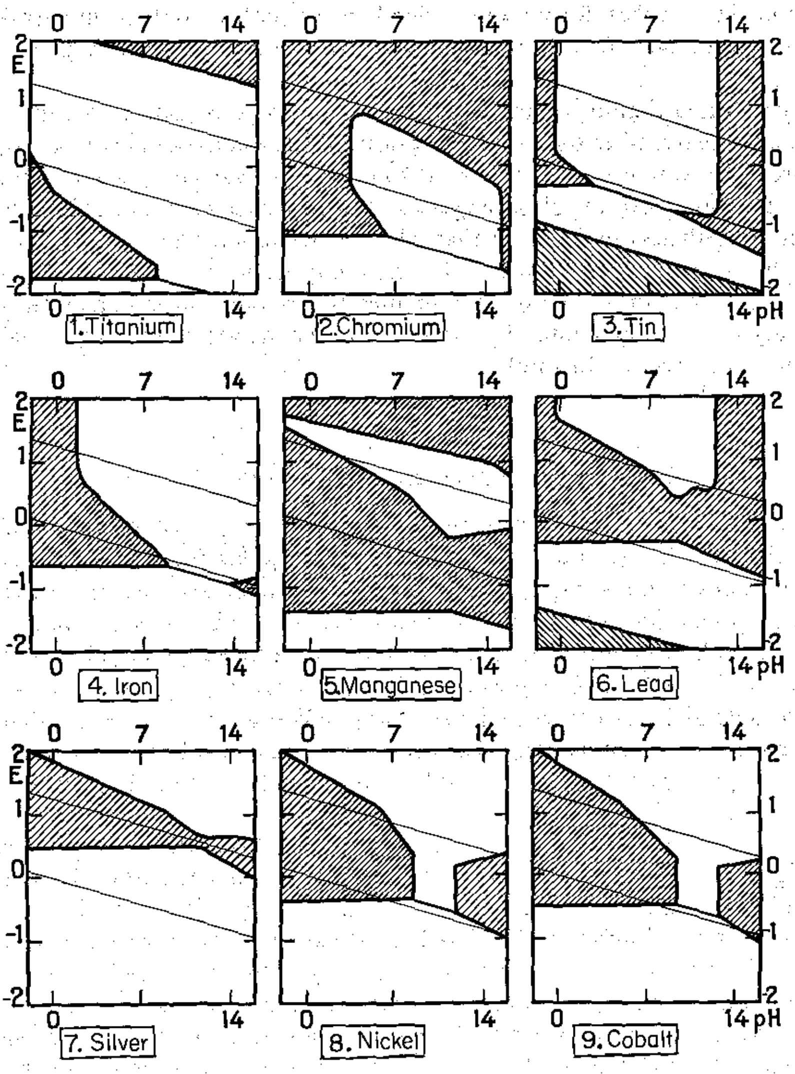


FIG. 2. Passive and active metals (as above).

For the three first metals (titanium, chromium and tin), the passivation domain of which, for an extensive pH range, is situated partly below the stability domain of water, passivation will be very easy and

---

(¹) Nickel and cobalt appear to be more easily passivated than the theoretical diagrams lead us to expect [see Chapter IV, sections 12.3 (nickel) and 12.2 (cobalt)].

will occur, more often than not, spontaneously, even in the absence of an oxidizing agent. Iron passivation will require an oxidizing action which, being weak for pH values between 9 and 13, will have to be relatively strong for other pH values. Passivation of the five other metals by the formation of an oxide layer will only be possible by means of a very strong oxidizing action (e.g. an anodization such as that which serves as the basis for charging lead batteries). It must however, be understood that, in spite of the difficulty of passivation, silver generally has a good corrosion resistance owing to the size of its immunity domain, and that, for reasons which have as yet been only insufficiently clarified, nickel (and perhaps cobalt too) can often be passivated at lower potentials than Fig. 2 leads us to anticipate.

Conversely, passivated titanium, chromium and tin can only be activated with relative difficulty: they generally remain passive after the oxidizing action, which would possibly have brought about passivation, has ceased. Activation of iron will be difficult for pH values between 9 and 13 and easy for other pH values. The other five metals (manganese, lead, silver, nickel and cobalt) will be very easily activated, it being nevertheless understood that whereas activation will always bring about corrosion of manganese (a by no means noble metal, the immunity domain of which exists only at very low electrode potentials), activation of the other four metals will only cause corrosion if there subsists a certain oxidizing action of variable intensity according to the metal (maintaining the electrode potential of the metal within its corrosion domain).

## 4. OXIDIZING CORROSION INHIBITORS (See Fig. 3)

The high susceptibility of iron to corrosion is mainly due to the existence, in the left-hand region of the part of Fig. 2 (No. 4) relating to this metal, of a large triangular domain of corrosion. In the case of solutions in presence of which the passivating iron oxide acts as an effective protector (which generally implies the absence of chloride), corrosion can be avoided by the introduction into the solution of an inhibitor having an oxidizing effect sufficient to enable the electrode potential of all the points on the surface of the iron to be high in the passivation domain of the metal. Protection will be particularly effective if, for the potential and pH conditions corresponding to the "corrosion domains" of the iron, the oxidizing inhibitor can be reduced together with formation of a solid: in becoming deposited on the "weak points" of the iron surface, this solid will improve the protective effect of the passivating oxide film.

This will thus enable us to obtain some data on the possible effectiveness of an oxidizing inhibitor by superimposing on the theoretical "corrosion, immunity and passivation" diagram for iron the potential–pH equilibrium diagram which shows the stability conditions of the solids which can be formed by reduction of this inhibitor. This has been done with Fig. 3, where consideration has been taken of 0·01 M solutions of the nine following oxidizing substances: hyperosmates, pertechnetates, chromates, molybdates, tungstates, vanadates, selenates, arsenates and antimonates.

A thick line indicates the potentials below which the inhibitor can be reduced; the shaded sections represent those parts of the corrosion domains of iron for which the products of the reduction of the oxidizing agent are not solids. If, as a first approximation, we assume that the reduction reactions of the oxidizing agent are reversible and that the solids formed in this reduction constitute a protective coating on the iron, the shaded sections in Fig. 3 show the theoretical conditions of corrosion, the non-shaded areas representing the theoretical areas of non-corrosion.

According to the first six diagrams in Fig. 3, the hyperosmates and pertechnetates are extremely effective inhibitors of iron corrosion, which coincides with Cartledge's observations(²); it is well known that the chromates, although less effective, are nevertheless very good inhibitors; the molybdates and tungstates are effective only to small extent; vanadates are hardly effective at all.

---

(²) See Chapter IV, sections 13.4 (osmium) and 11.2 (technetium).

On the other hand, the last three diagrams of Fig. 3 provide data on the efficacity of selenates, arsenates and antimonates.(³)

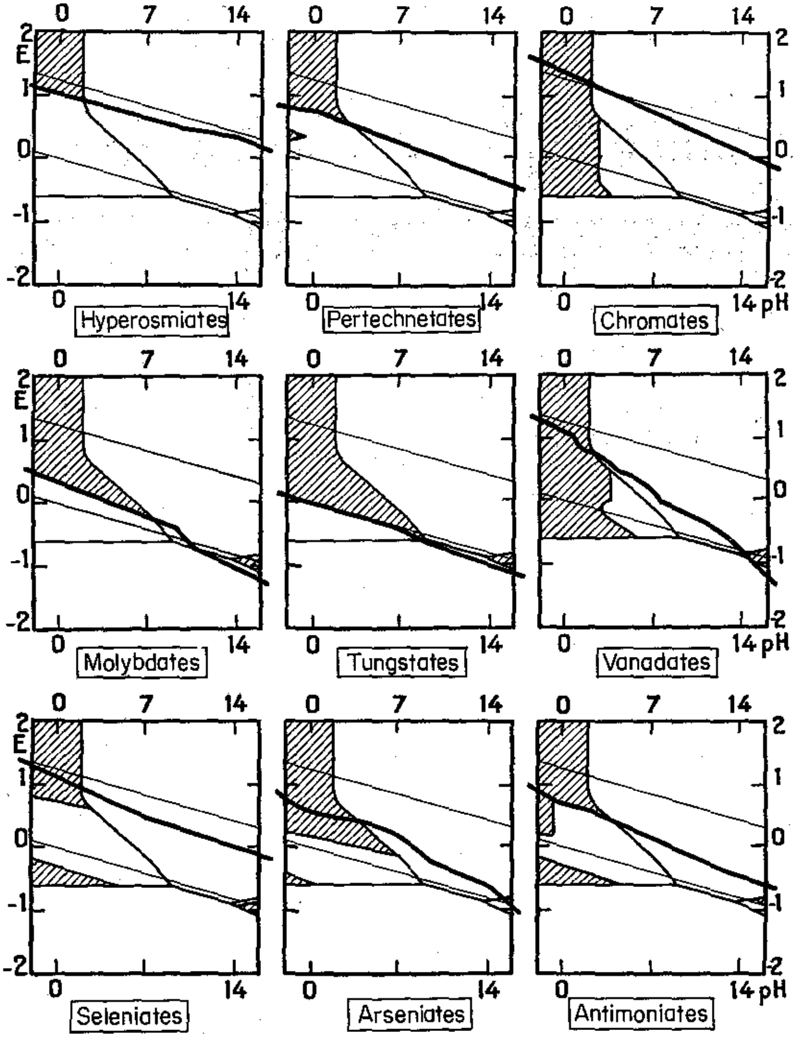


FIG. 3. Oxidizing corrosion inhibitors. The hatched regions indicate theoretical corrosion domains in the presence of 0·01 M solutions of inhibitor.

## 5. DEGREE OF NOBILITY OF METALS (See Fig. 4)

The Nernst scale of "solution potentials" allows us to classify the metals in order of "nobility", according to the value of the equilibrium potential of their reaction of dissolution in the form of a simple given ion considered in standard state (1 ion g/l): those metals are considered as noble which have an equilibrium potential higher than that of the standard hydrogen electrode and which,

---

(³) See primarily the work done in this field by Piontelli and Fagnani, Chapter IV, section 18.4 (antimony).

therefore, cannot be corroded with release of hydrogen in a solution with a zero pH value; the non-noble metals are those for which this condition does not arise and which can thus be corroded with release of hydrogen.

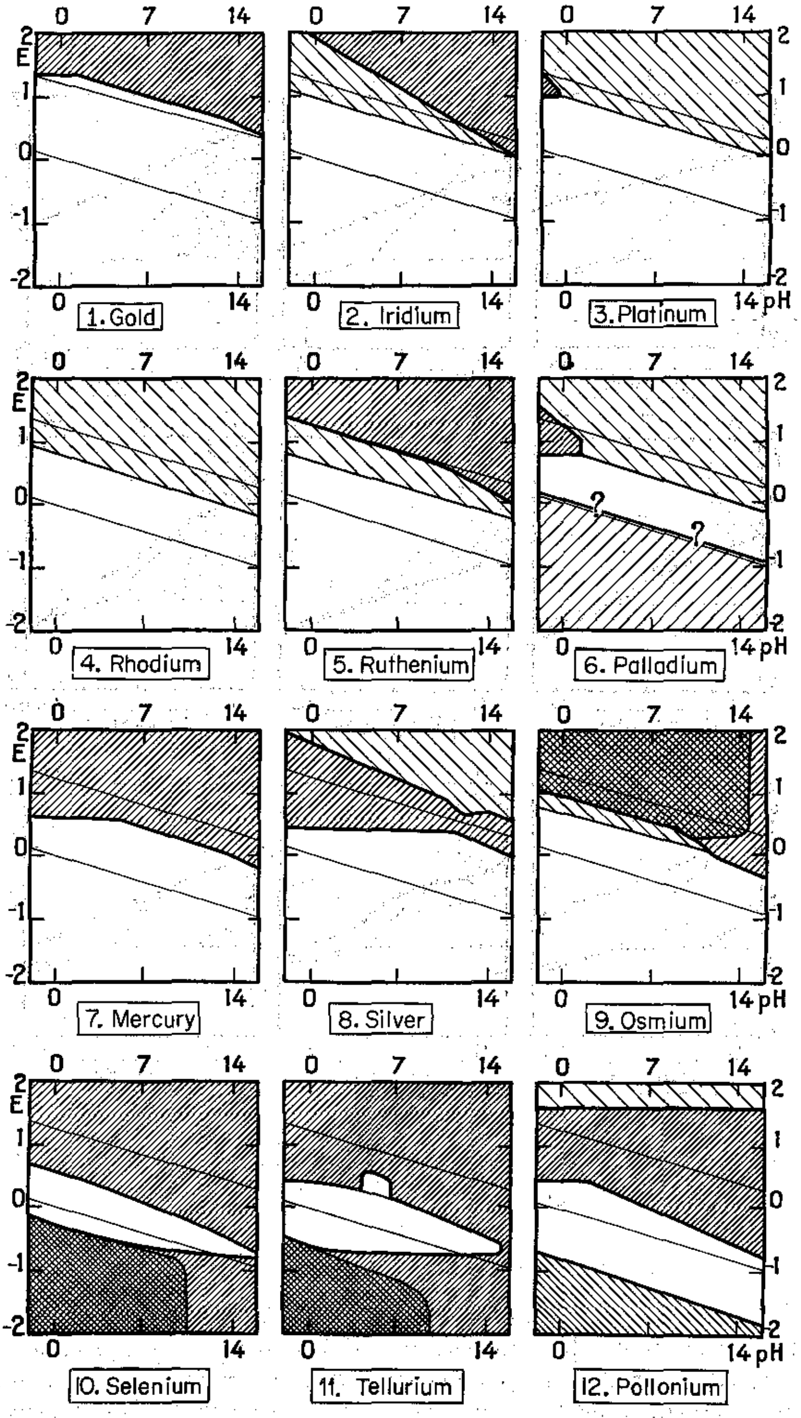


FIG. 4. Corrosion, immunity and passivation domains of metals and metalloids classified in order of thermodynamic nobility.

As R. Piontelli writes in his preface to this *Atlas*, this degree of "thermodynamic nobility" can differ appreciably from the "practical nobility" established experimentally. The divergence between these two degrees of nobility may be due to the following three facts:

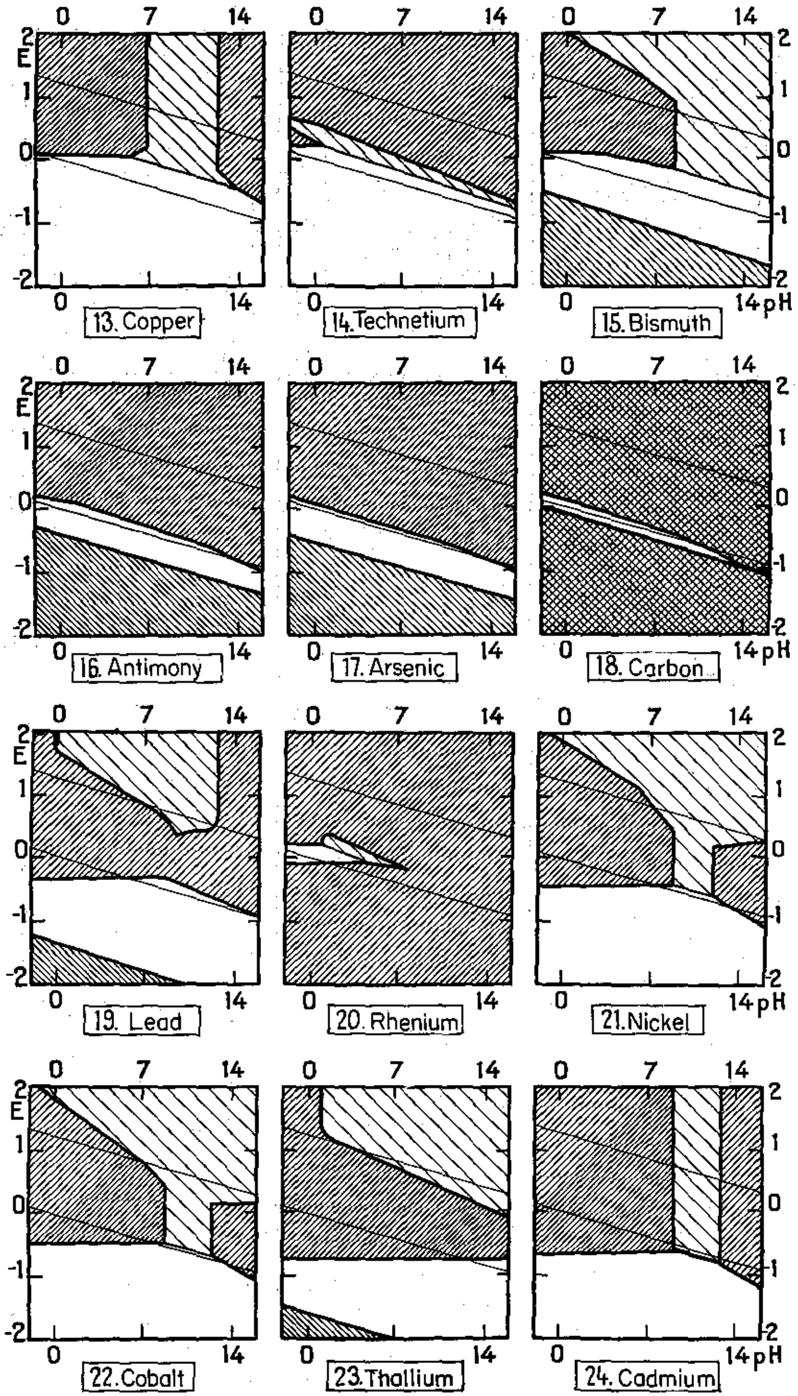


FIG. 4. (*continued*)

The metal is dissolved not in the form of a single simple ion (such as $Cu^+$), but in the form of two simple ions ($Cu^+$ and $Cu^{++}$) or oxygen ions ($CuO_2^{--}$) or in the form of complex ions [$Cu(CN)_2^-$, $CuCl_2^-$]; this results in a modification of the "solution potential" of the metal.

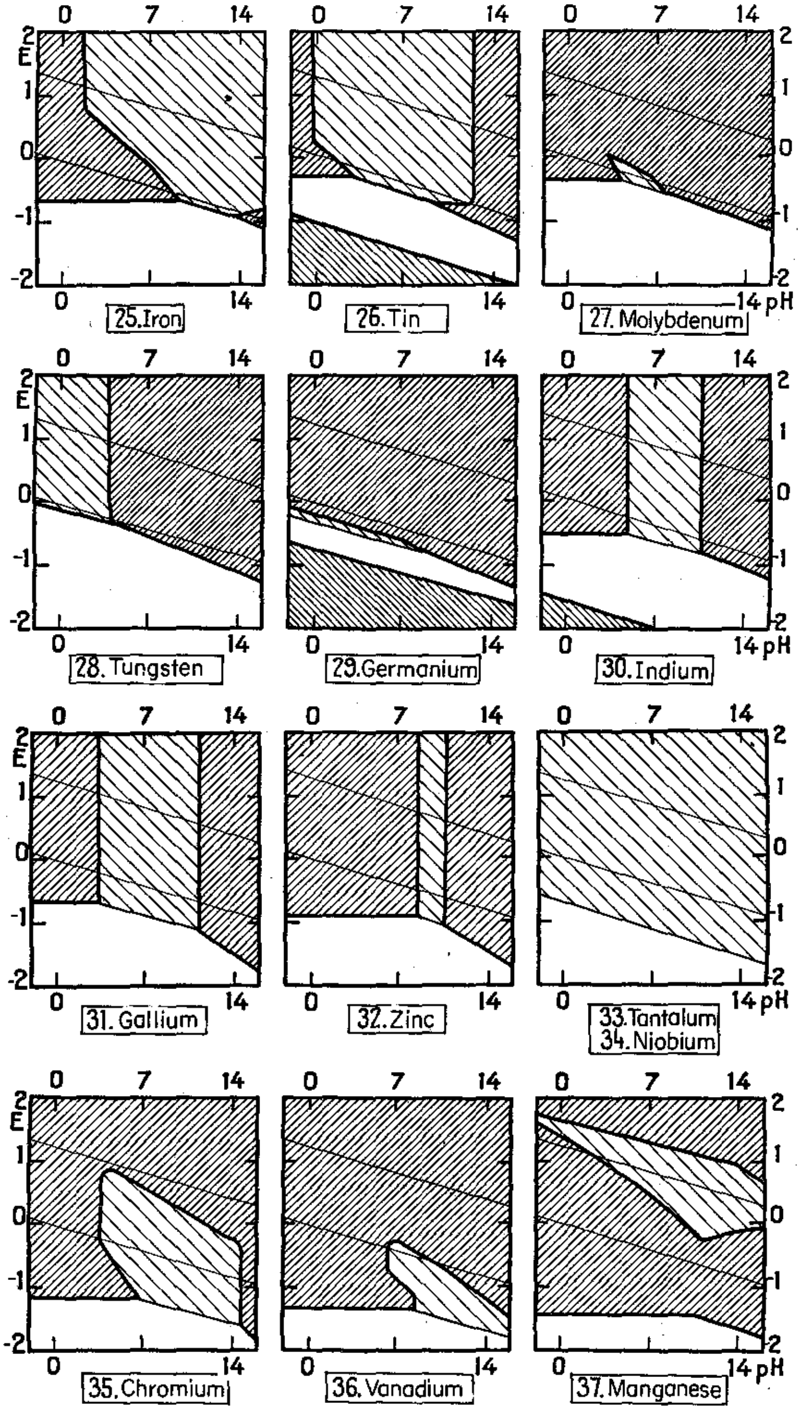


FIG. 4. (*continued*)

The metal is coated with a passivating film (oxide $Fe_2O_3$, hydride $UH_3$, salt $FePO_4$); the dissolution of the metal can thus be more or less completely braked by the interposition of a more or less protective film.

The dissolution reaction can be strongly irreversible (in the case of non-"normal" metals in the Piontelli classification, such as nickel), in which case the dissolution of the metal occurs effectively only through an appreciable potential-rise, at an electrode potential patently higher than the thermodynamic equilibrium potential.

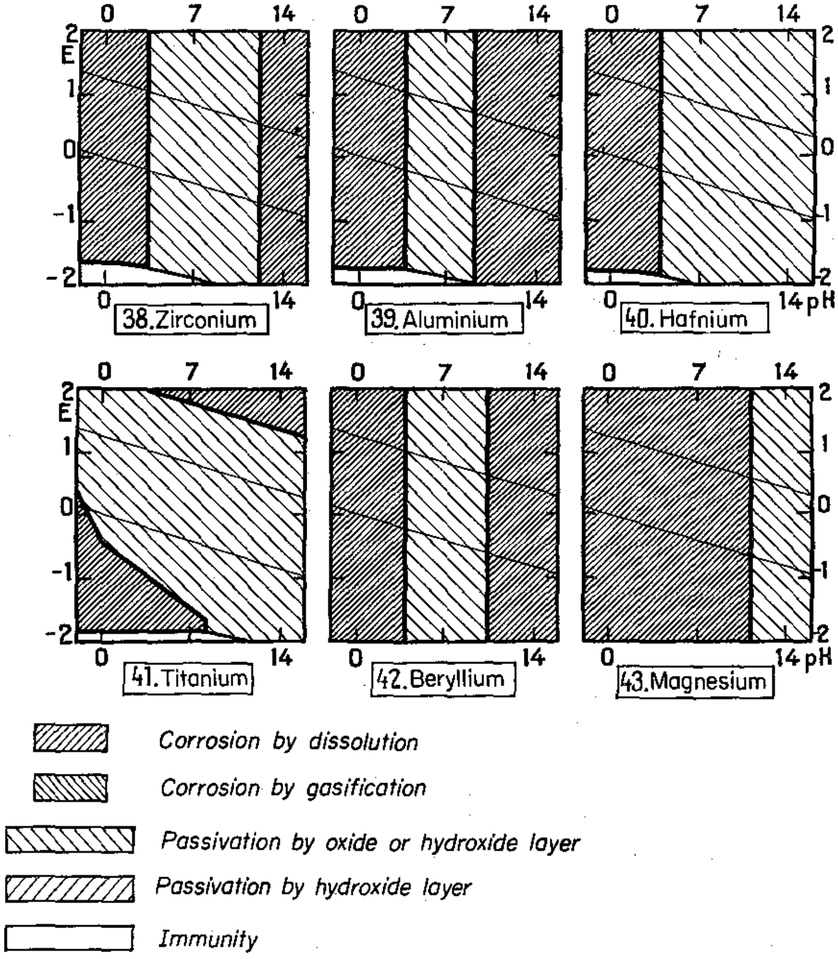


FIG. 4. (*end*)

The third cause of this divergence pertains to electrochemical kinetics and will be examined in paragraph 4.6; the first two causes can be studied on a thermodynamic basis with the aid of the potential–pH equilibrium diagrams if we adopt as the criteria of nobility, not the Nernst "solution potential", but the *immunity* conditions of the metal (in the presence of the total of the ions which this metal can produce) and the total of the *immunity* and *passivation* conditions of the metal respectively.

*Thermodynamic nobility and immunity*

Figure 4 gives the theoretical "corrosion, immunity and passivation" diagrams for forty-three metals and metalloids, classified in descending order of thermodynamic nobility. The shaded areas

TABLE I

Noble metals

| | A THERMODYNAMIC NOBILITY (immunity) | B PRACTICAL NOBILITY (immunity and passivation) | |
|---|---|---|---|
| 1 | Gold | Rhodium | 1 |
| 2 | Iridium | Niobium | 2 |
| 3 | Platinum | Tantalum | 3 |
| 4 | Rhodium | Gold | 4 |
| 5 | Ruthenium | Iridium | 5 |
| 6 | Palladium | Platinum | 6 |
| 7 | Mercury | Titanium | 7 |
| 8 | Silver | Palladium | 8 |
| 9 | Osmium | Ruthenium | 9 |
| 10 | Selenium | Osmium | 10 |
| 11 | Tellurium | Mercury | 11 |
| 12 | Polonium | Gallium | 12 |
| 13 | Copper | Zirconium | 13 |
| 14 | Technetium | Silver | 14 |
| 15 | Bismuth | Tin | 15 |
| 16 | Antimony | Copper | 16 |
| 17 | Arsenic | Hafnium | 17 |
| 18 | Carbon | Beryllium | 18 |
| 19 | Lead | Aluminium | 19 |
| 20 | Rhenium | Indium | 20 |
| 21 | Nickel | Chromium | 21 |
| 22 | Cobalt | Selenium | 22 |
| 23 | Thallium | Technetium | 23 |
| 24 | Cadmium | Tellurium | 24 |
| 25 | Iron | Bismuth | 25 |
| 26 | Tin | Polonium | 26 |
| 27 | Molybdenum | Tungsten | 27 |
| 28 | Tungsten | Iron | 28 |
| 29 | Germanium | Nickel | 29 |
| 30 | Indium | Cobalt | 30 |
| 31 | Gallium | Antimony | 31 |
| 32 | Zinc | Arsenic | 32 |
| 33 | Niobium | Carbon | 33 |
| 34 | Tantalum | Lead | 34 |
| 35 | Chromium | Rhenium | 35 |
| 36 | Vanadium | Cadmium | 36 |
| 37 | Manganese | Zinc | 37 |
| 38 | Zirconium | Molybdenum | 38 |
| 39 | Aluminium | Germanium | 39 |
| 40 | Hafnium | Vanadium | 40 |
| 41 | Titanium | Magnesium | 41 |
| 42 | Beryllium | Thallium | 42 |
| 43 | Magnesium | Manganese | 43 |

Non-noble metals

Classification of metals and metalloids in order of nobility represent the corrosion domains and were established by lines descending from right to left in the most frequent case of corrosion by dissolution, and by lines descending from left to right in the relatively rare case of corrosion by gasification (e.g. by formation of $OsO_4$, $H_2Se$, $H_2Te$, $CO_2$, $CH_4$, $AsH_3$, $SbH_3$, $BiH_3$, $GeH_4$, $SnH_4$, $PbH_2$, InH, TlH). The passivation domains are lightly hatched, the hatching descending from left to right in the very frequent case of passivation by formation of oxide or hydroxide and descending from right to left in the rare case of passivation by hydride formation ($Pd_2H$). The white areas represent the immunity domains.

It was considered that a metal is thermodynamically noble or non-noble according as its immunity domain (i.e. its thermodynamic stability domain) shows or does not show a section in common with the thermodynamic stability domain of water at a pressure of 1 atm.; this immunity domain is situated between two lines *a* and *b* traced on the equilibrium diagrams established in Chapter IV.

It was considered that the nobility of a metal is greater, the larger the surface common both to its immunity domain and to the stability domain of the water; it was considered that the greater the surface situated between the immunity domain of a non-noble metal and the stability domain of water, the more does the non-noble metal fall short of nobility.

### *Practical nobility, immunity and passivation*

Leaving aside, for the time being, the kinetic factors mentioned above, and assuming as a first approximation that the passivating films considered in Fig. 4 are perfectly protective, we considered that a metal is practically the more noble the greater the surface common both to the total of the immunity and passivation domains and to the stability domain of water. In the case of metals where these surfaces are preceptibly identical, it was accepted that this "practical nobility" is greater the more the immunity and passivation domains extend below and above the stability domain of water, and the more these domains overlap the section of the diagrams which corresponds to pH values between 4 and 10, which are most frequently met with in practice.

Table I shows, on the bases which have just been expounded, the classification of the forty-three elements examined on Fig. 4, on the one hand, according to "thermodynamic nobility" and, on the other, according to "practical nobility".

It must be understood that this table is to be regarded as a draft subject to considerable revision, notably because the electrochemical equilibrium diagrams on which it is based are themselves approximations and in some cases will call for drastic alteration (e.g. those for nickel and cobalt), and because the corrosion and/or passivation reactions represented are sometimes strongly irreversible (e.g. for carbon).

In its present form, this table brings out the considerable ennobling effect which passivation has on the ten following metals: niobium, tantalum, titanium, gallium, zirconium, hafnium, beryllium, aluminium, indium and chromium. According to this table, we must consider the first twenty-three items in column A as having thermodynamic nobility.

## 6. EXPERIMENTAL APPLICATIONS

As pointed out in section 1 (Generalities) of Chapter III, the electrochemical equilibrium diagrams cannot by themselves *solve* more than a limited number of problems. They are only one of the tools put at the disposal of the scientist, and they must almost always be employed in conjunction with other means of investigation, of which particular importance attaches to electrochemical kinetic studies, based on the judicious experimental definition of potential–current curves (e.g. by means of intensiostatic or potentiokinetic tests).

Analysis of such potential–current curves, together with the equilibrium diagrams, enables us to predetermine the theoretically possible and theoretically impossible reactions for each electrode potential value. If to this thermodynamic analysis, we add chemical, microscopic and other examinations it will generally be easy to change these theoretical possibilities into experimental certainties and thus, for example, to predetermine absolutely the conditions in which a metal alloy corrodes or does not corrode when in contact with a given aqueous solution.

Further on, the reader will find (Chapter IV, section 12.1) an exposé relating to iron, containing some examples for the application of an equilibrium diagram in the experimental study of corrosion and metal protection conditions. It would be useful: if such studies were carried out by electrochemists and metallurgists simultaneously; if they were used patiently for a systematic investigation of the effect produced by the composition of solution (pH, oxidizing agents, reducing agents, chlorides, phosphates...) and of the nature of the metal (chemical composition, structural state, heat treatment, cold working...); if they were applied progressively and thoroughly to different metals and their alloys; and if they were extended simultaneously to both the theoretical and the experimental fields to cover the behaviour of metals and alloys at high temperatures and pressures.

Such an effort would inevitably lead to better utilization of the existing metals and alloys, to new protection procedures and new alloys.

## 7. NOTE ON THE SIGNIFICANCE AND PRACTICAL IMPLICATIONS OF THE POTENTIAL–pH ELECTROCHEMICAL EQUILIBRIUM DIAGRAMS

In the course of "Study Sessions on the Electrochemical Behaviour and Corrosion of Metals and Stainless Steels" held in Brussels on 21 and 22 November 1957, C. Carius, C. Edeleanu and M. Pourbaix met and exchanged views on subjects of common interest. C. Edeleanu drew the attention of M. Pourbaix and C. Carius to the fact that the exact importance of the "potential–pH equilibrium diagrams" is often insufficiently realized in Great Britain and other countries, and that the interpretations made of them were therefore sometimes erroneous.

On the suggestion of C. Edeleanu, these three scientists drew up the following text, in which they express their agreement on the significance and implications of these diagrams.(4)

1. The metals having the greatest economic importance, and particularly iron, zinc and aluminium, belong, by virtue of their place in the dissolution potential scale, to the category of "non-noble" metals. The transformation of these metals into ions, forming a salt or oxide, is almost invariably accompanied by the liberation of energy, so that these metals tend to dissolve when certain favourable conditions are obtained (presence of humidity, access of atmospheric hydrogen).

   "Electrochemical equilibrium diagrams" are useful for obtaining as complete and overall a view as possible of the interface reactions thermodynamically practicable in a particular given case. Such diagrams indicate, notably as a function of the solution pH (a measure of the degree of acidity or alkalinity of that solution) and of the metal's electrode potential (which measures the reducing or oxidizing power of the interface), the thermodynamic limits of the stability of the metal in relation to its ions, to the ions of the water, and to the reaction products of these ions (hydroxides, oxides, etc.).

   These diagrams show the equilibrium potentials of the electrochemical reactions, the affinity of these reactions and the solubility of the solids for the given experimental conditions.
2. In the absence of any data indicating the contrary, the *electrochemical equilibrium diagrams* of the metals apply only to the behaviour of pure metals (pure iron, for example) in the presence of solutions not containing substances which might form soluble complexes with these metals (cyanides) or insoluble salts (phosphates). Thus these diagrams do not apply to alloys (alloy steels).

---

(4) See the Comptes Rendus de Séances d'Étude sur le comportement électrochimique et la corrosion des métaux et des aciers inoxydables, Brussels, 21 and 22 November 1957 (Rapport technique RT. 66 of CEBELCOR, May 1958), Appendix, pp. 9–11.

3. *The theoretical "corrosion, immunity and passivation" diagrams* which are deduced, by means of certain hypotheses, from these electrochemical equilibrium diagrams are only applicable in the cases defined under point 2 above, where the equilibrium diagrams are applied.
4. The *passivation* conditions of metals are defined as those in which the stable form of the metal in question is an insoluble oxide (or hydroxide or solid salt); if it is formed by direct contact with the metal, this oxide (or other solid product) "passivates" the metal to a greater or lesser extent and affords it a greater or lesser degree of protection against corrosion; generally speaking, protection will be complete where the film or deposit with which the metal is coated is absolutely adherent and non-porous; in all other cases, protection will be generally imperfect. Thus *passivation does not imply passivity*, if we define passivity as being the condition in which a metal does not corrode, although the metallic form is not thermodynamically stable and the metal thus tends to become transformed into another substance.

   This idea of passivity (caused by a *passivation*) differs from the idea of *immunity* (due, for example, to a *cathodic protection*), which means the condition in which a metal does not corrode because its metallic form is thermodynamically stable, thus making any transformation of the metal, and consequently corrosion, impossible.

   In the particular case of iron, for example, the oxide formed by passivation is often non-porous and thus protective in the solutions containing no chloride; it is generally porous and non-protective in chlorinated solutions.

   The pH value given in the *x*-axis of the electrochemical equilibrium diagrams is the pH of that fraction of the solution which is in direct contact with the surface (or with a fraction of the surface) of the metal under examination. This pH value is thus not necessarily the pH value of the bulk of the solution; the divergences between the local pH value and the bulk pH value can be considerable, particularly in cases of localized corrosion. In such cases there is generally an increase in the local pH value in the zones where reduction takes place (e.g. reduction of the dissolved oxygen) and a diminution of the local pH value in those zones where a solid oxide or hydroxide forms (e.g. rust).
5. The *electrochemical equilibrium diagrams* must be regarded primarily as patterns showing the reactions which are theoretically possible and impossible for different electrode potentials and pH conditions. If these diagrams are correctly drawn up, there can be no possibility of errors or exceptions; just as the fact that arithmetic is a formal and exact science does not prevent numerous errors in calculation from being made every day, so thermodynamics is exact, but those people who use thermodynamics may commit errors. The electrochemical equilibrium diagrams, which are of a thermodynamic character, must therefore be employed with a full realization of their significance and their conditions of validity. Essentially, these diagrams express that which is energetically *possible* or energetically *impossible*; now, numerous electrochemical reactions are irreversible, i.e. do not necessarily come about even when they are energetically possible. These diagrams, therefore, do not necessarily show what *actually* occurs; an absolute and definite reply to this point often requires *experimental kinetic studies*, consisting, for example, in the plotting of intensiostatic or potentiokinetic polarization curves.

   Electrochemical equilibrium diagrams can serve primarily as a guide in carrying out such experimental studies and in the interpretation of the results obtained.

## SECTION 5

# ELECTRODEPOSITION

T. P. HOAR

INFORMATION contained in potential–pH diagrams is useful in several ways for application to problems involved in electrodeposition. We consider below some representative problems associated with (a) cathodic processes, (b) anodic processes, (c) the solution.

### (a) CATHODIC PROCESSES

The desired cathodic reaction in electrowinning, electrorefining, electroplating and electroforming is ordinarily metal deposition. Hydrogen deposition, oxygen reduction and oxide or hydroxide deposition are usually undesirable, although the last of these side reactions has occasional usefulness.

Consider the deposition of nickel from sulphate solution open to the air; Fig. 1 shows the germane part of the nickel potential–pH diagram. At, say, pH 4·5 and $E_H = -0{\cdot}4$ V, evidently oxygen and hydrogen ion can be reduced as well as nickelous ion; however, the overpotentials required to reduce oxygen and hydrogen ion at sensible rates are fortunately considerably higher than that required for nickelous ion reduction, and this can consequently occur at *ca.* 96–98 per cent efficiency. Decrease of pH tends to increase the relative amount of hydrogen ion reduction. Nevertheless, the "acid" type of Watts nickel bath operating at *ca.* pH 2 can give good nickel deposition even though somewhat more hydrogen is evolved, because the pH of the solution next to the cathode rises, through hydrogen ion reduction, and under steady-state deposition conditions the relative amount of hydrogen ion reduction is not unduly large. On the other hand, increase of pH of the bulk solution beyond about 5 causes the catholyte, under deposition conditions, to contain sufficient nickelous hydroxide, present as positively charged colloidal particles, to lead to co-deposition of hydroxide with metal: this gives a harder and more brittle deposit that, although suitable for rather limited purposes, is in general undesirable. Deliberate cathodic deposition of beryllia and alumina from colloidal solutions has been used for the formation of protective oxide films; the suitable electrolytes are beryllium and aluminium sulphate solutions lightly buffered to *ca.* pH 6 and 4 respectively, so that a small increase of pH caused by hydrogen ion reduction, coupled with a very small faradaic current to discharge the colloidal particles, gives the required oxide deposition on the cathode. The very small faradaic current required for hydroxide or oxide deposition, due to the small charge/mass ratio of the colloidal particles, explains why a high pH nickel bath may give almost 100 per cent cathode current efficiency and yet yield deposits containing considerable hydroxide.

In certain special cases oxide can be formed by faradaic cathodic reduction of a soluble ion: thus cathodic deposits of cuprous oxide can be made from cupric sulphate solutions buffered at *ca.* pH 3·5, as shown by the portion of the copper diagram given in Fig. 2. The conditions for the further reduction of such deposits to metal can also be obtained from potential–pH diagrams; such reduction of cuprous oxide to copper is the basis of a decorative coating with a patterned structure caused by the spread of the reduction from widely dispersed nuclei.

The conditions for cathodic deposition from alkaline solutions containing metal hydroxy- or oxy-anions are likewise to be found on the appropriate potential–pH diagrams: tin and zinc deposition from stannate and zincate solutions are examples (see pp. 478, 409). Furthermore, the potential–pH conditions for cathodic deposition from baths containing other complexants, such as cyanide ion, ammonia, and substituted ammonias, can readily be seen on suitable potential–pH diagrams incorporating the complex-forming reactions. It is usually convenient to calculate such diagrams for one fixed activity of complexant, just as the simple diagrams are calculated for a fixed activity of water.

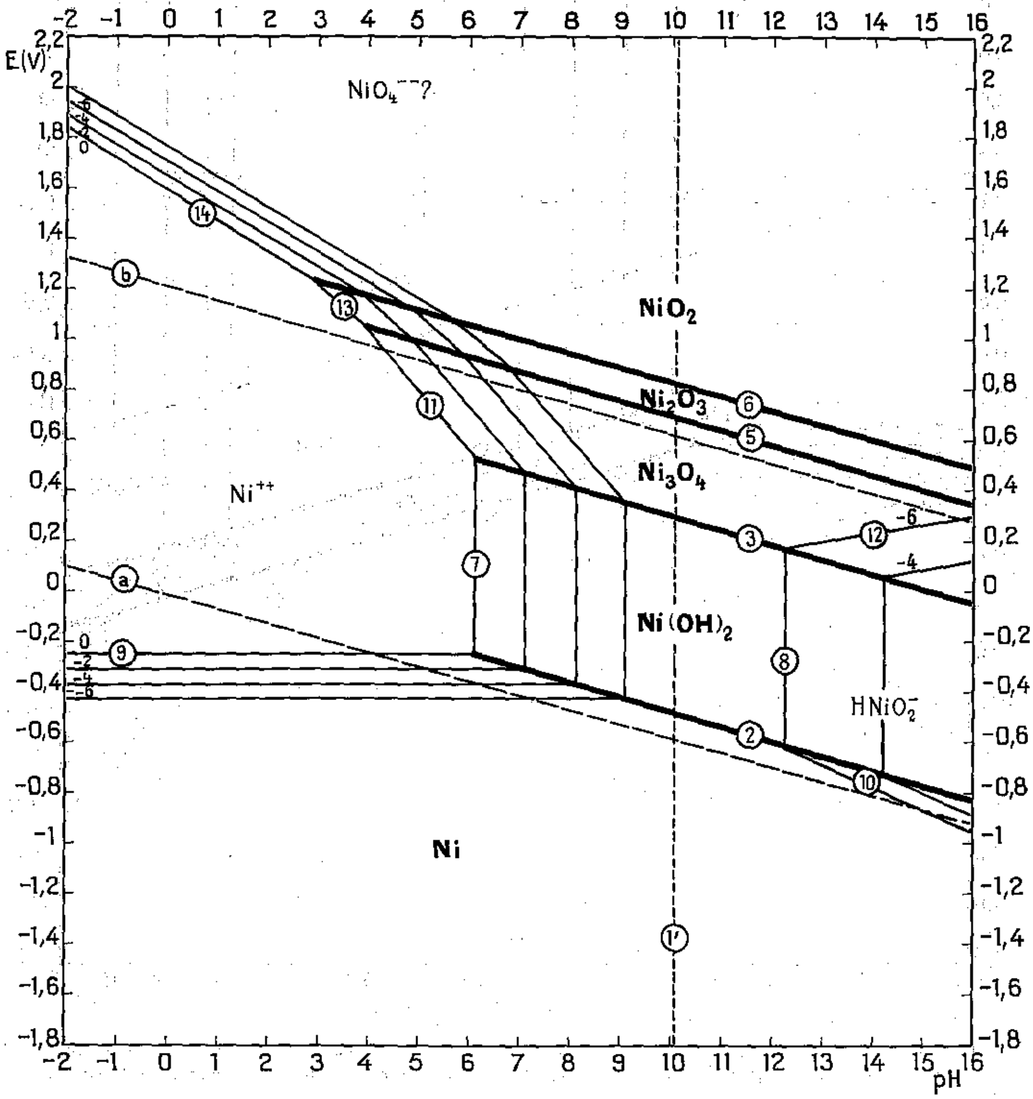


FIG. 1. Potential–pH equilibrium diagram for the nickel–water system, at 25°C.

Metals that form volatile hydrides, such as antimony (see p. 527), are occasionally electrodeposited.

Formation of the toxic hydride at high cathode polarization is a possible hazard, and the potential–pH conditions leading to it are easily seen on the appropriate diagram.

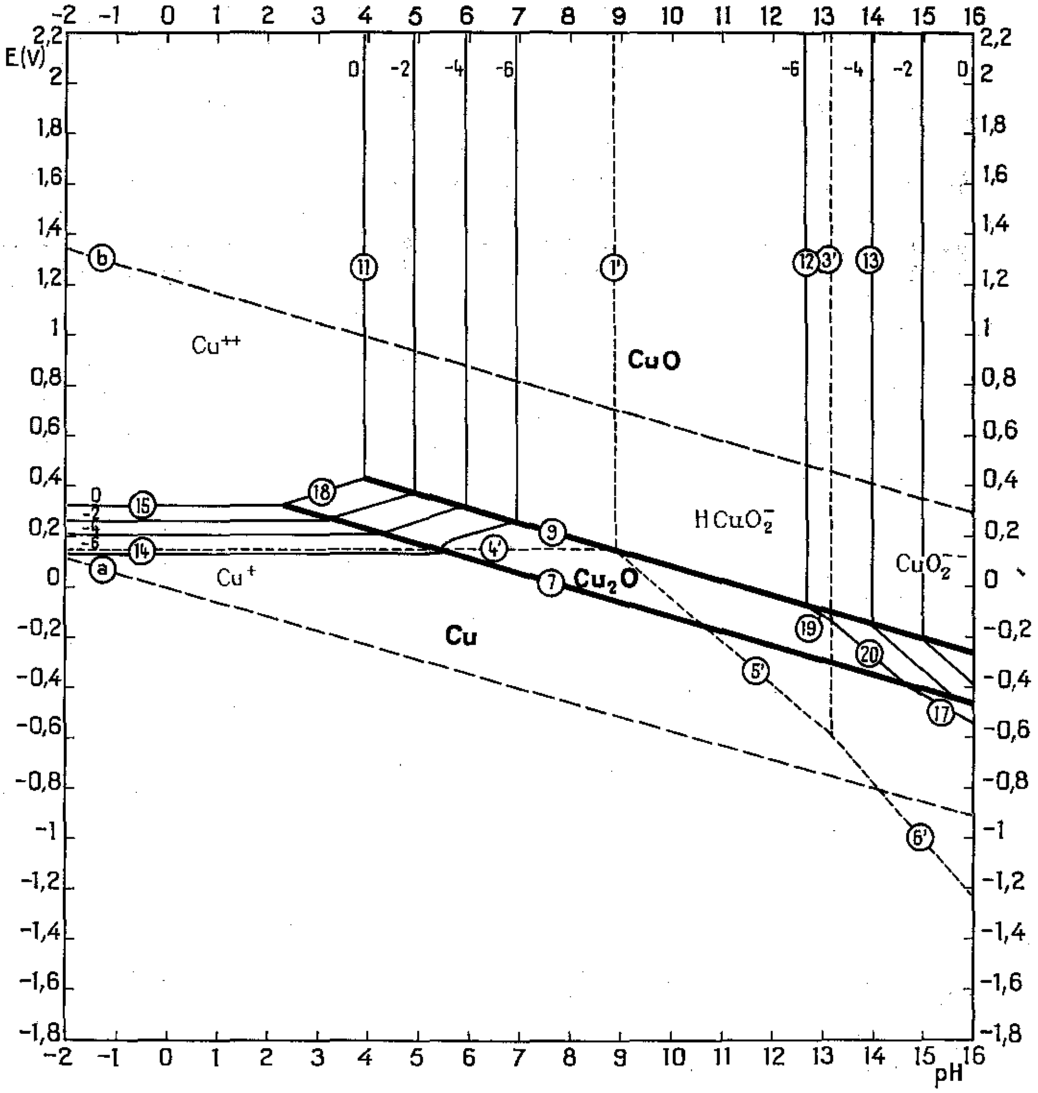


FIG. 2. Potential–pH equilibrium diagram for the copper–water system, at 25°C. [Only solid Cu, $Cu_2O$ and CuO are considered in the figure. $Cu(OH)_2$ and trivalent copper compounds have not been considered.]

### (b) ANODIC PROCESSES

In electrodeposition, it is usually desired to have either (a) an anode of the metal being deposited that dissolves at near 100 per cent current efficiency or (b) an anode that is totally insoluble and that acts merely as an inert basis for oxygen evolution. It is rarely desirable to have an anode that gives a mixture of these processes, or that operates consecutively in the dissolving and the passive states.

Again considering Fig. 1, we see, for example, that nickel dissolves to nickelous ion at unit activity at potentials more positive than −0·23 V and at pH less than about 6. At higher pH, solid nickelous hydroxide is the initial anodic product, and this is converted to higher oxides at higher anode potentials: under such conditions, passivation of a nickel anode occurs at once. However, passivation can also occur below pH 6, indeed, as low as *ca.* pH 0·5, because the anodic overpotential required to dissolve nickel to nickelous ions at the current densities required in electrodeposition process is considerable. Thus, if the polarization raises the anode potential above the broken-line extension of the $Ni/Ni(OH)_2$ line (Fig. 1), solid nickelous hydroxide may be formed at low pH; and since there is good evidence that its formation from the metal is *kinetically* easier than the formation of dissolved nickelous ion, its preferential formation is not surprising, and the tendency of nickel anodes to passivate is easily understood. In practice, this is remedied by the incorporation of a little oxide in the nickel anode and/or of chloride in the solution; the overpotential required for dissolution is thereby much reduced and the potential for passivation is not reached.

Soluble anodes operating in alkaline solution, such as tin and zinc, can also passivate at high current densities, mainly because the supply of complexing hydroxyl ions in the solution next to the anode becomes insufficient, so that insoluble hydroxides or oxides are formed. In the special case of tin anodes required to dissolve as stannate rather than stannite, a pseudo-passivation effect of this kind is advantageous; the anode is first passivated by the formation of stannic oxide at high current density, and subsequent operation at lower current density enables the stannic oxide to dissolve in the alkaline solution as stannate while being reformed anodically at the same rate. The potential–pH conditions for these transformations can be seen in the diagram for tin (p. 478).

Insoluble anodes are required in electrowinning and in some other electrodeposition processes. Lead is pre-eminently suitable owing to its easy passivation in sulphate solutions through the sparing solubility of its sulphate, and the fact that lead sulphate is readily converted anodically to the insoluble lead dioxide, which has good electron-conductivity and which is a good inert basis for hydroxyl-ion (or other anion) oxidation. Potential–pH conditions for the production and operation of lead-dioxide-coated lead anodes are shown in the diagram for the metal (p. 489). Platinum is another excellent inert anode, often used in practice for anodic oxidation processes, but usually too expensive for anodes used in electrodeposition. Chromium, on the other hand, while readily passivated like lead and platinum, enters a transpassive region at higher anode potentials and, as shown in the chromium diagram (p. 263), dissolves through the oxidation of its passivating chromic oxide film to soluble chromic acid or chromate. The same effect is found to a less extent in most of the "stainless" chromium irons and steels.

The "refractory" metals such as titanium, tantalum, etc., cannot be operated as inert anodes: although the potential–pH diagrams (pp. 217, 253) indicate the formation of oxide films over very wide ranges of pH and at very negative potentials, the films have very poor electron conductivity and the metals will not sustain any anodic reaction other than film thickening by ion transport under high-field conditions.

Anodic deposition of oxides from solution is occasionally a useful process, as in the electroanalysis of lead. As well as lead dioxide, cobaltic oxide, manganese dioxide and others can be deposited anodically by oxidation of soluble lower-valent ions; the suitable conditions of potential and pH can be readily seen in the relevant diagrams.

### (c) THE SOLUTION

Solutions used in electrodeposition need primarily to be stable except during the actual reactions at the electrodes. In particular, they should normally be operated under such pH conditions that hydroxide or oxide precipitation is negligible. These conditions, both for acid and alkaline solutions, are apparent in the relevant potential–pH diagrams. Buffering the solutions to the appropriate pH is frequently adopted to minimize changes due to adventitious absorption of atmospheric carbon dioxide, or to accidental contamination from acid pickling solutions or alkaline degreasants. Buffering also helps to maintain pH in the actual layer of solution next to the cathode or anode, although, as mentioned earlier, changes caused by hydrogen ion reduction may there be appreciable.

In some circumstances, alteration of pH or potential or both can be used to advantage in the purification of a solution used for electrodeposition. The removal of iron during the electrorefining of nickel is an example. Iron dissolves as ferrous ion from the impure nickel anodes into the fairly acid sulphate solution. The anolyte is freed from iron by raising the pH with lime and/or blowing with air, whereupon the very sparingly soluble *ferric* hydroxide is precipitated and can be removed by filtration. As can be seen in the germane part of the iron diagram (Fig. 3), both the rise of pH, and the presence of oxygen to effect oxidation and to raise the redox potential, contribute to the desired precipitation.

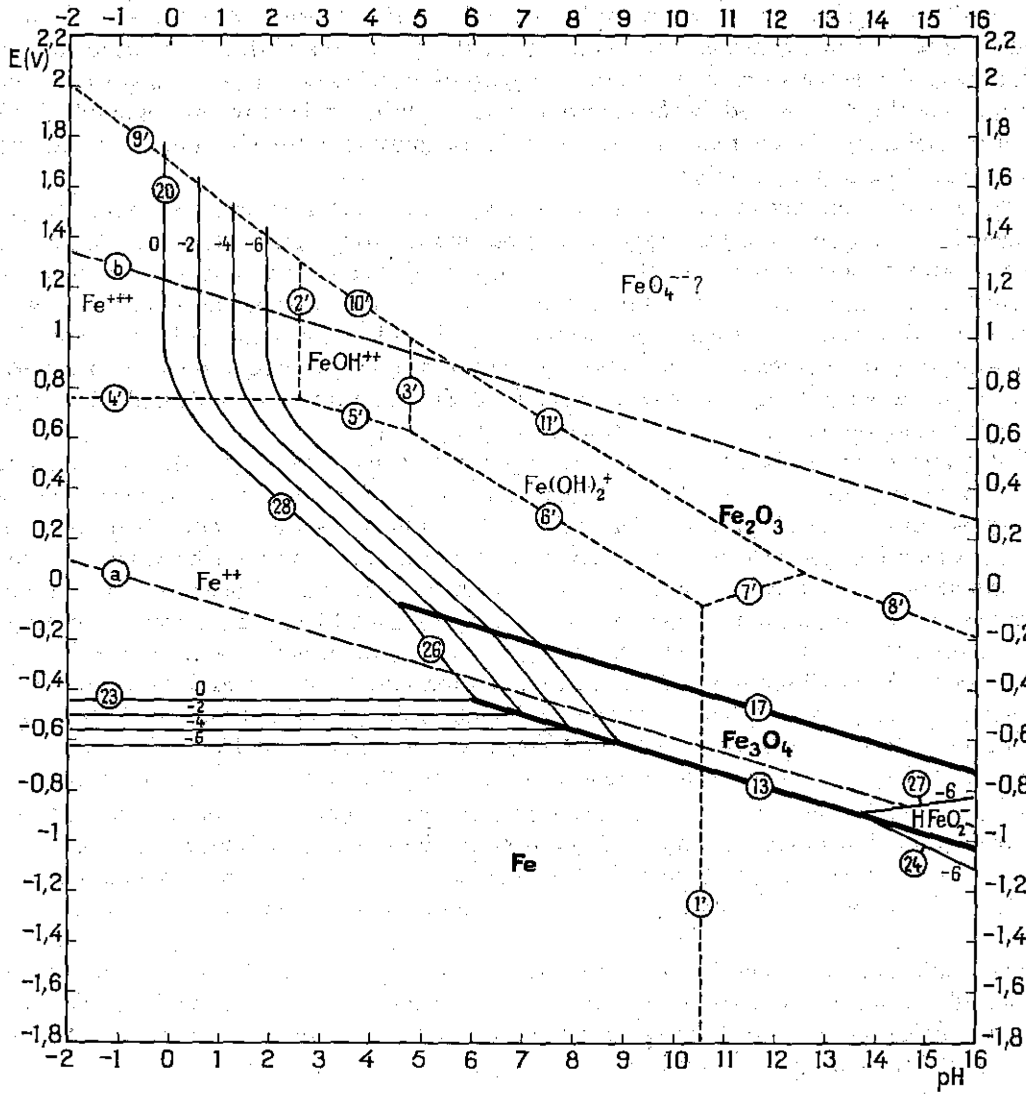


FIG. 3. Potential–pH equilibrium diagram for the iron–water system, at 25°C. (Only solid Fe, $Fe_3O_4$ and $Fe_2O_3$ are considered.)

## SECTION 6

# GEOLOGY

R. M. GARRELS

THE importance of pH and potential in reactions involving minerals has been recognized by geologists for several decades, and these two variables have been widely applied in geochemical work. On the other hand, the use of pH–potential diagrams depicting stability relations among solid phases is of relatively recent vintage (Blumer [1]; Krumbein and Garrels [2]).

The greatest use to date of pH–potential diagrams has been in the application to earth environments under surface or near-surface conditions inasmuch as most of the easily available thermochemical information has been compiled for use at 25°C and 1 atm. total pressure. However, the natural realm to which such data can be applied with fair accuracy should not be underestimated; it includes almost all of the earth that we can observe directly.

One major aspect of earth chemistry to which pH–potential diagrams have been applied profitably is the weathering process. This includes the zone in which minerals, originally formed under deep-seated high-temperature, high-pressure reducing conditions, become exposed to the atmosphere as uplift and erosion continuously wear away the earth's crust. The processes of rock-weathering and soil formation are those stemming from the superimposition of the acid oxidizing dilute aqueous environment of the earth's surface upon the alkaline, oxygen-free, more concentrated aqueous subsurface environment in which the rocks had been bathed for millions of years without gross alteration. Consequently there is a direct analogy in these processes to the corrosion of metals, which also are the products of high temperature and reducing conditions, and become exposed to the varied environments at the earth's surface.

A second major area of application of pH–potential diagrams is to the process complementary to weathering—chemical sedimentation. The waters of the earth span the range of pH from zero to 12 or perhaps a little higher, and that of potential from the breakdown of water into hydrogen to its equilibration with oxygen of the atmosphere (Fig. 1). The geologist needs to know, for a system of given composition, the mineral species that should coexist at equilibrium for each kind of environment. If the extent to which modern mineral assemblages equilibrate with their environments of deposition is deciphered, then a powerful tool has been developed for inquiry into the nature of environments of the geologic past by reversing the procedure and deducing the environment from the fossil mineral assemblage.

### SPECIFIC APPLICATIONS TO ROCK-WEATHERING

To date, most of the use of pH–potential diagrams in studying weathering processes has been devoted to the oxidation of mineral deposits. Attack on the major problem of the weathering of common rock minerals has been hindered by lack of thermochemical data on the silicates. The major minerals produced from mines, however, are sulphides, oxides, carbonates, hydroxycarbonates, sulphates, and hydrosulphates. Sufficient data are available to depict relations among many such mineral species. The major difficulty is related to the difference in composition between minerals and the pure chemical compounds for which thermochemical data are available.

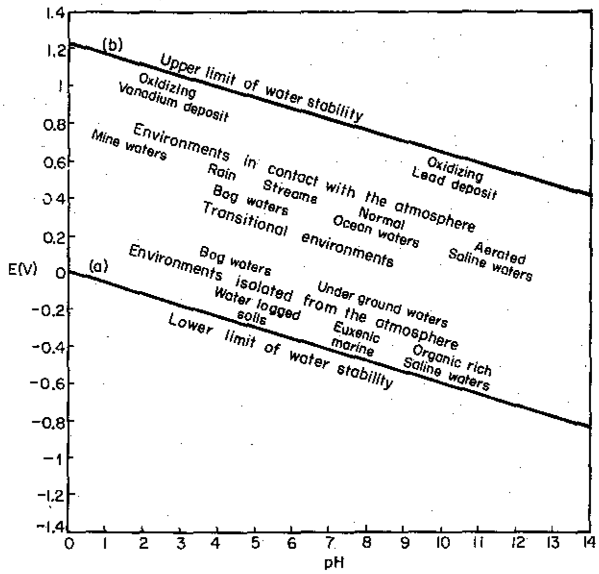


FIG. 1.

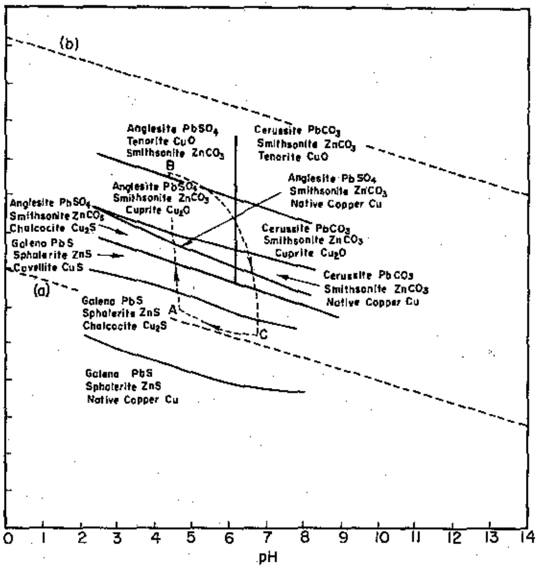


FIG. 2.

FIG. 1. Approximate positions of some natural environments as characterized by Eh and pH. (From R. M. GARRELS, *Mineral Equilibria*, Harper, New York, 1960, p. 201.)

FIG. 2. Mineral relations in an oxidizing ore body containing primary lead, zinc, and copper sulphide as functions of pH and potential. The dashed lines show deduced environmental changes with time during oxidation of a given sample of original ore. (From R. M. GARRELS, Mineral species as functions of pH and oxidation potentials, *Geochim. and Cosmochim. Acta*, **5**, 153–68 (1953).)

When sulphide ore bodies are weathered, the oxidation products are largely sulphates, oxides, and carbonates. Figure 2 shows an attempt to express mineral stability relations for an ore body containing lead, zinc, and copper sulphides as original minerals. Such a diagram can be viewed as a rough cross-section of such a deposit with the most highly oxidized compounds near the earth's surface at high potential, grading downward into the unaltered sulphides where oxygen is excluded in the zone of water saturation.

The uranium-vanadium deposits of the Colorado Plateau contain the mineral montroseite (VOOH) in the subsurface where the ores are protected from atmospheric oxygen. Evans and Garrels [3] have compared the results of oxidation as observed in nature (Fig. 3*a*) with those of the vanadium–water–

oxygen system, essentially as worked out by Deltombe *et al.* [4] (Fig. 3*b*). The remarkable correspondence between the calculated relations and those observed for the actual mineral species is apparent. Note how the sequence of environmental changes can be followed in terms of pH and potential.

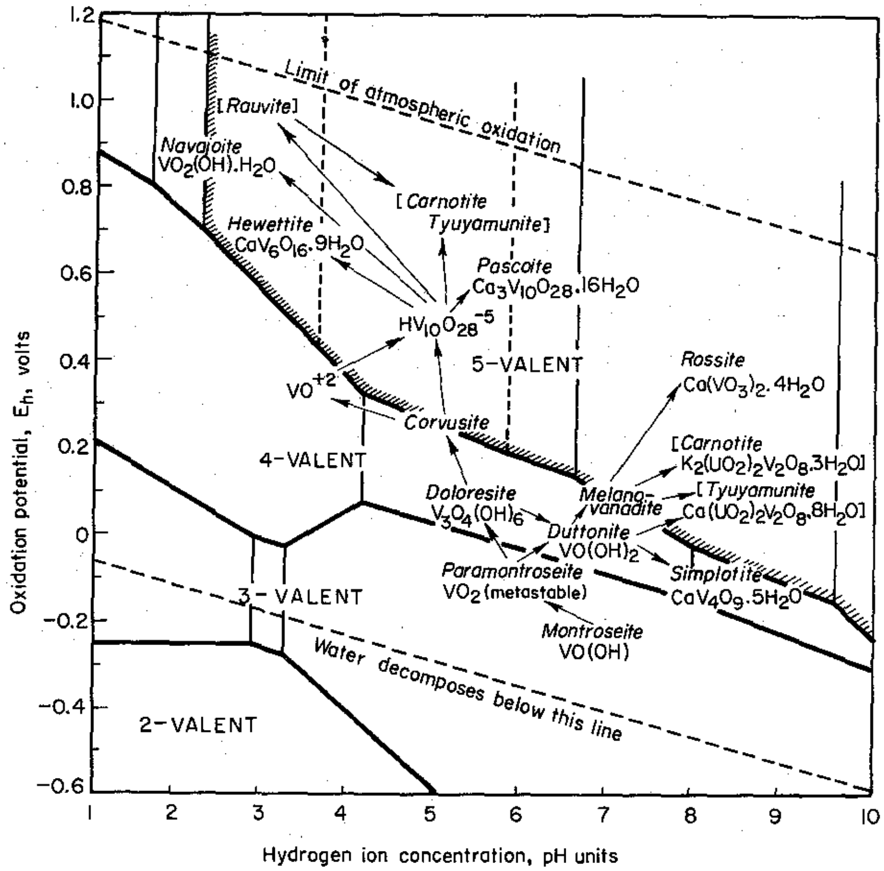


FIG. 3a. Aqueous equilibria of vanadium, showing the major aspects of relations among solids and important dissolved species. (From H. T. EVANS, Jr. and R. M. GARRELS, Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado Plateau ore deposits, *Geochim. and Cosmochim.* **15**, 131–9 (1958).)

These two examples show the kind of work that is in progress, but the major job is yet to be done when data for silicates are available and it becomes possible to depict in detail the changes that occur in the weathering of ordinary rocks.

## THE SPECIFIC APPLICATION TO CHEMICAL SEDIMENTATION

If the environment of a natural water changes, as where a stream enters the sea, or a portion of the sea becomes stagnant, precipitations of minerals usually occurs. The chemical sediments—those resulting from precipitation from homogeneous solution—have been classified on the basis of the pH and potential of their environment of formation (Fig. 4).

Only deposits of iron and manganese have been investigated in detail in so far as pH–potential diagrams of the important minerals are concerned (cf. Huber [5]; Krauskopf [6]).

A diagram illustrating relations among some major iron minerals is shown in Fig. 5. The use of diagrams including stability fields of sulphides and carbonates as well as those of oxides is common in the geologic literature. In many instances, the total dissolved sulphur and total dissolved carbon dioxide of the natural system can be estimated fairly accurately, so that the relations as depicted reflect nature without serious distortion. As shown by James [7] each mineral seen on Fig. 5 has a real counterpart in the Precambrian iron ores of the Lake Superior district of the United States. In some rocks, pyrite is the chief iron-bearing mineral; in others, siderite; in others, magnetite; and in still others, hematite. Thus the environments of deposition of these billion-and-a-half-year-old rocks can be read in terms of pH and potential.

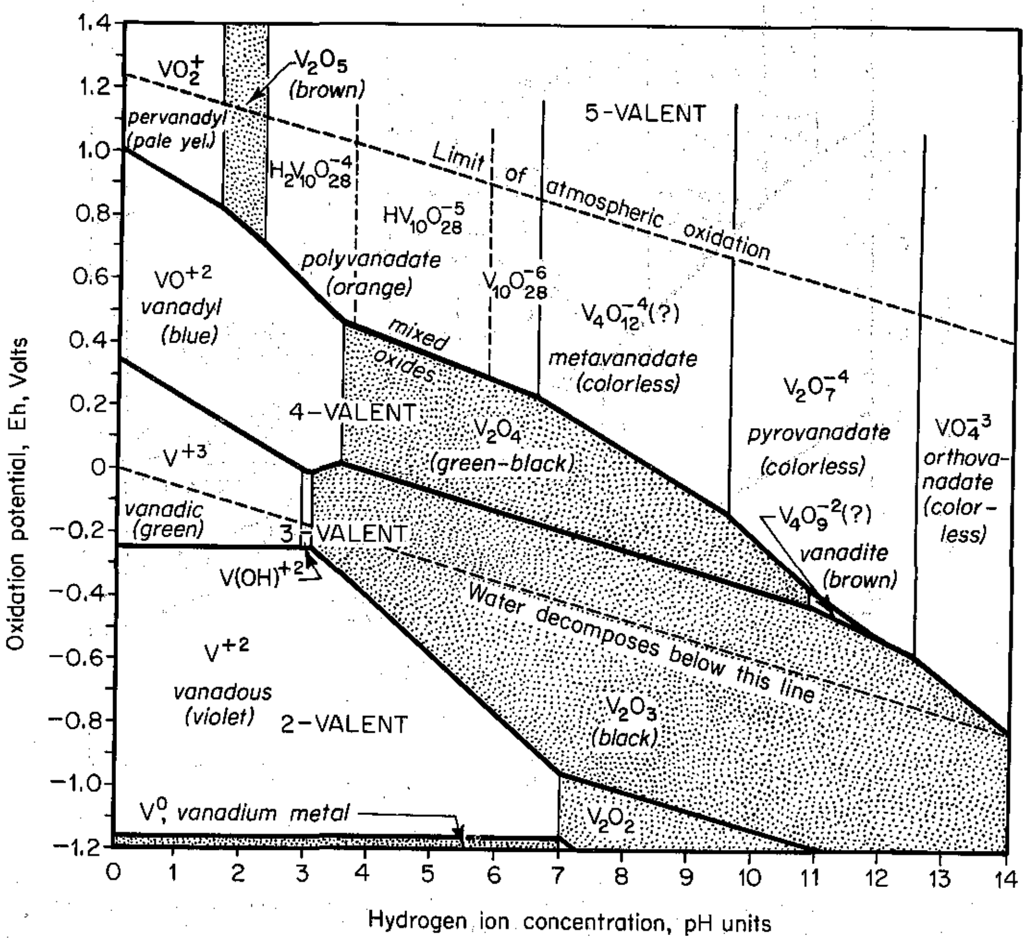


FIG. 3b. Aqueous equilibrium diagram for vanadium minerals showing stability regions for various minerals, and the paths followed during weathering. (From H. T. EVANS, Jr. and R. M. GARRELS, *loc. cit.*)

The future undoubtedly will see the development of diagrams representing stability relations of minerals involving essentially all the elements in the periodic table.

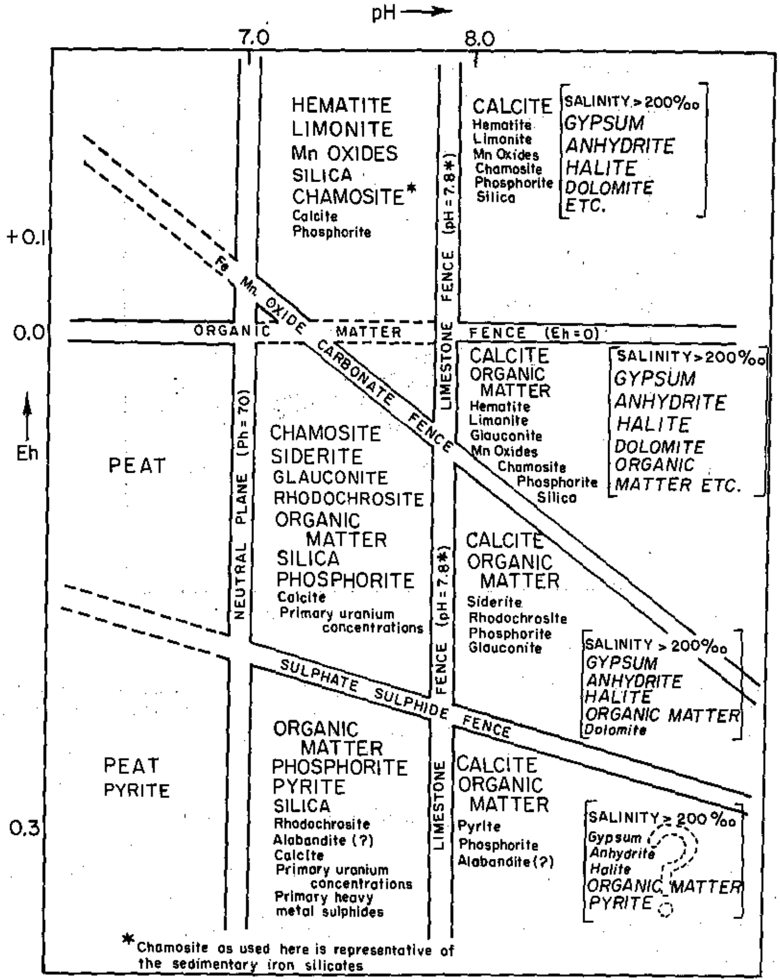


FIG. 4. Sedimentary chemical end-member associations in their relations to environmental limitations imposed by selected Eh and pH values. Associations in brackets refer to hypersaline solutions. (From W. C. KRUMBEIN and R. M. GARRELS, Origin and classification of chemical sediments in terms of pH and oxidation potentials, *J. Geol.* **60**, 1–33 (1952).)

## APPLICATION TO HIGH TEMPERATURE–HIGH PRESSURE MINERAL RELATIONS

Because most rocks of the earth sooner or later are subject to high temperature and high pressure conditions, the stability relations of minerals as functions of temperature and pressure have received a great deal of attention. Pressure–temperature–composition diagrams are in widespread use. As more thermochemical data become available, equilibrium relations among minerals will be portrayed in terms of as many variables as possible, so that we can gain maximum insight into environments inaccessible to us because of time or depth. We can look forward to the development of pH–potential diagrams for elevated temperatures and pressures as well as to three-dimensional diagrams with such variables as temperature, pressure, partial pressure of a gas, or activity of a particular dissolved species as the third axis. It should be clear that the role to be played by Eh–pH diagrams in geology is an important one, and that essentially every diagram that can be constructed involving any element in the periodic table will be of interest in this domain.

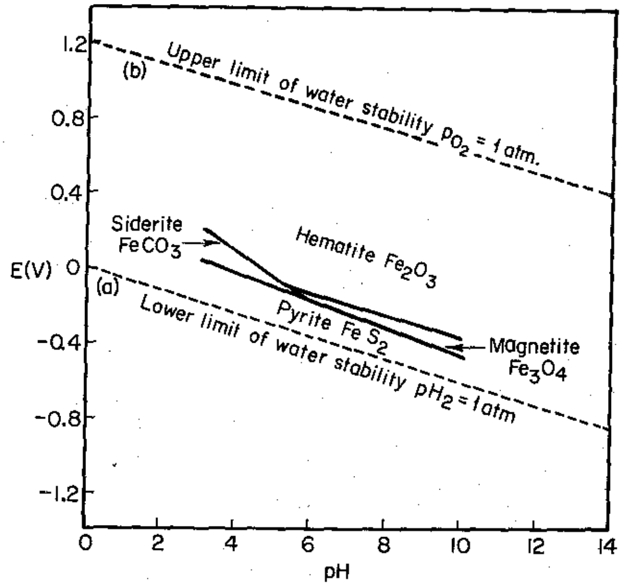


FIG. 5. Eh–pH stability fields of hematite, magnetite, siderite, and pyrite at 25°C, with carbonate equilibria as in normal sea water, and total sulphur as in average river or lake water. (Adapted from N. K. HUBER, The environmental control of iron minerals, *Econ. Geol.* **53**, 134 (1958).)

## BIBLIOGRAPHY

[1] M. BLUMER, *Die Existenzgrenzen anorganischer Ionen bei der Bildung von Sedimentgesteinen, Helv. Chim. Acta,* **33**, 1568–81 (1950).

[2] W. C. KRUMBEIN and R. M. GARRELS, Origin and classification of chemical sediments in terms of pH and oxidation potentials, *J. Geol.* **60**, 1–33 (1952).

[3] H. T. EVANS, JR. and R. M. GARRELS, Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado Plateau ore deposits, *Geochim. and Cosmochim. Acta,* **15**, 131–49 (1958).

[4] E. DELTOMBE, N. DE ZOUBOV and M. POURBAIX, *Comportement électrochimique du vanadium. Diagrammes d'équilibre tension–pH du système* V–$H_2O$ à 25°C, Rapport technique RT.29 of CEBELCOR, Brussels, 1956.

[5] N. K. HUBER, The environmental control of sedimentary iron minerals, *Econ. Geol.* **53**, 123–41 (1958).

[6] K. B. KRAUSKOPF, Separation of iron from manganese in sedimentary process, *Geochim. and Cosmochim. Acta,* **12**, 61–84 (1957).

[7] H. L. JAMES, Sedimentary facies of iron formation, *Econ. Geol.* **49**, 235–93 (1954).

[8] R. M. GARRELS, *Mineral Equilibria at Low Temperature and Pressure*, Harper, New York, 1960, p. 201.

## CHAPTER IV

# ESTABLISHMENT AND INTERPRETATION OF POTENTIAL–pH EQUILIBRIUM DIAGRAMS*

---

(*) Except where indicated, the standard free enthalpy values of formation given in this chapter are all taken from the works of W. M. Latimer (*Oxidation Potentials*, 2nd ed., Prentice-Hall, New York, 1952; *Recent References to Thermodynamic Data*, University of California, 1954).

## SECTION 1.1

# WATER (1)

M. POURBAIX and N. DE ZOUBOV

### SUMMARY

1. *Substances considered and substances not considered.*
2. *Reactions and equilibrium formulae.*
    - 2.1. Two dissolved substances.
        - 2.1.1. Relative stability of $H^+$, $OH^-$, $H^-$, $H_2O_2$ and $HO_2^-$.
        - 2.1.2. Limits of the domains of relative predominance of $H^+$, $OH^-$, $H^-$, $H_2O_2$ and $HO_2^-$.
    - 2.2. Two gaseous substances.
        - 2.2.1. Relative stability of $H_1$, $H_2$, $O_2$ and $O_3$.
        - 2.2.2. Limits of the domains of relative predominance of $H_2$, $O_2$ and $O_3$.
    - 2.3. One dissolved substance and one gaseous substance.
3. *Equilibrium diagrams and their interpretation.*
    - 3.1. Establishment of the diagrams.
    - 3.2. Thermodynamic stability of water.
    - 3.3. Acid and alkaline media. Oxidizing and reducing media; rH and rO. Absolute neutrality of aqueous solutions.
    - 3.4. Decomposition of water. Formation of hydrogen, oxygen, ozone and hydrogen peroxide.
4. *Bibliography.*

---

(1) Extract from the Rapport CEFA/R.2 of the Commission des Études Fondamentales et Applications of CEBELCOR; see also [1], [3] and [4].

## 1. SUBSTANCES CONSIDERED AND SUBSTANCES NOT CONSIDERED(²)

| | Considered | Not considered | $\mu^0$(cal.) | Names |
|---|---|---|---|---|
| Liquid substance | $\boldsymbol{H_2O}$ | – | $-56\,690$ | Water |
| Dissolved substances | $\mathrm{H^+}$ | – | $0$ | Hydrogen ion |
| | $\mathrm{OH^-}$ | – | $-37\,595$ | Hydroxide ion |
| | $\mathrm{H^-}$ | – | $51\,900$ | Hydride ion |
| | $\mathrm{H_2O_2}$ | – | $-31\,470$ | Hydrogen peroxide |
| | $\mathrm{HO_2^-}$ | – | $-15\,610$ | Hydrogen peroxide ion |
| | – | $\mathrm{OH}$ | $8\,530$ | Hydroxyl |
| | – | $\mathrm{HO_2}$ | $3\,000$ | Hydrogen peroxyl |
| | – | $\mathrm{O_2^-}$ | $13\,000$ | Hyperoxide ion |
| | – | $\mathrm{H_2}$ | $4\,230$ (*) | Natural hydrogen |
| | – | $\mathrm{O_2}$ | $3\,950$ (*) | Natural oxygen |
| Gaseous substances | $H_1$ | – | $48\,575$ | Atomic hydrogen |
| | $H_2$ | – | $0$ | Natural hydrogen |
| | – | $O_1$ | $54\,994$ | Atomic oxygen |
| | $O_2$ | – | $0$ | Natural oxygen |
| | $O_3$ | – | $39\,060$ | Ozone |
| | $H_2O$ | – | $-54\,635$ | Water |

## 2. REACTIONS AND EQUILIBRIUM FORMULAE (**)

### 2.1. TWO DISSOLVED SUBSTANCES

### 2.1.1. *Relative stability of* $\mathrm{H^+}$, $\mathrm{OH^-}$, $\mathrm{H^-}$, $\mathrm{H_2O_2}$ *and* $\mathrm{HO_2^-}$

1. $\boldsymbol{H_2O} = \mathrm{OH^-} + \mathrm{H^+}$ $\quad \log(\mathrm{OH^-}) = -14.00 + \mathrm{pH}$

2. $\mathrm{H_2O_2} = \mathrm{HO_2^-} + \mathrm{H^+}$ $\quad \log\frac{(\mathrm{HO_2^-})}{(\mathrm{H_2O_2})} = -11.63 + \mathrm{pH}$

3. $\mathrm{H^-} = \mathrm{H^+} + 2e^-$ $\quad \mathrm{E_0} = -1.125 + 0.0295 \log\frac{(\mathrm{H^+})}{(\mathrm{H^-})}$

4. $\mathrm{H^-} + \boldsymbol{H_2O} = \mathrm{OH^-} + 2\mathrm{H^+} + 2e^-$ $\quad \mathrm{E_0} = -0.711 - 0.0591\,\mathrm{pH} + 0.0295 \log\frac{(\mathrm{OH^-})}{(\mathrm{H^-})}$

5. $2\boldsymbol{H_2O} = \mathrm{H_2O_2} + 2\mathrm{H^+} + 2e^-$ $\quad \mathrm{E_0} = 1.776 - 0.0591\,\mathrm{pH} + 0.0295 \log(\mathrm{H_2O_2})$

6. $2\boldsymbol{H_2O} = \mathrm{HO_2^-} + 3\mathrm{H^+} + 2e^-$ $\quad \mathrm{E_0} = 2.119 - 0.0886\,\mathrm{pH} + 0.0295 \log(\mathrm{HO_2^-})$

7. $\mathrm{OH^-} + \boldsymbol{H_2O} = \mathrm{H_2O_2} + \mathrm{H^+} + 2e^-$ $\quad \mathrm{E_0} = 1.362 - 0.0295\,\mathrm{pH} + 0.0295 \log\frac{(\mathrm{H_2O_2})}{(\mathrm{OH^-})}$

8. $\mathrm{OH^-} + \boldsymbol{H_2O} = \mathrm{HO_2^-} + 2\mathrm{H^+} + 2e^-$ $\quad \mathrm{E_0} = 1.706 - 0.0591\,\mathrm{pH} + 0.0295 \log\frac{(\mathrm{HO_2^-})}{(\mathrm{OH^-})}$

---

(2) The radicals OH and $\mathrm{HO_2}$ which are not considered here have been dealt with in a previous study [2]. Monatomic gaseous hydrogen will be treated only very briefly here. It will be better considered when we study hydrogen (section 2). Monatomic gaseous oxygen will be considered when we study oxygen (section 19.1).

(*) We have calculated values from the solubilities of gaseous $\mathrm{H_2}$ and $\mathrm{O_2}$ in water.

(**) In the following general classification we have, with a view to simplification, taken water to be the solvent.

### 2.1.2. *Limits of the domains of relative predominance of* $H^+$, $OH^-$, $H^-$, $H_2O_2$ *and* $HO_2^-$

1'. $H^+ / OH^-$ $\quad pH = 7.00$

2'. $H_2O_2/HO_2^-$ $\quad pH = 11.63$

3'. $H^- / H^+$ $\quad E_0 = -1.125$

4'. $H^- / OH^-$ $\quad E_0 = -0.711 - 0.0591\ pH$

5'. $H^+ / H_2O_2$ $\quad E_0 = 1.776 - 0.0886\ pH$

6'. $H^+ / HO_2^-$ $\quad E_0 = 2.119 - 0.1181\ pH$

7'. $OH^- / H_2O_2$ $\quad E_0 = 1.362 - 0.0295\ pH$

8'. $OH^- / HO_2^-$ $\quad E_0 = 1.706 - 0.0591\ pH$

## 2.2. TWO GASEOUS SUBSTANCES

### 2.2.1. *Relative stability of* $H_1$, $H_2$, $O_2$ *and* $O_3$

9. $H_2 = H_1 + H^+ + e^-$ $\quad E_0 = 2.106 - 0.0591\ pH + 0.0591 \log \frac{p_{H_1}}{p_{H_2}}$

10. $H_2 + 2\mathbf{H_2O} = O_2 + 6H^+ + 6e^-$ $\quad E_0 = 0.819 - 0.0591\ pH + 0.0098 \log \frac{p_{O_2}}{p_{H_2}}$

11. $O_2 + \mathbf{H_2O} = O_3 + 2H^+ + 2e^-$ $\quad E_0 = 2.076 - 0.0591\ pH + 0.0295 \log \frac{p_{O_3}}{p_{O_2}}$

### 2.2.2. *Limits of the domains of relative predominance of* $H_2$, $O_2$ *and* $O_3$

9'. $H_2 / H_1$ $\quad E_0 = 2.106 - 0.0591\ pH$

10'. $H_2 / O_2$ $\quad E_0 = 0.819 - 0.0591\ pH$

11'. $O_2 / O_3$ $\quad E_0 = 2.076 - 0.0591\ pH$

## 2.3. ONE DISSOLVED SUBSTANCE AND ONE GASEOUS SUBSTANCE(³)

12. $\mathbf{H_2O} = H_2O$ $\quad \log p_{H_2O} = -1.505$

13. $H_1 = H^+ + e^-$ $\quad E_0 = -2.106 - 0.0591\ pH - 0.0591 \log p_{H_1}$

14. $H_2 = 2H^+ + 2e^-$ $\quad E_0 = 0.000 - 0.0591\ pH - 0.0295 \log p_{H_2}$

15. $2\mathbf{H_2O} = O_2 + 4H^+ + 4e^-$ $\quad E_0 = 1.228 - 0.0591\ pH + 0.0147 \log p_{O_2}$

16. $3\mathbf{H_2O} = O_3 + 6H^+ + 6e^-$ $\quad E_0 = 1.501 - 0.0591\ pH + 0.0098 \log p_{O_3}$

## 3. EQUILIBRIUM DIAGRAMS AND THEIR INTERPRETATION (³)

### 3.1. ESTABLISHMENT OF THE DIAGRAMS

Using formulae (1')–(8') we have represented in Fig. 1 the domains of relative predominance of the dissolved substances $H^-$, $H^+$, $OH^-$, $H_2O_2$ and $HO_2^-$; using formulae (10') and (11') we have represented in Fig. 2 the domains of relative predominance of the gaseous substances $H_2$, $O_2$ and $O_3$ (no domain of predominance exists for $H_1$). Using formulae (14) and (15) we have represented, notably in Figs. 3, 4 and 5, the domain of stability of water under atmospheric pressure (Fig. 3), the acid, alkaline,

---

(³) For further details, see *loc. cit.* [3] and [4].

oxidizing and reducing media (Fig. 4) and the values of rH and rO for aqueous solutions (Fig. 5). Finally, using all the formulae (1)–(16) we have represented in Fig. 6 all the oxidation and reduction reactions of water that are considered in this study.

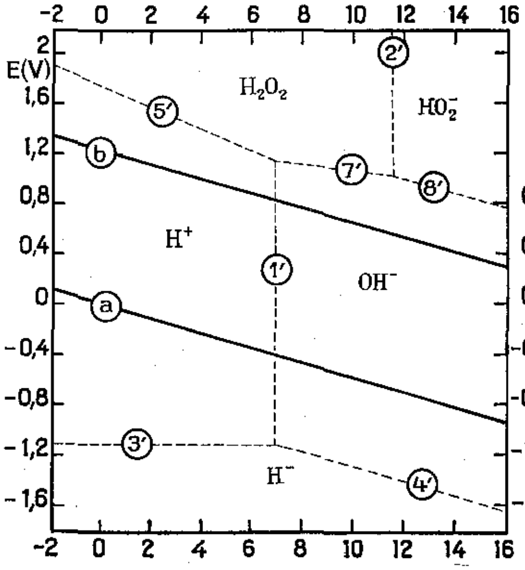


FIG. 1. Domains of relative predominance of the dissolved substances $H^-$, $H^+$, $OH^-$, $H_2O_2$ and $HO_2^-$.

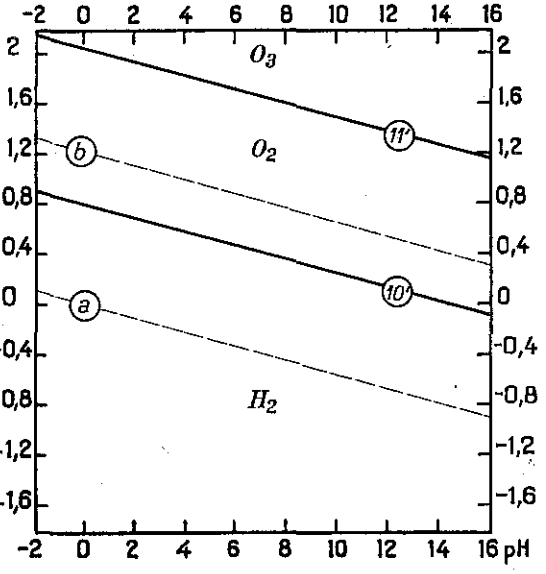


FIG. 2. Domains of relative predominance of the gaseous substances $H_2$, $O_2$ and $O_3$.

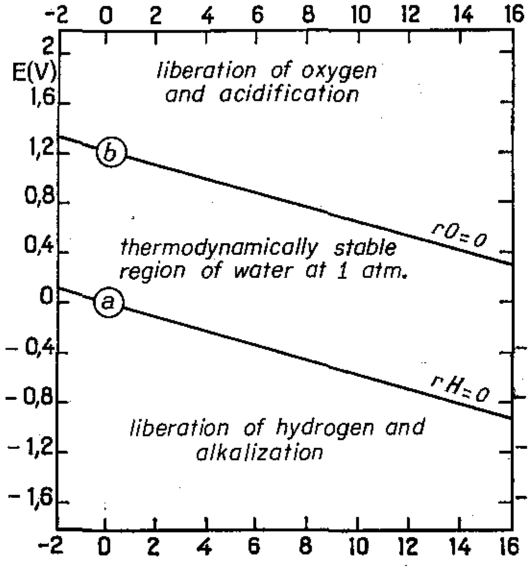


FIG. 3. Domain of thermodynamic stability of water under 1 atm. pressure.

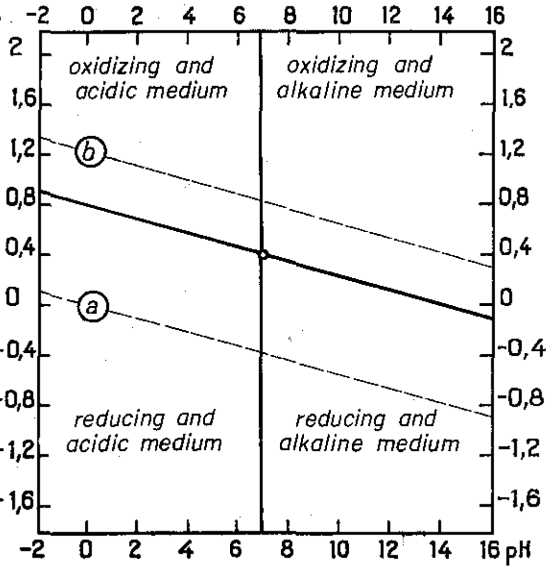


FIG. 4. Acid, alkaline, oxidizing and reducing media.

## 3.2. THERMODYNAMIC STABILITY OF WATER

In each of the Figs. 1–6, and notably in Fig. 3, we have drawn two parallel lines of slope −0·0591, labelled with the letters *a* and *b*, which represent respectively the equilibrium conditions of the reduction of water (or its $H^+$ ions) to gaseous hydrogen (reaction 14) and the oxidation of water to gaseous oxygen (reaction 15), when the partial pressure of hydrogen or oxygen is 1 atm. at 25°C.

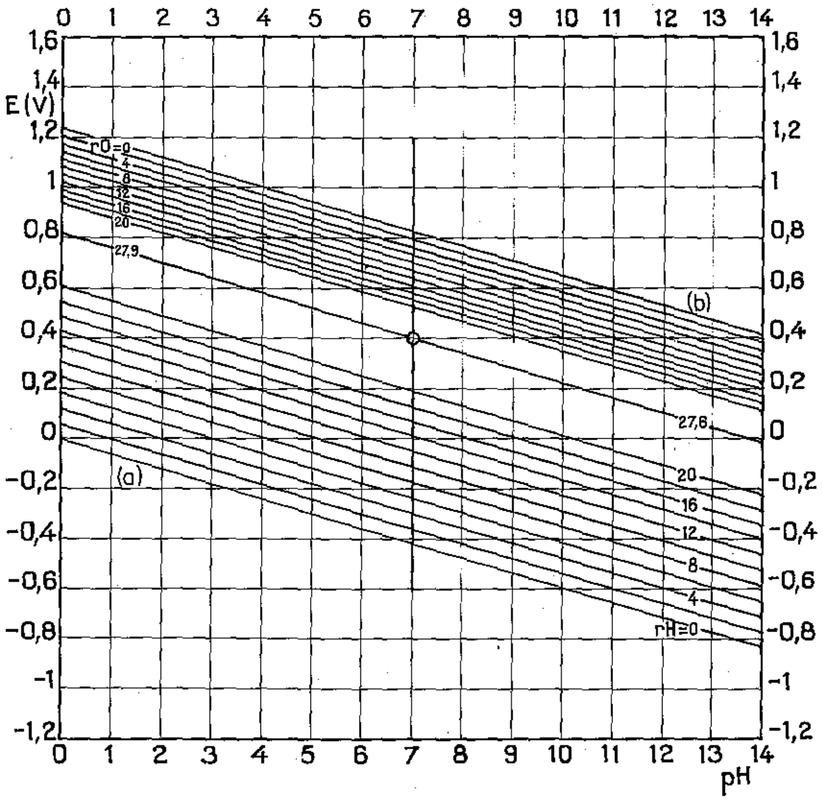


FIG. 5. rH and rO of aqueous solutions.

The equations of these two lines, obtained by equating to zero the term log $p_{H_2}$ of relation (14) and the term log $p_{O_2}$ of relation (15), are respectively:

(*a*) reaction $H_2 = 2H^+ + 2e^-$ : $E_0 = 0.000 - 0.0591\ pH$;
(*b*) reaction $2H_2O = O_2 + 4H^+ + 4e^-$ : $E_0 = 1.228 - 0.0591\ pH$.

In the portion of Fig. 3 below line (*a*), the equilibrium hydrogen pressure is above 1 atm., and water under atmospheric pressure therefore tends to be reduced with the evolution of hydrogen, becoming alkaline, according to the reaction

$$2H^+ + 2e^- \rightarrow H_2 \quad (14) \qquad \text{or} \qquad 2H_2O + 2e^- \rightarrow H_2 + 2OH^-.$$

In the portion of Fig. 3 above line (*b*), the equilibrium oxygen pressure is above 1 atm., and water under atmospheric pressure therefore tends to be oxidized with the evolution of oxygen, becoming acid, according to the reaction

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (15).$$

Between the two lines (*a*) and (*b*) in Fig. 3, the equilibrium pressures of hydrogen and oxygen are both below 1 atm.; the region included between these two lines is therefore the *domain of thermodynamic stability of water* under a pressure of 1 atm. Water will be thermodynamically stable in this

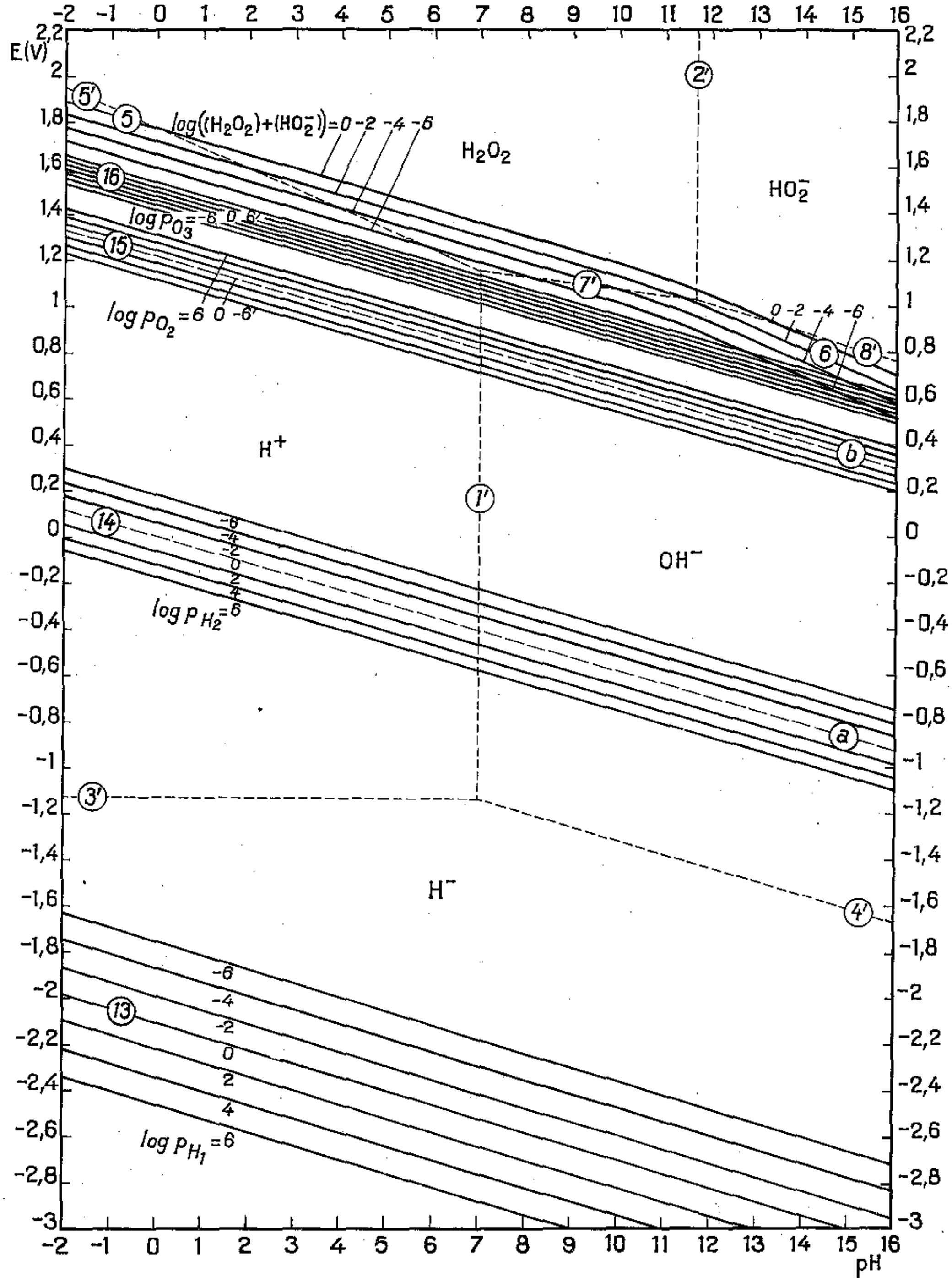


FIG. 6. Reduction and oxidation equilibria of water, with the formation of $H_1$, $H_2$, $O_2$, $O_3$, $H_2O_2$ and $HO_2^-$.

domain alone; this is true, not only for pure water, but also, to a first approximation,(4) for the water present in dilute aqueous solutions. Since, by definition, all aqueous solutions contain water, this domain of stability of water is important for all of them; for this reason *we shall reproduce its limits (a) and (b) in all the potential–pH diagrams that we establish.*

### 3.3. ACID AND ALKALINE MEDIA. OXIDIZING AND REDUCING MEDIA; rH AND rO. ABSOLUTE NEUTRALITY OF AQUEOUS SOLUTIONS

As is expressed by relation (1) above, water dissociates into $H^+$ and $OH^-$ ions according to the reaction $H_2O = H^+ + OH^-$ (1) whose equilibrium state, at 25°C, is

$$((H^+).(OH^-)) = 10^{-14{\cdot}00} \quad \text{or} \quad \log(H^+) + \log(OH^-) = -14{\cdot}00$$

or, by putting

$$pH = -\log(H^+), \quad \log(OH^-) = -14{\cdot}00 + pH.$$

It will be recalled that solutions are neutral, acid or alkaline depending on whether we have

$pH = 7{\cdot}00$ or $(H^+) = (OH^-)$ (neutral solutions),
$pH < 7{\cdot}00$ or $(H^+) > (OH^-)$ (acid solutions),
$pH > 7{\cdot}00$ or $(H^+) < (OH^-)$ (alkaline solutions).

The vertical line pH = 7 drawn in Fig. 4 therefore separates a domain in which there is a predominance of $H^+$ ions over $OH^-$ ions (acid solutions) from a domain in which there is a predominance of $OH^-$ ions over $H^+$ ions (alkaline solutions).

Another consideration is that water and its constituents can be reduced with the evolution of hydrogen, or oxidized with the evolution of oxygen, according to the reactions

$$2H^+ + 2e^- \rightarrow H_2 \text{ (reduction) and } 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \text{ (oxidation).}$$

The equilibrium conditions of these reactions at 25°C are respectively:

$$E_0 = 0{\cdot}000 - 0{\cdot}0591\,pH - 0{\cdot}0295 \log p_{H_2}, \quad (14)$$
$$E_0 = 1{\cdot}228 - 0{\cdot}0591\,pH + 0{\cdot}0147 \log p_{O_2}. \quad (15)$$

If, in the same way that we have put

$$pH = -\log(H^+)$$

we put

$$rH = -\log p_{H_2} \quad \text{and} \quad rO = -\log p_{O_2},$$

the two equilibrium reactions (14) and (15) can be written respectively

$$E_0 = 0{\cdot}000 - 0{\cdot}0591\,pH + 0{\cdot}0295\,rH, \quad (14')$$
$$E_0 = 1{\cdot}228 - 0{\cdot}0591\,pH - 0{\cdot}0147\,rO. \quad (15')$$

Now, in the same way that water can dissociate into $H^+$ and $OH^-$ ions according to the reaction $H_2O = H^+ + OH^-$ and is considered neutral from the acidity/alkalinity point of view if $(H^+) = (OH^-)$,

---

(4) More exactly, the lines (*a*) and (*b*) are practically valid for solutions in which the free enthalpy of formation of the water $\mu_{H_2O}$ is practically equal to the free enthalpy of formation of pure water, that is −56 690 cal. at 25°C. For most aqueous solutions $\mu_{H_2O}$ is below this value; this causes an increase in the stability of the water which is shown by an enlargement of its domain of stability in Fig. 1. This increase in stability of water when certain substances are dissolved in it shows itself in an analogous way as a function of the temperature, by an elevation of the boiling point (connected with a reduction of the vapour pressure) and by a depression of the freezing-point. *Loc. cit.* [3], pp. 12 and 13.

water can decompose into gaseous hydrogen and oxygen according to the reaction $2H_2O = 2H_2 + O_2$, and may be considered neutral from the oxidation/reduction point of view if $p_{H_2} = 2p_{O_2}$, i.e. if

$$\log p_{H_2} = \log p_{O_2} + \log 2 = \log p_{O_2} + 0{\cdot}30,$$

i.e. if

$$rH = rO - 0{\cdot}30.$$

If we combine this equation with the equations

$$E_0 = 0{\cdot}000 - 0{\cdot}0591\ pH + 0{\cdot}0295\ rH, \quad (14')$$
$$E_0 = 1{\cdot}228 - 0{\cdot}0591\ pH - 0{\cdot}0147\ rO, \quad (15')$$

we obtain, as the condition for the neutrality of water from the oxidation/reduction point of view

$$E_0 = 0{\cdot}813 - 0{\cdot}0591\ pH \quad \text{or} \quad rH = 27{\cdot}56 \quad \text{or} \quad rO = 27{\cdot}86.$$

By combining these relations with the relation $pH = 7{\cdot}00$ which expresses the neutrality of an aqueous solution from the acidity/alkalinity point of view, we obtain the following characteristics for the *condition of absolute neutrality* of a dilute aqueous solution, at 25°C:

$$pH = 7{\cdot}00, \quad rH = 27{\cdot}56, \quad rO = 27{\cdot}86, \quad E_0 = +0{\cdot}4\ V.$$

However, although the concept of neutrality from the acidity/alkalinity point of view has a great practical interest, the concept of neutrality from the oxidation/reduction point of view is of principally academic interest. rH, which is widely used in biological chemistry, is connected with pH and electrode potential E (calculated in volts with respect to the standard hydrogen electrode) by the following relation, valid for 25°C:

$$rH = 33{\cdot}9\ E + 2pH \quad (14'')$$

The neutrality characteristics that we have just defined enable a potential–pH diagram to be divided into the following four regions, shown in Fig. 4:

*top left:* oxidizing acid media;
*bottom left:* reducing acid media;
*bottom right:* reducing alkaline media;
*top right:* oxidizing alkaline media.

### 3.4. DECOMPOSITION OF WATER. FORMATION OF HYDROGEN, OXYGEN, OZONE AND HYDROGEN PEROXIDE

In the portion of Fig. 6 below line (*a*), relating to the equilibrium of the reaction $H_2 = 2H^+ + 2e^-$ (14) for a hydrogen pressure of 1 atm., it is thermodynamically possible to reduce water with the evolution of diatomic gaseous hydrogen at atmospheric pressure. This can be done using an electrolytic cathode or by the action of sufficiently powerful reducing agents, such as metals with low electrode potentials (iron, zinc, magnesium, sodium, etc.).

For electrode potentials below those indicated by lines (3′) and (4′), negative hydrogen ions $H^-$ can theoretically be formed; at very low potentials, below those indicated by the family of lines (13), it is theoretically possible for monatomic gaseous hydrogen to be evolved with an appreciable partial pressure, the equilibrium proportion of $H_1$ with respect to $H_2$, calculated from equation (9), remaining extremely small, however (of the order of $10^{-70}$).

In the portion of Fig. 6 above line (*b*), relating to the equilibrium of the reaction $2H_2O = O_2 + 4H^+ + 4e^-$ (15) for an oxygen pressure of 1 atm., it is thermodynamically possible to oxidize water with the evolution of diatomic gaseous oxygen at atmospheric pressure. This can be done by means of an electrolytic anode or by the action of sufficiently powerful oxidizing agents (permanganate, fluorine, etc.).

For electrode potentials above those indicated by the family of lines (16), it is theoretically possible for triatomic gaseous oxygen (ozone) to be evolved with an appreciable partial pressure, the equilibrium proportion of $O_3$ with respect to $O_2$, calculated from equation (11), remaining very small, however (of the order of $10^{-21}$ to $10^{-14}$). At potentials above those indicated by the family of lines (5–6), the evolution of gas may be accompanied by the formation of hydrogen peroxide and its ion $HO_2^-$.

Let us consider, as an example, the action of fluorine on water. As will be shown in section 20.1, concerning fluorine, the stable form of fluorine for potentials corresponding to the families of lines (14), (15) and (5–6) of Fig. 6 are hydrofluoric acid HF and fluoride ion $F^-$, with a possibility of the formation of gaseous fluorine monoxide $F_2O$ at high potentials. Gaseous fluorine tends therefore, in the presence of water, on the one hand, to turn into fluorine monoxide and hydrofluoric acid according to the reactions

$$\begin{array}{rlcl} & F_2 + 2e^- & \rightarrow & 2F^- \\ \text{and} & F_2 + H_2O & \rightarrow & F_2O + 2H^+ + 2e^- \\ \hline \text{overall reaction} & 2F_2 + H_2O & \rightarrow & F_2O + 2F^- + 2H^+ \end{array}$$

and, on the other hand, to be reduced according to the reaction

$$F_2 + 2e^- \rightarrow 2F^-.$$

Combining this last reaction with the three oxidations

$$\begin{array}{lcll} 2H_2O & \rightarrow & O_2 + 4H^+ + 4e^- & (15), \\ 3H_2O & \rightarrow & O_3 + 6H^+ + 6e^- & (16) \end{array}$$

and

$$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^- \quad (5),$$

this reduction of fluorine to fluoride gives rise to the following three simultaneous reactions:

$$\begin{array}{lcll} 2F_2 + 2H_2O & \rightarrow & O_2 + 4F^- + 4H^+ & \text{(formation of hydrofluoric acid and oxygen),} \\ 3F_2 + 3H_2O & \rightarrow & O_3 + 6F^- + 6H^+ & \text{(formation of hydrofluoric acid and ozone),} \\ \hline F_2 + 2H_2O & \rightarrow & H_2O_2 + 2F^- + 2H^+ & \text{(formation of hydrofluoric acid and hydrogen peroxide).} \end{array}$$

As a result of this, the action of fluorine on water can give rise to the simultaneous formation of fluorine monoxide, hydrofluoric acid, ozonized oxygen and hydrogen peroxide.

Some other considerations relating to the reduction and oxidation of water will be discussed later, when we study hydrogen peroxide (section 1.2), hydrogen (section 2) and oxygen (section 19.1).

## 4. BIBLIOGRAPHY

[1] M. Pourbaix, *Thermodynamique des solutions aqueuses diluées* (Thèse, Delft, 1945; Béranger, Paris and Liège, (1945). 3rd Edition, Cebelcor 1963.

[2] P. Delahay, M. Pourbaix and P. Van Rysselberghe, *Comportement électrochimique de l'oxygène, de l'eau oxygénée et des radicaux* OH *et* $HO_2$ (C.R. 2e Réunion du CITCE, Milan, 1950).

[3] M. Pourbaix, *Leçons sur la corrosion électrochimique* (2e fascicule) (Rapport technique RT.30, of CEBELCOR, 1956).

[4] M. Pourbaix, *Leçons sur la corrosion électrochimique* (3e fascicule) (Rapport technique RT.49, of CEBELCOR, 1957).

## SECTION 1.2

# HYDROGEN PEROXIDE(¹)

M. POURBAIX and N. DE ZOUBOV

## SUMMARY

---

(¹) Extract from the Rapport CEFA/R.2 of the Commission des Études Fondamentales et Applications of CEBELCOR; see also [1], [2], [3] and [4].

## 1. SUBSTANCES CONSIDERED AND SUBSTANCES NOT CONSIDERED (2)

| | Considered | Not considered | $\mu^0$(cal.) | Names |
|---|---|---|---|---|
| Liquid substance | $\boldsymbol{H_2O}$ | - | −56 690 | Water |
| Dissolved substances | $H^+$ | - | 0 | Hydrogen ion |
| | $OH^-$ | - | −37 595 | Hydroxide ion |
| | $H_2O_2$ | - | −31 470 | Hydrogen peroxide |
| | $HO_2^-$ | - | −15 610 | Hydrogen peroxide ion |
| | - | $OH$ | 8 530 | Hydroxyl |
| | - | $HO_2$ | 3 000 | Hydrogen peroxyl |
| | - | $O_2^-$ | 13 000 | Hyperoxide ion |
| Gaseous substances | $O_2$ | - | 0 | Natural oxygen |
| | - | $O_3$ | 39 060 | Ozone |

These free enthalpy values are all due to W. M. Latimer.

## 2. REACTIONS AND EQUILIBRIUM FORMULAE

### 2.1. TWO DISSOLVED SUBSTANCES(*)

### 2.1.1. *Relative stability of water, hydrogen peroxide and the* $HO_2^-$ *ion*

1. $H_2O_2 = HO_2^- + H^+$ $\quad \log \frac{(HO_2^-)}{(H_2O_2)} = -11.63 + pH$

2. $2\boldsymbol{H_2O} = H_2O_2 + 2H^+ + 2e^-$ $\quad E_0 = 1.776 - 0.0591\,pH + 0.0295 \log (H_2O_2)$

3. $2\boldsymbol{H_2O} = HO_2^- + 3H^+ + 2e^-$ $\quad E_0 = 2.119 - 0.0886\,pH + 0.0295 \log (HO_2^-)$

### 2.1.2. *Limit of the domains of relative predominance of* $H_2O_2$ *and* $HO_2^-$

1'. $H_2O_2/HO_2^-$ $\quad pH = 11.63$

### 2.2. ONE DISSOLVED SUBSTANCE AND ONE GASEOUS SUBSTANCE

*Relative stability of oxygen, hydrogen peroxide and the* $HO_2^-$ *ion*

4. $H_2O_2 = O_2 + 2H^+ + 2e^-$ $\quad E_0 = 0.682 - 0.0591\,pH + 0.0295 \log \frac{p_{O_2}}{(H_2O_2)}$

5. $HO_2^- = O_2 + H^+ + 2e^-$ $\quad E_0 = 0.338 - 0.0295\,pH + 0.0295 \log \frac{p_{O_2}}{(HO_2^-)}$

## 3. EQUILIBRIUM DIAGRAM AND ITS INTERPRETATION

### 3.1. ESTABLISHMENT OF THE DIAGRAM

The electrochemical equilibrium diagram 1 was constructed by means of equilibrium formulae 1–5. This diagram comprises two families of lines, relating respectively to certain fixed values of the concentration of hydrogen peroxide in the forms $H_2O_2$ and $HO_2^-$ (2 and 3) and to certain fixed values of the ratio $\frac{p_{O_2}}{(H_2O_2) + (HO_2^-)}$ (4 and 5).

---

(2) The radicals OH and $HO_2$, which are not considered here, are discussed in a previous study [1].

(*) In the following equations we have, with a view to simplification, taken water to be the solvent.

### 3.2. FORMATION OF HYDROGEN PEROXIDE

*Oxidizing and reducing properties; decomposition of hydrogen peroxide*

It is well known that hydrogen peroxide can be prepared by the low temperature electrolysis of sulphuric acid solutions using a platinum anode; it is also formed, in small quantities, when certain metals (zinc, aluminium) corrode in aqueous solution.

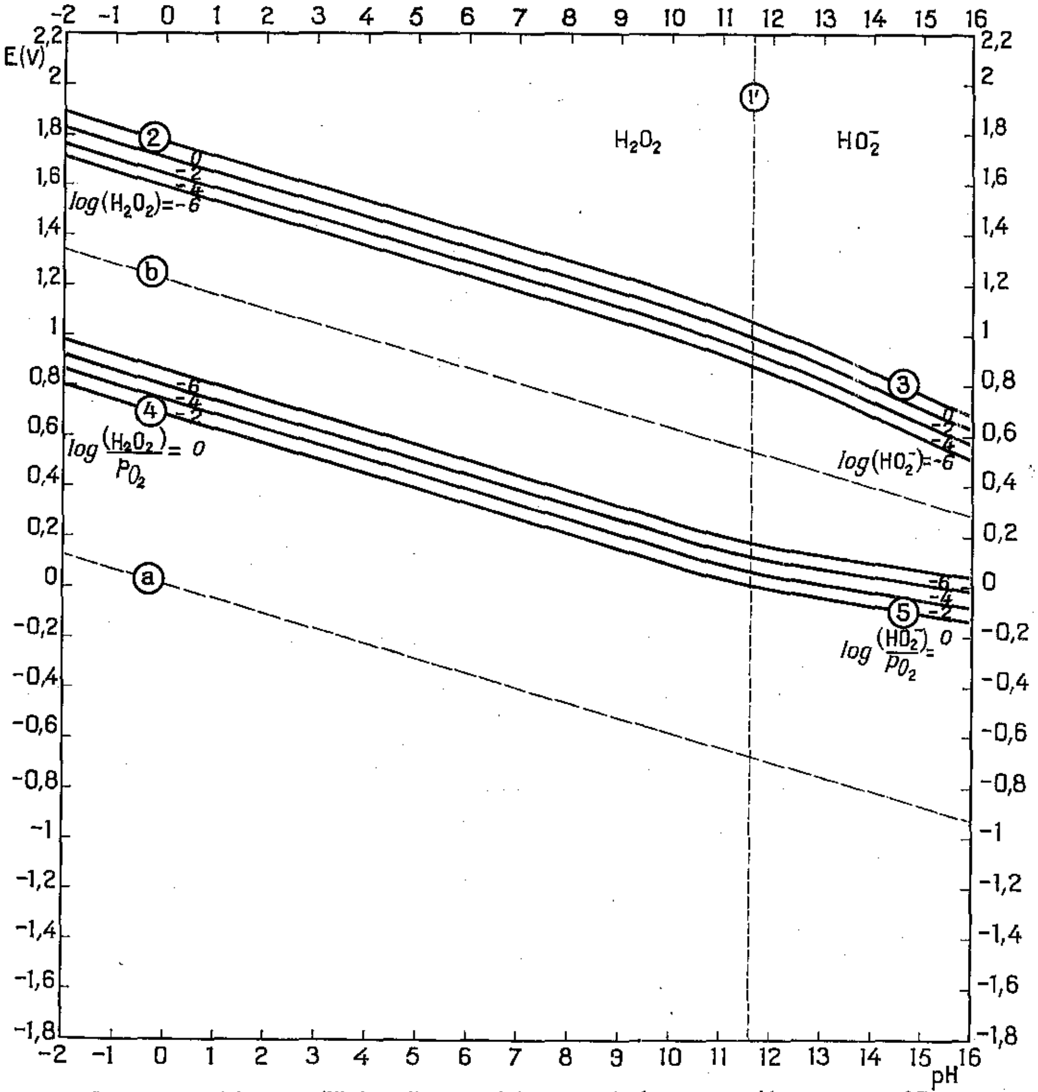


FIG. 1. Potential–pH equilibrium diagram of the system hydrogen peroxide–water, at 25°C.

In the first case, the hydrogen peroxide is formed by the oxidation of water according to the reaction $2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$ (2) at electrode potentials corresponding to the portion of Fig. 1 above the family of lines (2–3). In the second case, it is formed by the reduction of oxygen dissolved in the solution, according to the reaction $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ (4) at electrode potentials corresponding to the portion of Fig. 1 below the family of lines (4–5).

As shown in Figs. 2 and 3, these two families of lines enable us to represent, on the one hand, domains in which hydrogen peroxide can be formed by the oxidation of water (Fig. 2) or by the reduction of oxygen (Fig. 3), and, on the other hand, domains in which hydrogen peroxide can be reduced to water (Fig. 2), or oxidized to oxygen (Fig. 3). Below the family of lines (2–3) (Fig. 2) hydrogen peroxide can act as an oxidizing agent with the formation of water; for instance it oxidizes ferrous ions to ferric ions according to the reactions

$$\begin{array}{lrcll}
 & H_2O_2 + 2H^+ + 2e^- & \rightarrow & 2H_2O & (2) \\
\text{and} & 2Fe^{++} & \rightarrow & 2Fe^{+++} + 2e^- & \\
\hline
\text{overall reaction} & H_2O_2 + 2H^+ + 2Fe^{++} & \rightarrow & 2H_2O \quad + 2Fe^{+++}. &
\end{array}$$

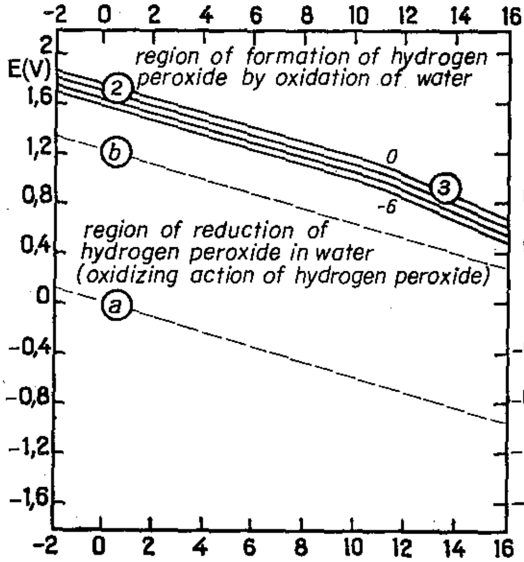


FIG. 2. Formation of hydrogen peroxide by the oxidation of water. Oxidizing action of hydrogen peroxide.

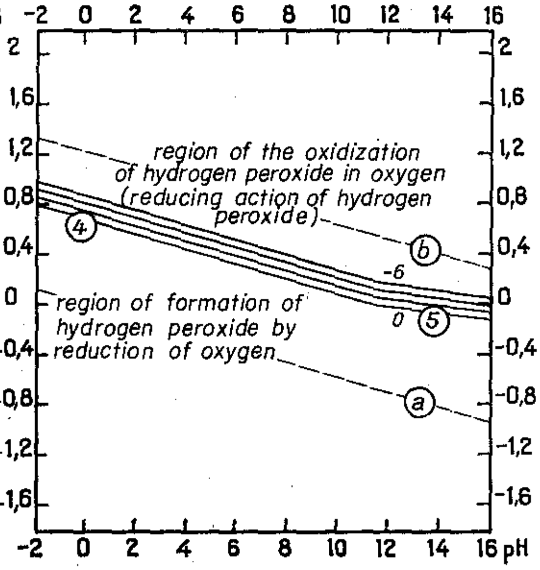


FIG. 3. Formation of hydrogen peroxide by the reduction of oxygen. Reducing action of hydrogen peroxide.

Above the family of lines (4–5) (Fig. 3) hydrogen peroxide can act as a reducing agent with the formation of oxygen; for instance it reduces permanganate to manganous ions according to the reactions:

$$\begin{array}{lrcll}
 & 5H_2O_2 & \rightarrow & 5O_2 + 10H^+ + 10e^- & (4) \\
\text{and} & 2MnO_4^- + 16H^+ + 10e^- & \rightarrow & 2Mn^{++} + 8H_2O & \\
\hline
\text{overall reaction} & 5H_2O_2 + 2MnO_4^- + 6H^+ & \rightarrow & 5O_2 + 2Mn^{++} + 8H_2O. &
\end{array}$$

Hydrogen peroxide thus appears unstable and reducible to water below the family of lines (2–3) (Fig. 2); it appears unstable and oxidizable to oxygen above the family of lines (4–5) (Fig. 3). If these two families of lines are plotted on a simple diagram (Fig. 4) it is found that these two domains of instability have a common area, in which hydrogen peroxide is doubly unstable and can decompose into water and oxygen according to the reactions

$$\begin{array}{lrcll}
 & H_2O_2 + 2H^+ + 2e^- & \rightarrow & 2H_2O & (2) \\
\text{and} & H_2O_2 & \rightarrow & O_2 + 2H^+ + 2e^- & (4) \\
\hline
\text{overall reaction} & 2H_2O_2 & \rightarrow & 2H_2O + O_2. &
\end{array}$$

In the domain of double instability, and only in this domain, hydrogen peroxide can decompose chemically into water and oxygen.

Consequently, if a solution of hydrogen peroxide is in contact with a metallic surface whose electrode potential is situated in this domain of double instability, the hydrogen peroxide can decompose spontaneously into water and oxygen according to the reaction $2H_2O_2 \rightarrow 2H_2 + O_2$, and, conversely, if hydrogen peroxide decomposes spontaneously into water and oxygen on a metallic surface, then this surface must necessarily exert an electrode potential whose position on the diagram is situated in the domain of double instability. We have here an example of the *electrochemical catalysis of a chemical reaction.*

On the other hand, in the presence of metallic surfaces whose condition is represented by a point not included in this domain of double instability, the decomposition of hydrogen peroxide into water and oxygen is impossible: the hydrogen peroxide will either be practically stable; or else it will be reduced to water (below this domain) *or* oxidized to oxygen (above this domain).

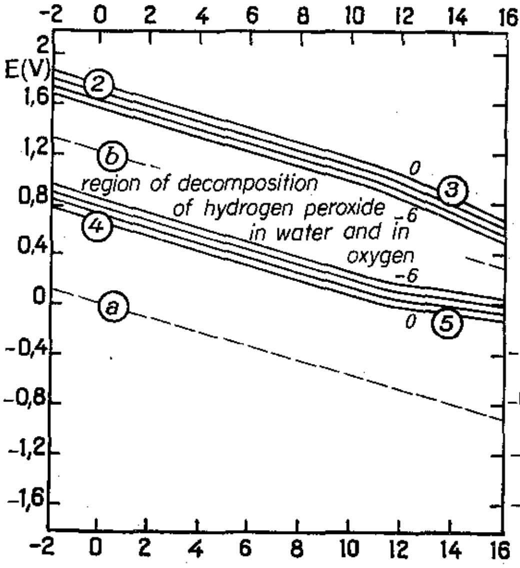


FIG. 4. Decomposition of hydrogen peroxide to water and oxygen.

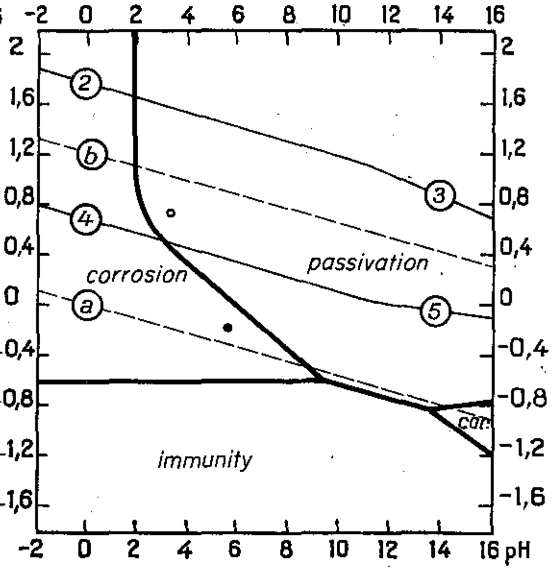


FIG. 5. Corrosion and passivation of iron by hydrogen peroxide. Reduction and decomposition of hydrogen peroxide by iron.

● Iron in the presence of a solution of $H_2O_2$ of 0·3 g/l. (corrosion).
○ Iron in the presence of a solution of $H_2O_2$ of 3·0 g/l. (passivation).

### 3.3. ACTION OF HYDROGEN PEROXIDE ON IRON

We have verified two of these facts in the particular case of the action of hydrogen peroxide solutions on iron ([2], [3]): some piano-wires were put into two glass flasks containing respectively a relatively dilute solution of hydrogen peroxide (0·3 g/l) and a relatively concentrated solution of hydrogen peroxide (3·0 g/l).

After a few hours the pH of the solution and the electrode potential of the iron were measured, and the state of the metal surface was noted. The conditions of pH and potential obtained were marked on Fig. 5, a potential–pH diagram representing, on the one hand, the theoretical conditions of instability and double instability of hydrogen peroxide solutions, and, on the other hand, the theoretical conditions of corrosion, immunity and passivation of iron.

We see in Fig. 5 that, for the relatively dilute solution of hydrogen peroxide, the point representing the condition of the iron ($E = -0{\cdot}200$ V; pH = 5·7) is situated in the domain of corrosion of iron and in the domain of reduction of hydrogen peroxide; therefore corrosion of the metal without evolution of gas takes place according to the reactions:

$$\begin{array}{rrcl} & \mathrm{Fe} & \rightarrow & \mathrm{Fe}^{++} + 2e^- \\ \text{and} & \mathrm{H_2O_2} + 2\mathrm{H}^+ + 2e^- & \rightarrow & 2\mathrm{H_2O} \\ \hline \text{overall reaction} & \mathrm{Fe} + \mathrm{H_2O_2} + 2\mathrm{H}^+ & \rightarrow & \mathrm{Fe}^{++} + 2\mathrm{H_2O}. \end{array}$$

For the relatively concentrated solution of hydrogen peroxide, the point representing the condition of the iron ($E = +0{\cdot}720$ V; $pH = 3{\cdot}4$) is in the domain of passivation of iron and in the domain of double instability of hydrogen peroxide; therefore passivation of the iron occurs without corrosion (probably by the formation of a protective film of $Fe_2O_3$), and evolution of gaseous oxygen is noticed on the surface of the metal, resulting from the decomposition of hydrogen peroxide according to the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$. Moreover, it is noticed, after some time, and as a result of this decomposition which causes a reduction in the concentration of hydrogen peroxide to below the critical concentration necessary to ensure passivation of the metal, that the electrode potential of the iron decreases abruptly and takes up a position, as in the previous case, in the domain of corrosion of iron and in the domain of reduction of hydrogen peroxide. The evolution of oxygen is seen to stop, passivation ceases and the metal begins to corrode.

## 4. BIBLIOGRAPHY

[1] P. Delahay, M. Pourbaix and P. Van Rysselberghe, *Comportement électrochimique de l'oxygène, de l'eau oxygénée et des radicaux* OH *et* $HO_2$ (C. R. 2$^e$ Réunion du CITCE, Milan, 1950).
[2] M. Pourbaix, *Applications de diagrammes potentiel–pH relatifs au fer et à l'eau oxygénée. Expériences de démonstration* (Rapport technique RT.2 of CEBELCOR, 1954).
[3] M. Pourbaix, *Leçons sur la corrosion électrochimique* (1$^{er}$ fascicule) (Rapport technique RT.57 of CEBELCOR, 1957).
[4] M. Pourbaix, *Leçons sur la corrosion électrochimique* (3$^e$ fascicule) (Rapport technique RT.49 of CEBELCOR, 1957).

## SECTION 5.2

# ALUMINIUM (¹)

E. Deltombe, C. Vanleugenhaghe and M. Pourbaix

## SUMMARY

---

(¹) Shortened and adapted version of the Rapport technique RT.42 of CEBELCOR (December 1956) [1]. A preliminary work was published by Delahay *et al.* [2]. The same method was used by Patrie [3] to study the formation of layers of oxide on aluminium in nitric acid solutions; Groot and Peekema [4] have also established a corrosion diagram for aluminium for a concentration of $3 \times 10^{-6}$ g-ion Al/l.

## 1. SUBSTANCES CONSIDERED AND SUBSTANCES NOT CONSIDERED

| | Oxidation number (Z) | Considered | Not considered | $\mu^0$ (cal.) | Name, colour, crystalline system |
|---|---|---|---|---|---|
| Solid substances | 0 | **Al** | – | 0 | Aluminium, tin-white, f.c. cub. |
| | +3 | $\mathbf{Al_2O_3}$ hydr. | – | *a*. −384 530 (²) | Trihydrated aluminium oxide (hydrargillite) $Al_2O_3 . 3H_2O$, white monocl.⁽³⁾ |
| | » | » » | – | *b*. −382 400 (²) | Trihydrated aluminium oxide (bayerite) $Al_2O_3 . 3H_2O$, white, monocl.⁽³⁾ |
| | » | » » | – | *c*. −378 310 | Monohydrated aluminium oxide (böhmite) $Al_2O_3 . H_2O\gamma$, white, rhomb. |
| | » | » anh. | – | *d*. −376 770 | Anhydrous aluminium oxide (corundum) $Al_2O_3\alpha$, white, rhomb. |
| | » | » hydr. | – | *e*. −373 730 | Aluminium hydroxide $Al(OH)_3$, white, amorphous⁽³⁾ |
| Dissolved substances | +1 | – | $Al^+$ | – | Aluminous ion, colourless |
| | +3 | $Al^{+++}$ | – | −115 000 | Aluminic ion, colourless |
| | » | – | $AlOH^{++}$ ? | – | ? |
| | » | – | $AlO^+$? | – | ? |
| | » | $AlO_2^-$ | – | −200 710 (²) | Aluminate ion, colourless |

## 2. REACTIONS AND EQUILIBRIUM FORMULAE

### 2.1. TWO DISSOLVED SUBSTANCES

### 2.1.1. *Relative stability of* $Al^{+++}$ *and* $AlO_2^-$

$Z = +3$

1. $Al^{+++} + 2H_2O = AlO_2^- + 4H^+$  $\log \frac{(AlO_2^-)}{(Al^{+++})} = -20.30 + 4\,pH$

### 2.1.2. *Limit of the domains of relative predominance of* $Al^{+++}$ *and* $AlO_2^-$

1'. $Al^{+++}/AlO_2^-$  $pH = 5.07$

### 2.2. TWO SOLID SUBSTANCES

*Limits of the domains of relative stability of aluminium and its oxides*

$0 \rightarrow +3$

2. $\mathbf{Al} + 3H_2O = \mathbf{Al_2O_3} + 6H^+ + 6e^-$

$$
\begin{aligned}
a.\ E_0 &= -1.550 - 0.0591\,pH\\
b.\ \phantom{E_0} &= -1.535 - 0.0591\,pH\\
c.\ \phantom{E_0} &= -1.505 - 0.0591\,pH\\
d.\ \phantom{E_0} &= -1.494 - 0.0591\,pH\\
e.\ \phantom{E_0} &= -1.471 - 0.0591\,pH
\end{aligned}
$$

---

(²) We have calculated the standard free enthalpy of formation of hydrargillite [1] starting from the solubility product of hydrargillite $10^{-14.60}$ calculated by Fricke and Jucaitis [5]: that of bayerite starting from its solubility product $10^{-13.82}$ determined by Fricke and Meyring [6]. The standard free enthalpy of formation of the $AlO_2^-$ ion was calculated from the solubility product of böhmite $(AlO_2^-)(H^+) = 10^{-12.32}$, given by Fricke and Meyring [6].

(³) These values of $\mu^0$ for the oxides correspond to the following values for the hydrated oxides and hydroxide:

| | | | |
|---|---|---|---|
| $Al_2O_3.3H_2O$ hydrargillite: | −554 600 cal. | $Al_2O_3.H_2O$ böhmite: | −435 000 cal. |
| $Al_2O_3.3H_2O$ bayerite: | −552 470 cal. | $Al(OH)_3$ hydroxide: | −271 900 cal. |

### 2.3. ONE SOLID SUBSTANCE AND ONE DISSOLVED SUBSTANCE

*Solubility of aluminium and its oxides*

$Z = +3$

3. $2\,Al^{+++} + 3\,H_2O = \mathbf{Al_2O_3} + 6\,H^+$
$a.\ \log(Al^{+++}) = 5{,}70 - 3\,pH$
$b.\ = 6.48 - 3\,pH$
$c.\ = 7.98 - 3\,pH$
$d.\ = 8.55 - 3\,pH$
$e.\ = 9{,}66 - 3\,pH$

4 $\mathbf{Al_2O_3} + H_2O = 2\,AlO_2^- + 2\,H^+$
$a.\ \log(AlO_2^-) = -14{,}60 + pH$
$b.\ = -13{,}82 + pH$
$c\ = -12{,}32 + pH$
$d.\ = -11.76 + pH$
$e.\ = -10.64 + pH$

$0 \rightarrow +3$

5. $\mathbf{Al} = Al^{+++} + 3e^-$ $E_0 = 1{,}663 + 0{,}0197 \log(Al^{+++})$
6. $\mathbf{Al} + 2\,H_2O = AlO_2^- + 4\,H^+ + 3e^-$ $E_0 = 1.262 - 0{,}0788\,pH + 0{,}0197 \log(AlO_2^-)$

## 3. EQUILIBRIUM DIAGRAM AND ITS INTERPRETATION

### 3.1. ESTABLISHMENT OF THE DIAGRAM

Using formulae (1)–(6) given in paragraph 2, we have drawn in Fig. 1 a potential–pH equilibrium diagram for the system aluminium–water at 25°C considering as the form of $Al_2O_3$ the most stable of the forms quoted in paragraph 1, i.e. hydrargillite.

In establishing the diagram we have not taken into account the cations $Al(OH)^{++}$ and $Al(OH)_2^+$ (or $AlO^+$) which seem to relate only to chloride complexes.

The equilibrium diagram in Fig. 1 is valid only in the absence of substances with which aluminium can form soluble complexes or insoluble salts. According to Charlot [7] the principal aluminium complexes are those formed with the anions of organic compounds (acetic, citric, tartaric, oxalic ions, etc.) and also the fluorine complexes. As sparingly soluble salts, the phosphate and oxinate may be mentioned. Calcium aluminate is also sparingly soluble.

### 3.2. STABILITY AND CORROSION OF ALUMINIUM

Figures 2*a* and 2*b* represent the theoretical conditions of corrosion, immunity and passivation of aluminium at 25°C, in the absence of substances with which aluminium forms soluble complexes or insoluble salts. Figure 2*a*, deduced from Fig. 1, refers to passivation by the formation of a layer of hydrargillite $Al_2O_3 \cdot 3H_2O$. Figure 2*b* refers to passivation by the formation of a layer of böhmite $Al_2O_3 \cdot H_2O$, which is usually the practical case, notably when the metal becomes covered with a layer of anodic oxide (see paragraph 3.3).

From Figs. 1 and 2 aluminium is seen to be a very base metal, as the whole of its domain of stability lies below that of water. In the presence of sufficiently acid solutions, it decomposes water with the evolution of hydrogen, dissolving as trivalent $Al^{+++}$ ions; under certain conditions which are little known at present this dissolution occurs with the formation of monovalent $Al^+$ ions. In the presence of sufficiently alkaline solutions aluminium decomposes water with the evolution of hydrogen, dissolving as aluminate ions $AlO_2^-$.

In non-complexing solutions of pH roughly between 4 and 9, aluminium tends to become covered with a film of oxide; the nature of the film is generally complex (see paragraph 3.3).

In practice, the corrosion behaviour of aluminium is determined essentially by the behaviour of the oxide film with which it is almost always covered towards the corroding media to be considered. Cases of bad resistance to corrosion are often connected with a change in this oxide film, notably in its degree of hydration and porosity.

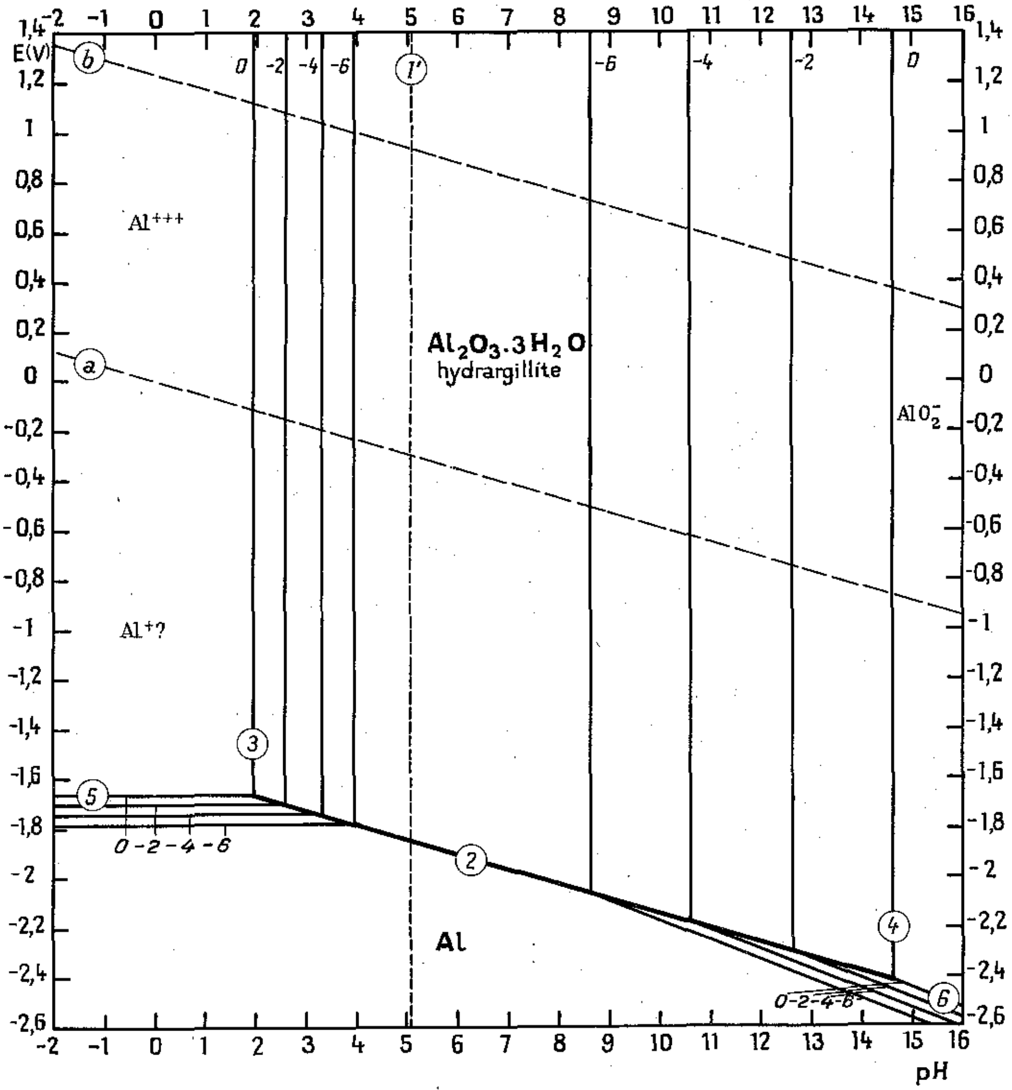
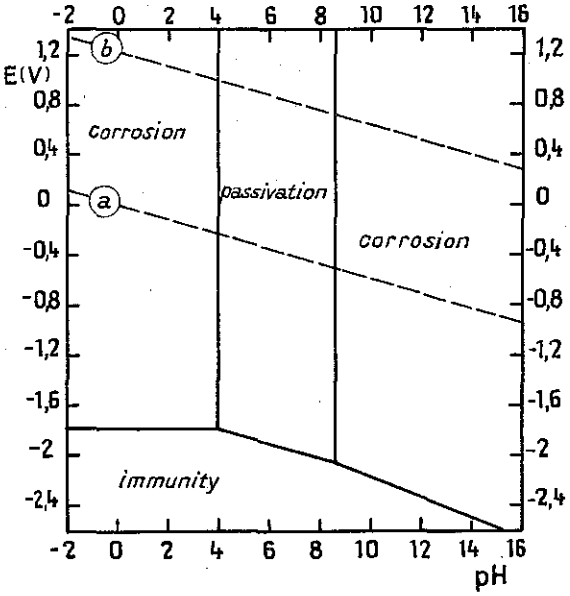


FIG. 1. Potential–pH equilibrium diagram for the system aluminium–water, at 25°C.

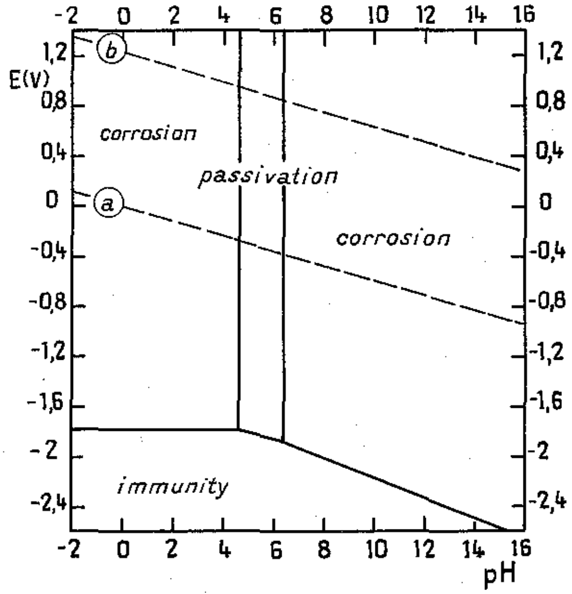
Chatalov [8] has studied the corrosion rate of aluminium as a function of the pH in various buffer solutions; his results are reproduced in Figs. 3*a* and 3*b*.

The equilibrium potential of the reaction $Al \rightarrow Al^{+++} + 3e^-$ (5) is practically impossible to measure directly, on account of the great tendency for hydrogen to be evolved at such low potentials; the measurements are also complicated by the great tendency of aluminium to cover itself with a layer of non-conducting oxide. Heyrovsky [9] used a liquid aluminium amalgam, enabling him to practically eliminate the secondary reaction $H_2 \rightarrow 2H^+ + 2e^-$.

As stated above (pp. 15 and 137), pitting of passivable metals (including aluminium) due to chlorides may sometimes be avoided by a cathodic treatment which brings the metal into a state of perfect passivation, by improving the quality of the protective oxide film. But cathodic protection of aluminium by bringing the metal into a state of immunity (without protective oxide) is practically impossible on account of the very low equilibrium potential of the metal. For the same reason it is practically impossible to electrodeposit aluminium from aqueous solutions, although, under very special conditions, aluminium has been deposited electrochemically. The classical process for the electrolytic separation of the metal remains that of igneous electrolysis.



(*a*) Passivation by a film of hydrargillite $Al_2O_3.3H_2O$.



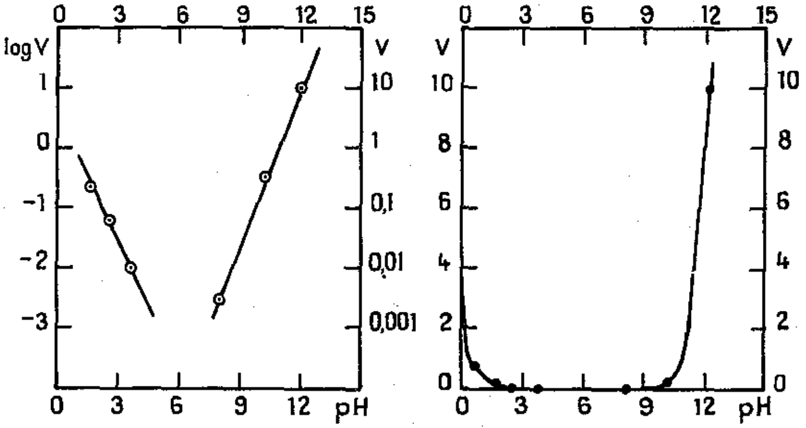
(*b*) Passivation by a film of böhmite $Al_2O_3.H_2O$.

FIG. 2. Theoretical conditions of corrosion, immunity and passivation of aluminium, at 25°C.

### 3.3. STABILITY OF ALUMINIUM OXIDE AND ITS HYDRATES. ANODIC OXIDATION OF ALUMINIUM

Aluminium oxide, or alumina, $Al_2O_3$ occurs in various forms: the ordinary variety is corundum or α-alumina, crystallizing in the rhombohedral system; the other varieties are β-alumina (hexagonal crystals), γ-alumina (cubic crystals) and δ-alumina (rhombohedral crystals). The physical and chemical properties of alumina depend to a large extent on the temperature reached during its preparation; thus, when heated to a high temperature, alumina loses its property of being a hygroscopic substance and at the same time becomes practically insoluble in acids and bases.

When alkali is added to a solution of an aluminium salt, or acid is added to an aluminate, a precipitate is obtained which is a hydroxide gel, corresponding practically to the composition $Al(OH)_3$ and amphoteric in nature.



(*a*) log V as a function of pH. (*b*) log V as a function of pH.
(V, corrosion rate in mg/dm$^2$ h).

FIG. 3. Influence of pH on the corrosion rate of aluminium (Chatalov).

This aluminium hydroxide gel is not stable, however; it crystallizes in the course of time to give first the monohydrate $\gamma\text{-}Al_2O_3 . H_2O$ or böhmite, crystallizing in the rhombohedral system, then the trihydrate $Al_2O_3 . 3H_2O$ or bayerite, crystallizing in the monoclinic system, and, finally another trihydrate, hydrargillite, crystallizing in the same system. This development of aluminium hydroxide is known as "ageing".

The various hydrates formed during the ageing are characterized by an increasing stability and an accompanying variation in all their properties, in particular their solubility in acids, bases and pure water. In Fig. 4 we have drawn a series of curves expressing the influence of pH on the solubility of the various compounds for which we have free enthalpy values; these curves are deduced from the equilibrium relations established in paragraph 2. In Table I we give for each of these compounds the logarithm of the acid and alkaline solubility products, the logarithm of the minimum solubility which occurs at a pH of 5·1, the logarithm of the solubility in pure water, the pH obtained by dissolution in pure water and finally the crystallographic system.

In Fig. 4 we have drawn, from formulae (3) and (4), a series of curves expressing the influence of pH on the solubility of the five forms of alumina for which we know the free enthalpies of formation. We have also reproduced Kolthoff's experimental data [10] which Latimer considered to refer to the amorphous hydroxide but are much nearer to those of böhmite. This is probably due to the fact that Kolthoff gave the precipitated hydroxide time to stabilize itself. Thus when the measurements were made it is most likely that the substance in question was no longer an $Al(OH)_3$ gel.

TABLE I. Solubility of aluminium oxide and its hydrates

| | Formula | log $[(Al^{+++})(OH^-)^3]$ | log $[(AlO_2^-)(H^+)]$ | log (minimum solubility) (g-at Al/l) | log (solubility in pure water) (g-at Al/l) | pH on dissolution in water | Crystallographic system |
|---|---|---|---|---|---|---|---|
| Hydrargillite | $Al_2O_3 . 3H_2O$ | −36·30 | −14·60 | −9·2 | −7·8 | 6·8 | Monocl. |
| Bayerite | $Al_2O_3 . 3H_2O$ | −35·52 | −13·82 | −8·5 | −7·2 | 6·7 | Monocl. |
| Böhmite | $\gamma$-$Al_2O_3 . H_2O$ | −34·02 | −12·32 | −7·0 | −6·2 | 6·1 | Tern. |
| Corundum | $\alpha$-$Al_2O_3$ | −33·45 | −11·76 | −6·4 | −5·9 | 5·9 | Tern. |
| Amorphous hydroxide | $Al(OH)_3$ | −32·34 | −10·64 | −5·3 | −5·3 | 5·3 | Amorphous |

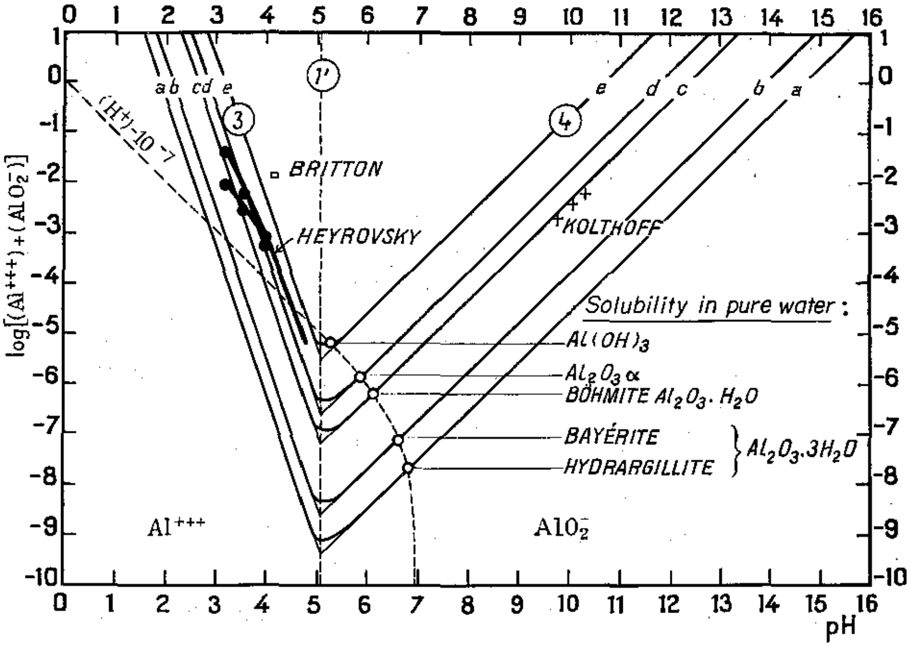


FIG. 4. Influence of pH on the solubility of $Al_2O_3$ and its hydrates, at 25°C.

The alkaline solubility products of böhmite, bayerite and hydrargillite are those given by Fricke and Meyring [6] and Fricke and Jucaitis [5]. They have been used to calculate the free enthalpies of these compounds [1].

The solubility product in acid solution has been calculated by Heyrovsky [11]. In Fig. 4 we have drawn the section of the straight line corresponding to Heyrovsky's solubility product $10^{-32\cdot97}$ for concentrations below $10^{-4}$ M. For higher concentrations we have represented the lower and higher limits assumed by Heyrovsky for the value of $(Al^{+++})$ as a function of pH. We have also marked on Fig. 4 a point representing a result obtained by Britton [12], concerning freshly precipitated $Al(OH)_3$.

With regard to the minimum solubility of the hydrates, Edwards and Buswell [13] point out that, when town-water is clarified by means of aluminium compounds, the residual aluminium concentration in the treated water rarely exceeds 2 mg Al/l, i.e. $10^{-4\cdot1}$ g-at Al/l.

Concerning the solubilities in pure water, Remy and Kuhlmann [14] calculated that of $Al_2O_3$ at 20°C, first by conductiometric titration ($10^{-4\cdot74}$ g-at Al/l) and then by specific conductivity measurement ($10^{-4\cdot69}$ g-at Al/l). Busch [15] obtained the value $10^{-4\cdot72}$ g-at Al/l by acidimetric titration of a saturated solution at 29°C. Jander and Ruperti [16] determined analytically the percentage of $Al_2O_3$ in a saturated solution of $Al(OH)_3$ at 12–15°C and found it to be $10^{-5\cdot 11}$ g-at Al/l.

All these values agree well enough among themselves, but leave open the question of exactly which form of oxide or hydroxide they represent; they are all greater than the solubilities in pure water calculated from Fig. 4; the greatest one of these for amorphous $Al(OH)_3$ is $10^{-5\cdot 3}$ g-at Al/l, i.e. 0·13 mg Al/l.

*The anodic behaviour* of aluminium is affected by the formation of a passivating layer of oxide on the surface of the metal. Much use is made of anodically treated aluminium. This treatment covers the metal with a layer of oxide which gives it desirable properties, such as the absorption of coloured materials and resistance to chemical reagents and to the passage of electric currents.

The structure of the anodic deposit has been the object of numerous studies. The X-ray identification of alumina was carried out by Burgers *et al.* [17], in 1932. Belwe identified the same substance by electron diffraction [18].

When the oxide layer is clogged up by boiling water, the $\gamma$-oxide is converted into böhmite. It follows that the layer of oxide is made up of a thin film of anhydrous $\gamma$-$Al_2O_3$, directly in contact with the metal, while the part in contact with the bath consists of monohydrated alumina [19]. According to a recent study by Hart [20], the film formed on extra pure aluminium immersed in water not above 60°C develops in three stages: first of all amorphous hydroxide is formed, then orthorhombic $\gamma$-$AlO\,.\,OH$ and then bayerite $Al_2O_3\,.\,3H_2O$; the final film will therefore, according to Hart, be made up of three layers.

As we have said in paragraph 3.2, the corrosion resistance of aluminium is determined essentially by the behaviour of its layer of oxide. Practically neutral solutions are in general without action, except in the particular cases when there is danger of pitting, which occurs mainly in the presence of chlorides. In acid or alkaline solutions, the aluminium will be attacked as soon as the oxide film is eliminated. This dissolution is slower in acid solutions than in alkaline solutions.

## 4. BIBLIOGRAPHY

[1] E. Deltombe and M. Pourbaix, *Comportement électrochimique de l'aluminium. Diagrammes d'équilibres tension–pH du système* Al–$H_2O$ *à* 25°C (Rapport technique RT.42 of CEBELCOR, December 1955).

[2] P. Delahay, M. Pourbaix and P. Van Rysselberghe, *Diagrammes d'équilibres potentiel–pH de quelques éléments* (C. R. 3e réunion du CITCE, Berne, 1951).

[3] J. Patrie, *Contribution à l'étude des phénomènes de passivation de l'aluminium immergé en milieu nitrique* (Thèse, Grenoble, 1952).

[4] C. Groot and R. M. Peekema, *The Potential-pH Diagram for Aluminium,* U.S. Atomic Energy Comm. Publ. H.W.28556, 1953, 13 pages.

[5] R. Fricke and P. Jucaitis, Untersuchungen über die Gleichgewichte in den Systemen $Al_2O_3$, $Na_2O\,.\,H_2O$ und $Al_2O_3$, $K_2O\,.\,H_2O$, *Z. anorg. allgem. Chem.* **191**, 129–49 (1930).

[6] R. Fricke and K. Meyring, Zur Älterung junger Aluminium Hydroxydgel, *Z. anorg. allgem. Chem.* **214**, 269–74 (1933).

[7] G. Charlot, *L'analyse qualitative et les réactions en solution,* 2nd ed., Masson, Paris, 1957.

[8] A. Ya. Chatalov, Effet du pH sur le comportement électrochimique des métaux et leur résistance à la corrosion, *Dokl. Akad. Naouk S.S.S.R.* **86**, 775–7 (1952).

[9] J. Heyrovsky, The Electroaffinity of Aluminium. Part II. The aluminium electrode, *J. Chem. Soc.* **117**, 27–36 (1920).

[10] I. M. Kolthoff, Die azidimetrische Bestimmung schwerer Metalle in ihren salzen, *Z. anorg. allgem. Chem.* **112**, 172–86 (1920).

[11] J. Heyrovsky, The electroaffinity of aluminium. Part I. The ionisation and hydrolysis of aluminium chloride, *J. Chem. Soc.* **117**, 11–26 (1920).

[12] H. T. S. Britton, Electrometric studies of the precipitation of hydroxides. Part II. The precipitation of hydroxides of zinc, chromium, beryllium, aluminium, bivalent tin and zirconium by use of the hydrogen electrode and their alleged atmospheric nature, *J. Chem. Soc.*, 2120–41 (1925).

[13] G. P. Edwards and A. M. Buswell, La relation entre la concentration en ion hydrogène et les propriétés de l'aluminium floculé, *Illinois State Water Surv. Bull.* **22**, 47–72 (1925); *Z.B.*, 1927, I, p. 1718.

[14] H. Remy and A. Kuhlmann, Löslichkeitsbestimmungen an schwerlöslichen Stoffen. II. Wasserlöslichkeit der Oxyde von Beryllium, Aluminium, Zink, Cadmium, Blei, Kupfer und Silber, *Z. anal. Chem.* **65**, 161–81 (1924–5).

[15] W. Busch, Ueber die Verwendbarkeit der electrometrischen Titration zur Löslichkeitsbestimmung schwerlöslicher Oxyde, *Z. anorg. allgem. Chem.* **161**, 161–79 (1927).

[16] G. Jander and O. Ruperti, Zur Fällung des Aluminiums als Oxydhydrat mittels Ammoniaks, *Z. anorg. allgem. Chem.* **153**, 253–9 (1926).

[17] W. G. Burgers, A. Claasen and I. Zernike, Ueber die chemische Natur des Oxydschichten welche sich bei anodischer Polarisation auf Metallen Aluminium, Zirkon, Titan und Tantal bilden, *Z. Phys.* **74**, 593–603 (1932).

[18] E. Belwe, Untersuchung von Aluminiumoxyden mittels Elektroneinterferenzen, *Z. Phys.* **100**, 192–6 (1936).

[19] J. Patrie, Le mécanisme de l'oxydation électrolytique et la formation des couches d'oxyde d'alumine, *Rev. Aluminium,* **26**, 397–403 (1949); **27**, 3–7 (1950).

[20] R. K. Hart, The formation of films on aluminium immersed in water, *Trans. Faraday Soc.* **53**, No. 7, 1020–7 (1957).

## SECTION 12.1

# IRON[1]

M. POURBAIX and N. DE ZOUBOV

SUMMARY

---

(1) Adapted version of the Rapport CEFA/R.13 of the Commission des Études Fondamentales et Applications of CEBELCOR.

## 1. SUBSTANCES CONSIDERED AND SUBSTANCES NOT CONSIDERED

| | Oxidation number (Z) | Considered | Not considered | $\mu^0$(cal.) | Name, colour, crystalline system |
|---|---|---|---|---|---|
| Solid substances | 0 | **Fe** | – | 0 | α-Iron, light grey, f.c.cub. |
| | +2 | **FeO** hydr. | – | — 58 880 (²) | Ferrous hydroxide $Fe(OH)_2$, white, rhomb. |
| | » | – | **FeO** anh. | – | Ferrous oxide, black, cub. |
| | +2.67 | **$Fe_3O_4$** anh. | – | —242 400 | Magnetite, black, cub. |
| | » | – | **$Fe_3O_4$**$.xH_2O$ | – | Hydrated magnetite, green–black |
| | +3 | **$Fe_2O_3$** anh. | – | a. —177 100 | Haematite, red–brown, rhomb. or cub. |
| | » | » hydr. | – | b. —161 930 (³) | Ferric hydroxide $Fe(OH)_3$, red–brown, f.c.cub. |
| Dissolved substances | +2 | $Fe^{++}$ | – | — 20 300 | Ferrous ion, green |
| | » | $HFeO_2^-$ | – | — 90 627 (*) | Dihypoferrite ion, green |
| | » | – | $FeO_2^{--}$ | – | Hypoferrite ion |
| | +3 | $Fe^{+++}$ | – | — 2 530 | Ferric ion, colourless |
| | » | $FeOH^{++}$ | – | — 55 910 | Ferric ion, colourless |
| | » | $Fe(OH)_2^+$ | – | —106 200 | Ferric ion, colourless |
| | » | – | $FeO_2^-$ | – | Ferrite ion |
| | +4 | – | $FeO^{++}$ | – | Ferryl ion |
| | » | – | $FeO_3^{--}$ | – | Perferrite ion |
| | +5 | – | $FeO_2^+$ | – | Perferryl ion |
| | +6 | $FeO_4^{--}$? | – | —111 685 ? (*) | Ferrate ion, violet |

These values are indicated by W. M. Latimer, except for the two values given below which were calculated by us as follows (see [1], pp. 83 and 84):

(*) for $HFeO_2^-$: We have assumed, as the solubility product $(HFeO_2^-).(H^+)$ relating to the reaction $Fe(OH)_2 = HFeO_2^- + H^+$, the value $10^{-18.3}$ (Schrager [2]);

(*) for $FeO_4^{--}$: for want of more precise data we have provisionally assumed, for the standard equilibrium potential of the reaction $Fe^{+++} + 4H_2O = FeO_4^{--} + 8H^+ + 3e^-$, the approximate value $E_0^0 = +1.7$ V given by Hodgmann ([3], p. 951), whose origin we have not been able to find.(⁴)

## 2. REACTIONS AND EQUILIBRIUM FORMULAE

### 2.1. TWO DISSOLVED SUBSTANCES

### 2.1.1. *Relative stability of the dissolved substances*

$Z = +2$

1. $Fe^{++} + 2H_2O = HFeO_2^- + 3H^+$ $\qquad \log\frac{(HFeO_2^-)}{(Fe^{++})} = -31.58 + 3\,pH$

$Z = +3$

2. $Fe^{+++} + H_2O = FeOH^{++} + H^+$ $\qquad \log\frac{(FeOH^{++})}{(Fe^{+++})} = -\ 2.43 + pH$

3. $FeOH^{++} + H_2O = Fe(OH)_2^+ + H^+$ $\qquad \log\frac{(Fe(OH)_2^+)}{(FeOH^{++})} = -\ 4.69 + pH$

---

(²) This value of $\mu^0_{FeO\,hydr.}$ corresponds to $\mu^0_{Fe(OH)_2} = -115\,570$ cal.

(³) This value of $\mu^0_{Fe_2O_3\,hydr.}$ corresponds to $\mu^0_{Fe(OH)_3} = -166\,000$ cal.

(⁴) We point out that Latimer gives two approximate values for the equilibrium potentials of the oxidation-reduction reactions: $FeO_2^-/FeO_4^{--} = V^0 > +0.9$ V at pH 14 and $Fe^{+++}/FeO_4^{--} = V^0 > +1.9$ V at pH 0.

$+2 \rightarrow +3$

4. $Fe^{++} = Fe^{+++} + e^-$ $E_0 = 0.771 + 0.0591 \log \frac{(Fe^{+++})}{(Fe^{++})}$

5. $Fe^{++} + H_2O = FeOH^{++} + H^+ + e^-$ $E_0 = 0.914 - 0.0591\ pH + 0.0591 \log \frac{(FeOH^{++})}{(Fe^{++})}$

6. $Fe^{++} + 2H_2O = Fe(OH)_2^+ + 2H^+ + e^-$ $E_0 = 1.191 - 0.1182\ pH + 0.0591 \log \frac{(Fe(OH)_2^+)}{(Fe^{++})}$

7. $HFeO_2^- + H^+ = Fe(OH)_2^+ + e^-$ $E_0 = -0.675 + 0.0591\ pH + 0.0591 \log \frac{(Fe(OH)_2^+)}{(HFeO_2^-)}$

$+2 \rightarrow +6$

8. $HFeO_2^- + 2H_2O = FeO_4^{--} + 5H^+ + 4e^-$ $E_0 = 1.001 - 0.0738\ pH + 0.0148 \log \frac{(FeO_4^{--})}{(HFeO_2^-)}$

$+3 \rightarrow +6$

9. $Fe^{+++} + 4H_2O = FeO_4^{--} + 8H^+ + 3e^-$ $E_0 = 1.700 - 0.1580\ pH + 0.0197 \log \frac{(FeO_4^{--})}{(Fe^{+++})}$

10. $FeOH^{++} + 3H_2O = FeO_4^{--} + 7H^+ + 3e^-$ $E_0 = 1.652 - 0.1379\ pH + 0.0197 \log \frac{(FeO_4^{--})}{(FeOH^{++})}$

11. $Fe(OH)_2^+ + 2H_2O = FeO_4^{--} + 6H^+ + 3e^-$ $E_0 = 1.559 - 0.1182\ pH + 0.0197 \log \frac{(FeO_4^{--})}{(Fe(OH)_2^+)}$

### 2.1.2. *Limits of the domains of relative predominance of the dissolved substances*

1'. $Fe^{++}/HFeO_2^-$ pH = 10.53
2'. $Fe^{+++}/FeOH^{++}$ pH = 2.43
3'. $FeOH^{++}/Fe(OH)_2^+$ pH = 4.69

4'. $Fe^{++}/Fe^{+++}$ $E_0 = 0.771$
5'. $Fe^{++}/FeOH^{++}$ $E_0 = 0.914 - 0.0591\ pH$
6'. $Fe^{++}/Fe(OH)_2^+$ $E_0 = 1.191 - 0.1182\ pH$
7'. $HFeO_2^-/Fe(OH)_2^+$ $E_0 = -0.675 + 0.0591\ pH$
8'. $HFeO_2^-/FeO_4^{--}$ $E_0 = 1.001 - 0.0738\ pH$
9'. $Fe^{+++}/FeO_4^{--}$ $E_0 = 1.700 - 0.1580\ pH$
10'. $FeOH^{++}/FeO_4^{--}$ $E_0 = 1.652 - 0.1379\ pH$
11'. $Fe(OH)_2^+/FeO_4^{--}$ $E_0 = 1.559 - 0.1182\ pH$

## 2.2. TWO SOLID SUBSTANCES (⁵)

### *Limits of the domains of relative stability of iron and its oxides and hydroxides*

$0 \rightarrow +2$

12. $\mathbf{Fe} + H_2O = \mathbf{FeO} + 2H^+ + 2e^-$ $E_0 = -0.047 - 0.0591\ pH$

$0 \rightarrow +2.67$

13. $3\mathbf{Fe} + 4H_2O = \mathbf{Fe_3O_4} + 8H^+ + 8e^-$ $E_0 = -0.085 - 0.0591\ pH$

$0 \rightarrow +3$

14. $2\mathbf{Fe} + 3H_2O = \mathbf{Fe_2O_3} + 6H^+ + 6e^-$
*a.* $E_0 = -0.051 - 0.0591\ pH$
*b.* $= 0.059 - 0.0591\ pH$

$+2 \rightarrow 2.67$

15. $3\mathbf{FeO} + H_2O = \mathbf{Fe_3O_4} + 2H^+ + 2e^-$ $E_0 = -0.197 - 0.0591\ pH$

$+2 \rightarrow +3$

16. $2\mathbf{FeO} + H_2O = \mathbf{Fe_2O_3} + 2H^+ + 2e^-$
*a.* $E_0 = -0.057 - 0.0591\ pH$
*b.* $= 0.271 - 0.0591\ pH$

$+2.67 \rightarrow +3$

17. $2\mathbf{Fe_3O_4} + H_2O = 3\mathbf{Fe_2O_3} + 2H^+ + 2e^-$
*a.* $E_0 = 0.221 - 0.0591\ pH$
*b.* $= 1.208 - 0.0591\ pH$

---

(⁵) For the reactions involving $Fe_2O_3$, the letter *a* relates to anhydrous $Fe_2O_3$, whose free enthalpy of formation is −177 100 cal.; the letter *b* relates to $Fe(OH)_3$, whose free enthalpy of formation is −166 000 cal.

### 2.3. ONE SOLID SUBSTANCE AND ONE DISSOLVED SUBSTANCE ($^5$)

*Solubility of iron and its oxides and hydroxides*

$Z = +2$

18. $Fe^{++} + H_2O = \mathbf{FeO} + 2H^+$ $\qquad \log(Fe^{++}) = 13.29 - 2\,pH$

19. $\mathbf{FeO} + H_2O = HFeO_2^- + H^+$ $\qquad \log(HFeO_2^-) = -18.30 + pH$

$Z = +3$

20. $2Fe^{+++} + 3H_2O = \mathbf{Fe_2O_3} + 6H^+$ $\qquad$ *a*. $\log(Fe^{+++}) = -0.72 - 3\,pH$
*b*. $= 4.84 - 3\,pH$

21. $2FeOH^{++} + H_2O = \mathbf{Fe_2O_3} + 4H^+$ $\qquad$ *a*. $\log(FeOH^{++}) = -3.15 - 2\,pH$
*b*. $= 2.41 - 2\,pH$

22. $2Fe(OH)_2^+ = \mathbf{Fe_2O_3} + H_2O + 2H^+$ $\qquad$ *a*. $\log(Fe(OH)_2^+) = -7.84 - pH$
*b*. $= -2.28 - pH$

$0 \rightarrow +2$

23. $\mathbf{Fe} = Fe^{++} + 2e^-$ $\qquad E_0 = -0.440 + 0.0295 \log(Fe^{++})$

24. $\mathbf{Fe} + 2H_2O = HFeO_2^- + 3H^+ + 2e^-$ $\qquad E_0 = 0.493 - 0.0886\,pH + 0.0295 \log(HFeO_2^-)$

$0 \rightarrow +3$

25. $\mathbf{Fe} = Fe^{+++} + 3e^-$ $\qquad E_0 = -0.037 + 0.0197 \log(Fe^{+++})$

$+2 \rightarrow +2.67$

26. $3Fe^{++} + 4H_2O = \mathbf{Fe_3O_4} + 8H^+ + 2e^-$ $\qquad E_0 = 0.980 - 0.2364\,pH - 0.0886 \log(Fe^{++})$

27. $3HFeO_2^- + H^+ = \mathbf{Fe_3O_4} + 2H_2O + 2e^-$ $\qquad E_0 = -1.819 + 0.0295\,pH - 0.0886 \log(HFeO_2^-)$

$+2 \rightarrow +3$

28. $2Fe^{++} + 3H_2O = \mathbf{Fe_2O_3} + 6H^+ + 2e^-$ $\qquad$ *a*. $E_0 = 0.728 - 0.1773\,pH - 0.0591 \log(Fe^{++})$
*b*. $= 1.057 - 0.1773\,pH - 0.0591 \log(Fe^{++})$

29. $2HFeO_2^- = \mathbf{Fe_2O_3} + H_2O + 2e^-$ $\qquad$ *a*. $E_0 = -1.139 - 0.0591 \log(HFeO_2^-)$
*b*. $= -0.810 - 0.0591 \log(HFeO_2^-)$

## 3. EQUILIBRIUM DIAGRAMS AND THEIR INTERPRETATION

### 3.1. ESTABLISHMENT OF THE DIAGRAMS

Using formulae (1′)–(11′) we have represented in Fig. 1 the domains of relative predominance of the dissolved substances $Fe^{++}$, $HFeO_2^-$, $Fe^{+++}$, $FeOH^{++}$, $Fe(OH)_2^+$ and $FeO_4^{--}$. Using formulae (18)–(29) we have represented in Figs. 2 and 3 the influence of pH on the solubility of $Fe(OH)_2$ (Fig. 2) and on the solubility of $Fe_2O_3$ and $Fe(OH)_3$ (Fig. 3).

Using all the formulae (1)–(29) we have given in Figs. 4 and 5 two general equilibrium diagrams for the system iron–water, on the one hand considering as solid substances only Fe, $Fe_3O_4$ and $Fe_2O_3$ (Fig. 4), and, on the other hand considering as solid substances only Fe, $Fe(OH)_2$ and $Fe(OH)_3$ (Fig. 5).

From Fig. 4 we have derived two theoretical diagrams, Figs. 6*a* and *b*, of "corrosion, immunity and passivation" of iron, on the one hand assuming passivation by $Fe_2O_3$ alone (Fig. 6*a*), and on the other hand assuming passivation by $Fe_2O_3$ and $Fe_3O_4$ (Fig. 6*b*). These figures are valid only in the absence of substances which can form soluble complexes or insoluble salts with iron. According to Charlot [4], divalent iron forms the following complexes: ammine complexes, complexes with organic hydroxyl compounds and with hypophosphite, oxalate and cyanide ions. Trivalent iron forms numerous complexes: hydrochloric (lemon–yellow), sulphuric (yellow), thiocyanic (deep red) and acetic, which are not very stable; hydrofluoric (colourless), pyrophosphoric, phosphoric, organic hydroxyl and oxalic (green), which are more stable, and the very stable orange–yellow ferricyanide $Fe(CN)_6^{---}$ and ferrinitrosocyanide complexes.

The following compounds are sparingly soluble [4]: carbonates, cyanides, oxalates, phosphates, sulphides, etc. of divalent iron; phosphates and sulphides (in alkaline media) of trivalent iron.

## 3.2. FORMATION, STABILITY AND CORROSION OF IRON

### 3.2.1. *Theoretical considerations*

From Figs. 4 and 5 iron appears to be a base metal, as its domain of thermodynamic stability, at 25°C and atmospheric pressure, has no portion in common with that of water.

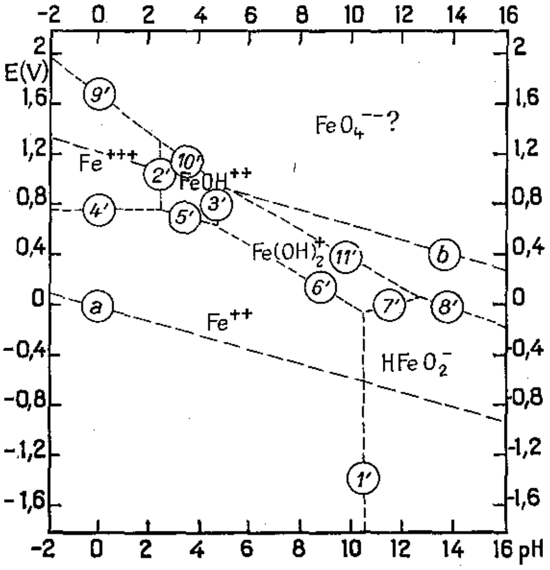


FIG. 1. Domains of relative predominance of the dissolved substances $Fe^{++}$, $HFeO_2^-$, $Fe^{+++}$, $FeOH^{++}$, $Fe(OH)_2^+$ and $FeO_4^{--}$.

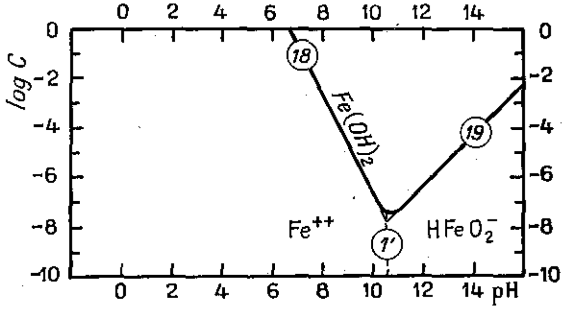


FIG. 2. Influence of pH on the solubility of $Fe(OH)_2$.

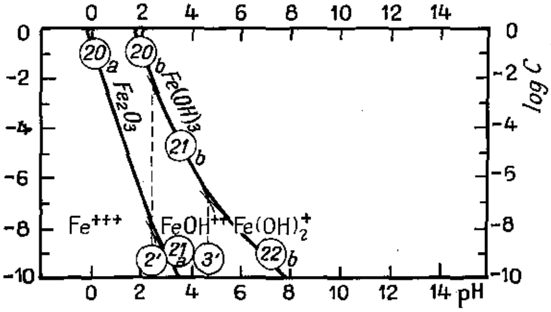


FIG. 3. Influence of pH on the solubility of $Fe_2O_3$ and $Fe(OH)_3$.

Unstable in the presence of water and a large number of aqueous *non-oxidizing* solutions, iron will therefore corrode in such solutions with the evolution of hydrogen; this reaction, which will be very vigorous in acid solutions, will become progressively less vigorous as the pH of the solution increases, and will almost cease at pH's around 10–13 when the iron will become covered with a film of oxide; at very high pH's, above about 13, solutions free from oxidizing agents will be corrosive.

The electrode potential of iron immersed in a solution is increased by the presence of oxidizing agents. The addition of such compounds will therefore have the effect either of passivating the metal more or less perfectly, or, on the other hand, of increasing its corrosion rate, depending on whether or not the increase in potential is sufficient to bring the metal into the passivation domain. The ease with which iron is passivated by oxidizing agents will therefore be the greater the smaller the range of electrode potentials at which corrosion is possible. From Fig. 6*a* passivation will therefore be relatively difficult, or even impossible, at pH's below about 8; it will be relatively easy at pH's above about 8, and very easy at pH's between about 10 and 12.

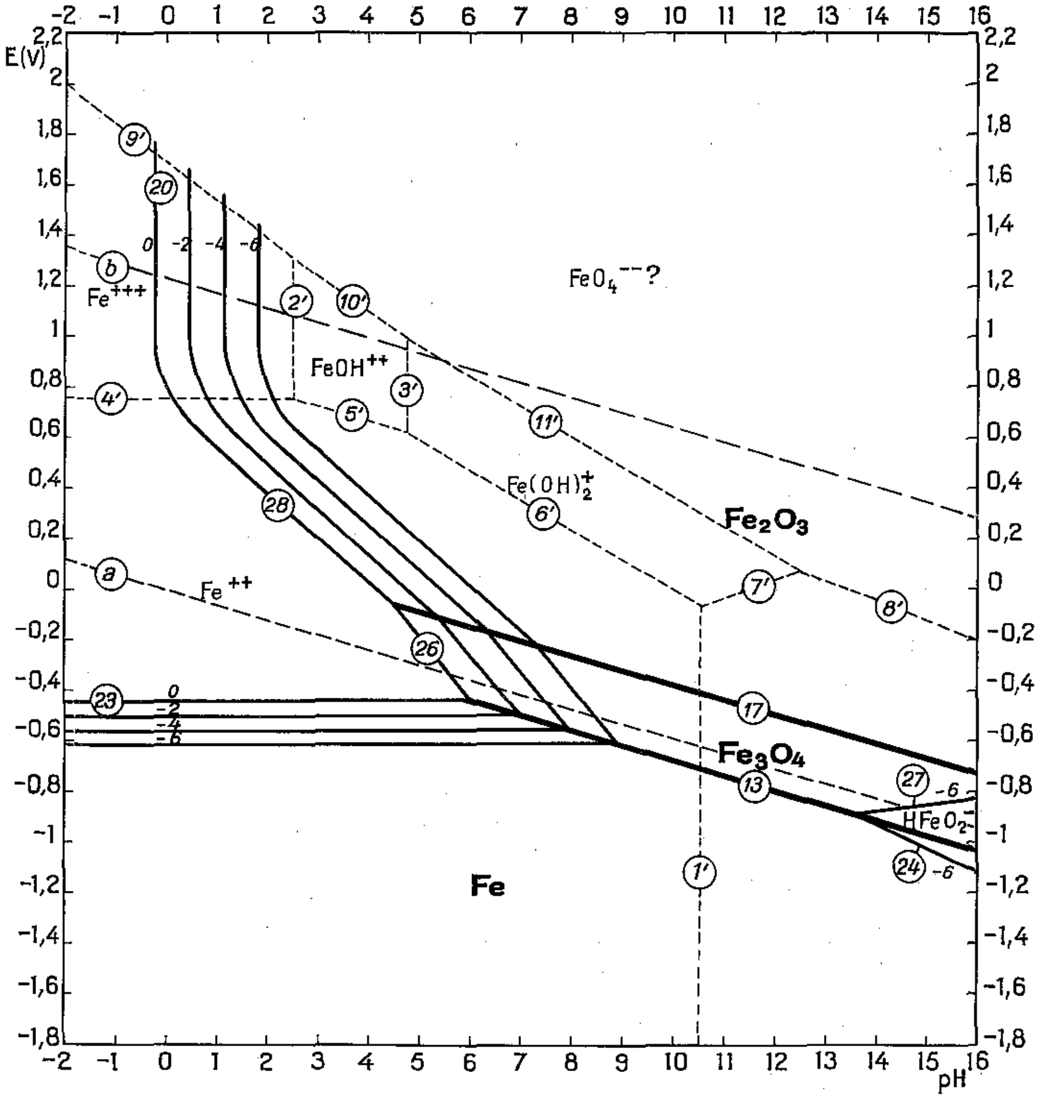


FIG. 4. Potential–pH equilibrium diagram for the system iron–water, at 25°C (considering as solid substances only Fe, $Fe_3O_4$ and $Fe_2O_3$).

This, however, concerns the behaviour of iron at 25°C and atmospheric pressure. When the pressure is above 1 atm. the domain of stability of water extends beyond lines (*a*) and (*b*) in Fig. 4; when the hydrogen pressure reaches 740 atm. (i.e. rH = −2·87) the lower limit of the domain of stability of water merges with the line $E_0 = -0{\cdot}085 - 0{\cdot}0591\,\text{pH}$ (volt) which represents the conditions of the equilibrium between Fe and $Fe_3O_4$ according to reaction (13) (see § 2). At these pressures and within certain limits of pH (between about 10 and 12), iron can therefore be thermodynamically stable in the presence of water, without necessarily being covered with a film of oxide; at pressures above 740 atm. (at 25°C) the domain of stability of iron and that of water have a portion in common, which confers upon iron the characteristics of a noble metal, within very narrow limits however.

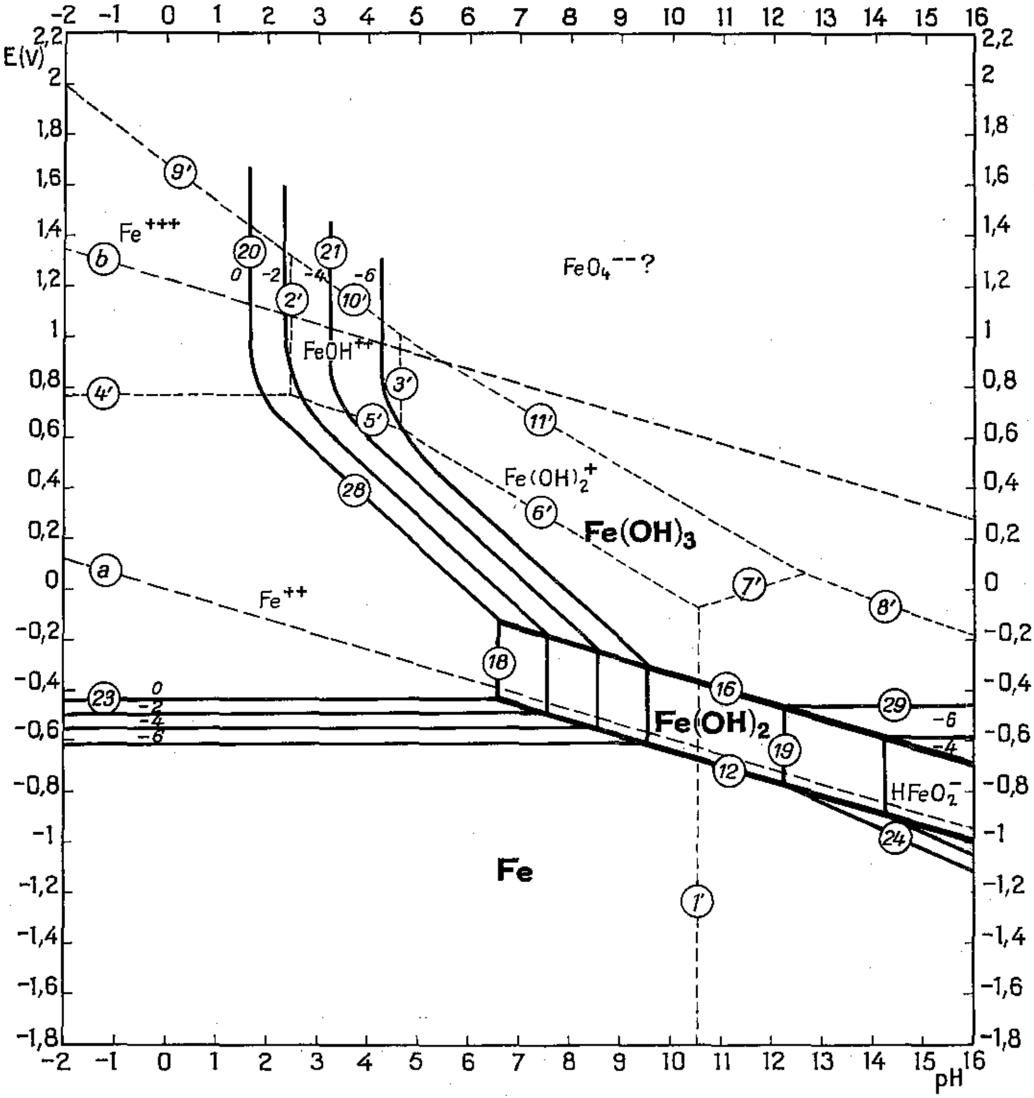


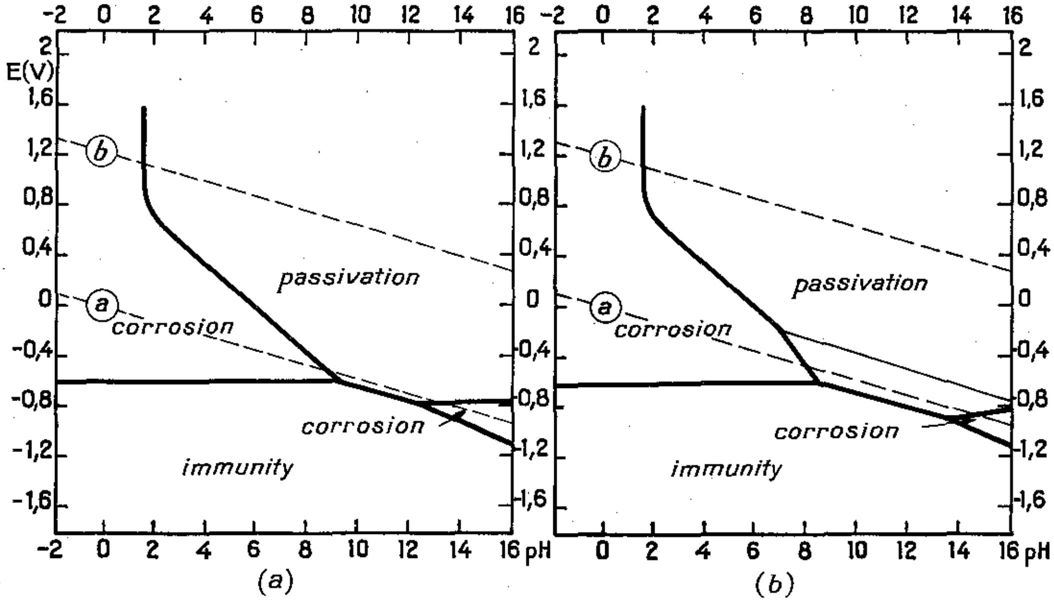
FIG. 5. Potential–pH equilibrium diagram for the system iron–water, at 25°C [considering as solid substances only Fe, Fe(OH)$_2$ and Fe(OH)$_3$].

In agreement with Figs. 4 and 5, metallic iron can be obtained, together with some hydrogen, by the reduction of acid solutions of ferrous salts.

### 3.2.2. *Experimental verification and detailed investigation*

(*a*) *General conditions of corrosion, immunity and passivation.* In order to verify and make a detailed investigation of these conclusions, we have performed several series of experiments since 1937 in order to examine the behaviour of iron in the presence of various aqueous solutions and under various conditions of pH and electrode potential.

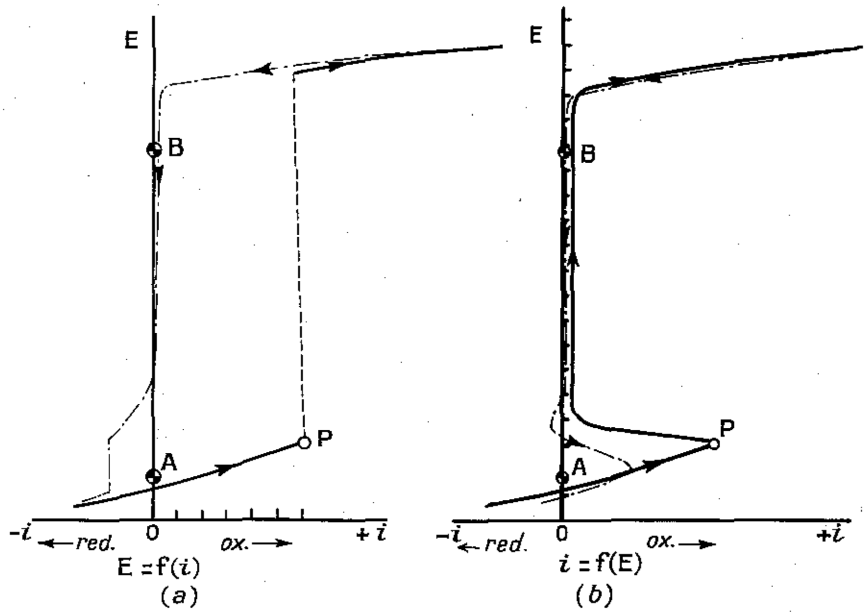
First of all, in order to verify experimentally the possible existence of the domains of corrosion, immunity and passivation shown in the theoretical Figs. 6*a* and *b*, we determined polarization curves



(*a*) Assuming passivation by a film of $Fe_2O_3$.

(*b*) Assuming passivation by films of $Fe_2O_3$ and $Fe_3O_4$.

FIG. 6. Theoretical conditions of corrosion, immunity and passivation of iron.

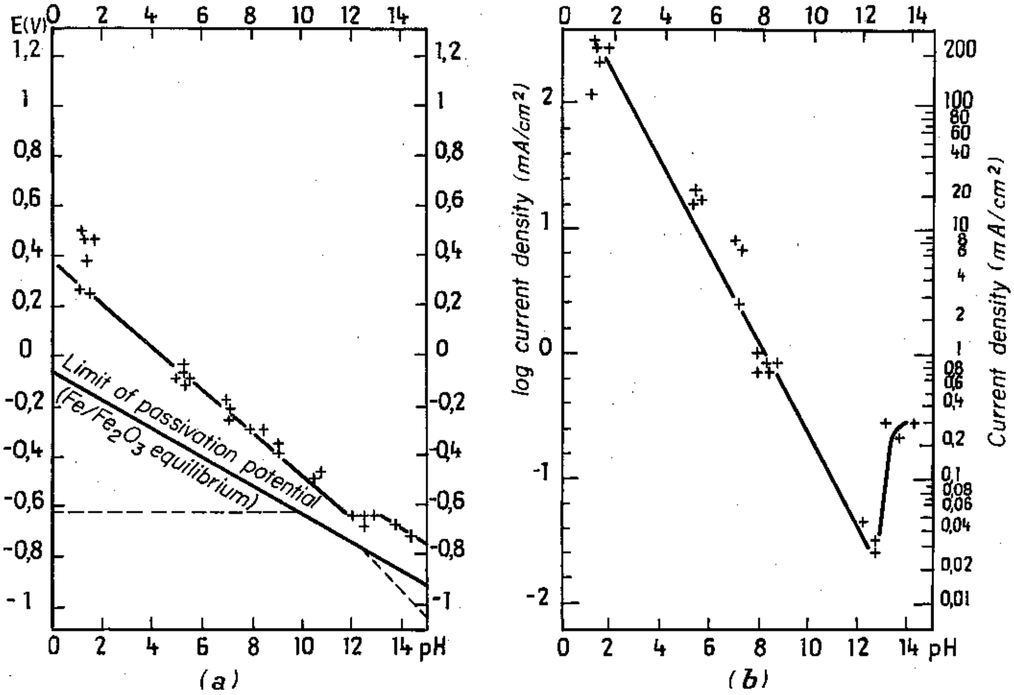


(*a*) Galvanostatic method.

(*b*) Potentiokinetic method.

FIG. 7. Polarization curves for iron in 0·10 M $NaHCO_3$ solutions (pH = 8·4).

for iron in various agitated buffer solutions of pH between 1 and 15, using a method that has been described elsewhere (*loc. cit.* [1]; stelling No. 7; [5], [6]). Figures 7*a* and *b* show two examples of such polarization curves, determined respectively by a manual galvanostatic method and an automatic potentiokinetic method ([7], [8]). These experiments showed that iron is actually passivated under definite conditions of electrode potential and current density; the passivation potential and passivation current density depend on the pH as indicated in Figs. 8*a* and *b*. These experiments also enabled us to establish Figs. 9*a* and *b* which represent diagrammatically the *experimental* conditions of corrosion, immunity and passivation of iron in agitated solutions, with a schematic indication of the corrosion rates of the metal.



(*a*) Passivation potentials. (*b*) Passivation current densities.

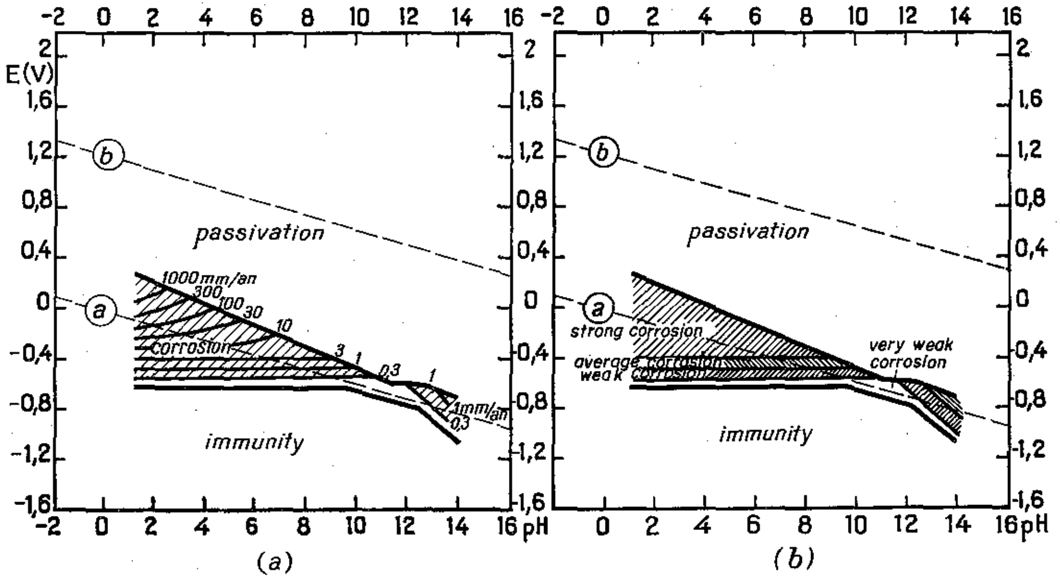
FIG. 8. Influence of pH on the conditions of anodic passivation of iron.

By comparing the experimental diagrams Figs. 8*a* and *b* with the theoretical diagrams Figs. 6*a* and *b*, it can be seen that the theoretical predictions are verified as far as the principal lines are concerned: there actually exist two domains of corrosion (connected, nevertheless, by a narrow domain in which a slight amount of corrosion is possible), one domain of immunity and one domain of passivation; the line separating the domain of passivation from the domains of corrosion does not, however, correspond exactly with the line predicted theoretically.(6) From the above it appears most probable that the thermodynamic method used in this *Atlas* to predict the general conditions of corrosion, immunity and passivation is practically exact, in the particular case of iron at least; more especially this implies the validity of the theory of passivation by an oxide film. This theory was suspected towards 1836 by Michael Faraday and contested for a long time, receiving formal ratification in 1930 when Evans [9] isolated the film formed on iron passivated by anodic treatment in a dilute solution of sulphuric acid,

---

(6) The limits of the theoretical domains of passivation represented in Figs. 6*a* and *b* relate to solutions containing $10^{-6}$ g-at Fe/l (i.e. 0·06 mg/l). This, of course, does not necessarily correspond to the experimental cases practically experienced.

thus making visible a film that was invisible when in contact with the metal; Mayne and Pryor in 1949 and 1950 produced some important information in support of this theory, namely that in the presence of an aerated caustic soda solution iron covers itself with a protective film of $\gamma$-$Fe_2O_3$ [10].



(*a*) Corrosion rates. (*b*) Corrosion intensities.

FIG. 9. Experimental conditions of corrosion, immunity and passivation of iron in the presence of agitated aqueous solutions.

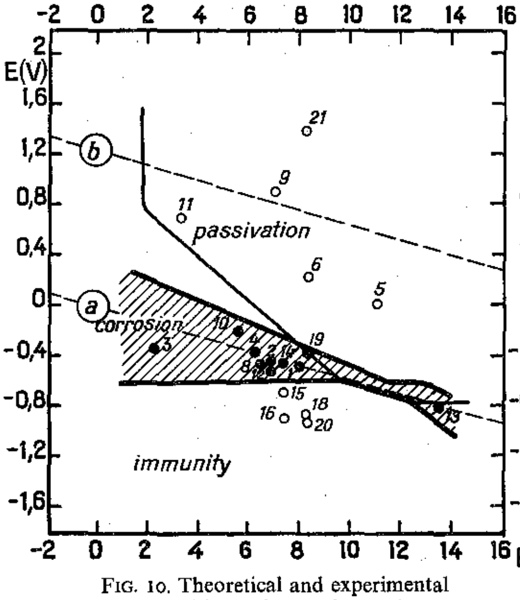


FIG. 10. Theoretical and experimental conditions of corrosion and non-corrosion of iron.

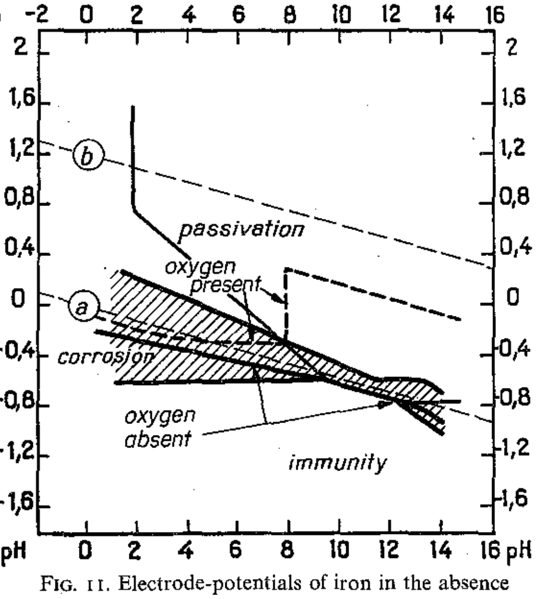


FIG. 11. Electrode-potentials of iron in the absence and in the presence of oxygen.

We also point out that Fig. 8*b* indicates the critical oxidation rate, one side of which an oxidation is passivating and the other side of which it is activating. From this figure it results that iron is most easily passivated at pH's around 12: a very mild oxidizing action is then sufficient to produce passivation.

In Fig. 10. we have reproduced the theoretical and experimental boundaries of the domains of corrosion, immunity and passivation of iron, already represented respectively in Figs. 6*a* and 9*a*. Also shown are the results of various experiments relating to the behaviour of iron in the presence of aqueous solutions. We give below some information concerning these experiments, already shown in previous publications ([11], [12], [13], [14]). Marked in Fig. 10 are the electrode potentials exerted by specimens of iron immersed in solutions of various pH's, these specimens of iron being either electrically insulated, or coupled to another metal, or used as an electrolytic anode or cathode. The cases in which corrosion took place are represented by a black disc ●, and the cases in which there was no corrosion are represented by a white disc ○. The characteristics of the specimens of iron and the solutions were as follows:

| No. | | pH | E (volt) | |
|---|---|---|---|---|
| | *Insulated iron* | | | |
| 1. | Distilled water | 8·1 | −0·486 | ● |
| 2. | NaCl, 1 g/l | 6·9 | −0·445 | ● |
| 3. | $H_2SO_4$, 1 „ | 2·3 | −0·351 | ● |
| 4. | $NaHSO_3$, 1 „ | 6·4 | −0·372 | ● |
| 5. | NaOH, 1 „ | 11·2 | +0·026 | ○ |
| 6. | $K_2CrO_4$, 1 „ | 8·5 | +0·235 | ○ |
| 8. | $KMnO_4$, 0·3 „ | 6·7 | −0·460 | ● |
| 9. | $KMnO_4$, 1 „ | 7·1 | +0·900 | ○ |
| 10. | $H_2O_2$, 0·3 „ | 5·7 | −0·200 | ● |
| 11. | $H_2O_2$, 3 „ | 3·4 | +0·720 | ○ |
| 12. | Brussels tap-water | 7·0 | −0·450 | ● |
| 13. | Air-free NaOH, 40 g/l | 13·7 | −0·810 | ● |
| | *Iron coupled to another metal* | | | |
| 14. | Tap–water, iron–copper | 7·5 | −0·445 | ● |
| 15. | „ iron–zinc | 7·5 | −0·690 | ○ |
| 16. | „ iron–magnesium | 7·5 | −0·910 | ○ |
| | *Iron used as an electrode* | | | |
| 18. | 0·10 M $NaHCO_3$, $-^{ve}$ pole | 8·4 | −0·860 | ○ |
| 19. | „ $+^{ve}$ pole | 8·4 | −0·350 | ● |
| 20. | „ $-^{ve}$ pole | 8·4 | −0·885 | ○ |
| 21. | „ $+^{ve}$ pole | 8·4 | +1·380 | ○ |

It can be seen that, without exception, there is actually corrosion or non-corrosion of the iron depending on whether the point representing the condition of the metal lies in the domain of corrosion, in Fig. 10, or in the domains of immunity or passivation; this agreement holds good not only for the experimental corrosion–immunity–passivation diagram drawn in Fig. 9*a*, but also for the theoretical diagrams in Figs. 6*a* and *b*.

(*b*) *Activating or passivating action of oxygen and other oxidizing agents.* In Fig. 11 we have represented the influence of pH on the electrode potential of electrically insulated iron, on the one hand, in the presence of solutions free from oxygen and other oxidizing agents, and, on the other hand, in the presence of solutions saturated with oxygen at atmospheric pressure.

It can be seen from this figure that, *for solutions free from oxygen*, the potential of the iron is always below line *a*, which implies the possibility of hydrogen evolution. At pH's below about 9·5 or above about 12·5 the potential lies inside the corrosion domains, which means that iron is corroded with the evolution of hydrogen. The corrosion will progressively increase in intensity as the pH decreases below 9·5 or increases above 12·5. At pH's between about 9·5 and 12·5, the potential is near the boundary of the immunity domain and is practically the same as the equilibrium potential of the system Fe–$Fe_3O_4$, the value of which depends on the pH as shown by relation (13) in paragraph 2.2; under these pH conditions iron will tend to be converted into magnetite with the evolution of hydrogen; however, this conversion will be slow, and will stop completely if the magnetite thus produced forms a protective film on the metal.

The *presence of oxygen* in the solution will have the effect of increasing the electrode potential of the metal. At pH's below about 8 this increase will be insufficient to bring about passivation of the iron; oxygen will therefore increase the corrosion rate. At pH's above about 8 oxygen will bring about passivation by forming a film on the metal, most probably made up of $\gamma$-$Fe_2O_3$ (Mayne and Pryor [10]), which will, in general, be protective in the case of solutions not containing chloride.

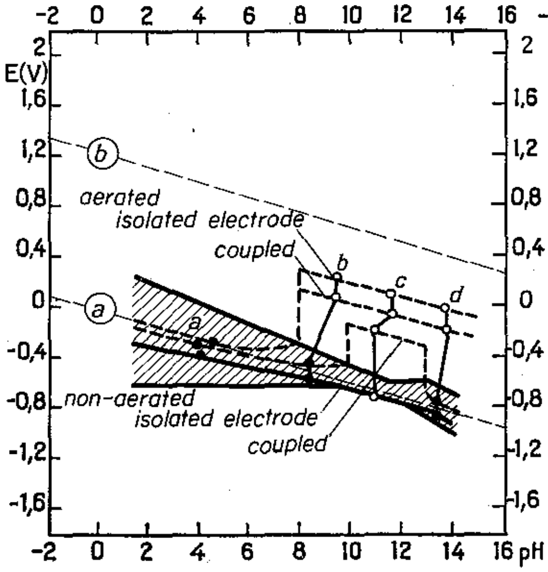


FIG. 12. Differential aeration of iron (Evans cells).

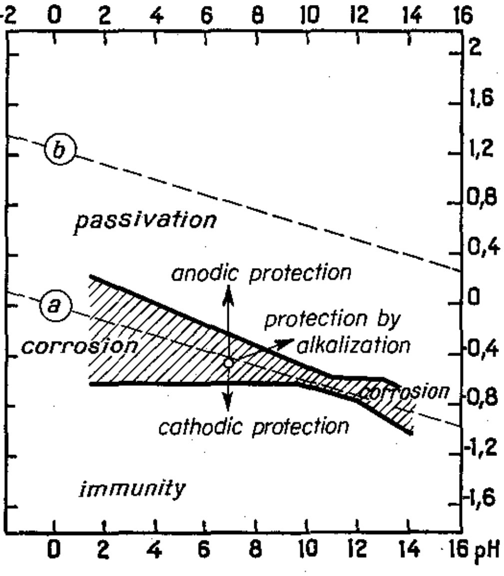


FIG. 13. Protection of iron against corrosion.

(*c*) *Differential aeration.* Figure 11 leads to the following interpretation of the differential aeration phenomena discovered in 1923 by Evans [15]: when a piece of iron is immersed in a practically neutral non-buffered solution, which is aerated in one region and not aerated in another, it is noticed that this "differential aeration" produces an increase in the corrosion rate in the non-aerated regions, and a decrease in the corrosion rate in the aerated regions, with a flow of electric current between these regions. It results from Fig. 11 that, on account of the increase of the pH above 8 due to the reduction of oxygen by the reaction $O_2+2H_2O+4e^- \rightarrow 4OH^-$, the aerated regions will be passivated and the non-aerated regions will not be passivated (Fig. 12); the short-circuiting of aerated regions of high electrode potential and non-aerated regions of low electrode potential will cause electric currents to flow with the reduction of oxygen in the aerated regions and an increase in corrosion in the non-aerated regions. Figure 11 also shows that, for solutions of various pH's, the mode of operation of these "Evans differential aeration cells" will in general vary with the pH as follows:

(*a*) pH below 7: "abnormal" operation: aeration will cause an *increase* in the corrosion rate of the aerated zones with a *small* flow of current between the aerated and non-aerated zones and a *small* increase in the corrosion rate of the non-aerated zones.

(*b*) pH approximately 7–10: "normal" operation: passivation of the aerated zones, a large current and a large corrosion rate in the non-aerated zones;

(*c*) pH approximately 10–13: "abnormal" operation: passivation of the aerated and non-aerated zones without a flow of current;

(*d*) pH above 13: "normal" operation, qualitatively the same as for pH's of approximately 7–10, but less vigorous.

### 3.2.3. *Processes for the protection of iron against corrosion*

The corrosion of iron by natural waters, and by a large number of moist materials, is due to the existence in Figs. 6*a* and *b* of a large "dangerous triangle" in which the electrode potential of the metal very often is situated.

In order to protect iron against corrosion, therefore, three groups of processes are theoretically possible(7): as shown in Fig. 13, the point representing the condition of the metal can be displaced downwards (*cathodic protection*), upwards (*anodic protection or protection by passivation*) or to the right (*protection by passivating alkalinization*).

A detailed account of this is beyond the scope of the present book. We shall content ourselves with giving a brief description of each of the three groups of processes.

*Cathodic protection* is based on the fact that the potential of iron is lowered, on reduction, into the domain of immunity in which the corrosion of iron is theoretically impossible, i.e. appreciably below the following values (Fig. 6):

for pH's below about 10: $E_0 = -0{\cdot}62$ (volt)
„ between about 10 and 13: $E_0 = -0{\cdot}08 - 0{\cdot}059\ \text{pH}$ „
„ above about 13: $E_0 = +0{\cdot}31 - 0{\cdot}088\ \text{pH}$ „

Cathodic protection can be brought about either by making the structure to be protected the negative electrode of a source of direct current, or by connecting the structure to a "reactive anode" of zinc or magnesium which corrodes sacrificially; cathodic protection is *generally* free from dangers and affords *perfect* protection of structures in permanent contact with water or a moist medium (soil, porous concrete, etc.) even if the water or other medium is strongly corrosive.

*Anodic protection* or *protection by passivation* is based on the fact that the potential of iron is raised, on oxidation, into the domain of passivation in which the metal can become covered with a more or less protective film of oxide, i.e. appreciably above the following values (Fig. 8*a*):

for pH's below about 12: $E_0 = +0{\cdot}40 - 0{\cdot}085\ \text{pH}$ (volt)
„ between 12 and 13: $E_0 = -0{\cdot}63$ „
„ above 13: $E_0 = +0{\cdot}20 - 0{\cdot}062\ \text{pH}$ „

Anodic protection or protection by passivation can be brought about either by making the structure to be protected the positive electrode of a source of direct current, or by the use of oxidizing substances (which are introduced into the corrosive medium or applied to the surface of the metal); the latter method is sometimes dangerous for the following two reasons: firstly, if the oxidizing action is insufficient there is a generalized increase in corrosion instead of passivation; secondly, if the passivating film is porous and insufficiently protective (which is frequently the case with media containing chloride), the protection is imperfect and corrosion takes place in the form of localized "pitting" at certain points of the structure. Based upon this method of protection is the action of a large number of "anodic" inhibitors (chromates, nitrites, oxygen, etc.) which are added to the corrosive medium or used as constituents of a primary coat of paint, for satisfactory results to be obtained the method must be used with care and with a perfect knowledge of the problem to be solved.

---

(7) We shall not consider here protection by the application of coatings (paints, galvanization, electro-plating, etc.) which are intended to prevent completely any direct contact between the metal and the solution.

Finally, *protection by alkalinization*, which is a variation of protection by passivation, consists of the addition of alkaline substances to the water or corrosive medium, producing a pH at which passivation is particularly easy (for instance 10–13). This method is used principally in the treatment of waters with trisodium phosphate or caustic soda, and also in protection by cement coatings. It must also be used with care. It is as well to make sure that the medium treated in this way is oxidizing, in particular if the pH is very high, in order to avoid the metal taking up a position in the small corrosion domain which is shown in Figs. 6 and 9 for alkaline reducing media, and which is one of the principal causes of the caustic embrittlement of boilers.

### 3.3. SIGNIFICANCE AND PRACTICAL IMPORTANCE OF THE ELECTROCHEMICAL EQUILIBRIUM DIAGRAMS FOR IRON

At this stage we should like to emphasize the fact that potential–pH electrochemical equilibrium diagrams, such as those given in Figs. 4 and 5 of this section of the *Atlas*, represent essentially the conditions under which the reactions considered for their establishment are theoretically possible or impossible, from the thermodynamic point of view. However, a large number of electrochemical reactions are irreversible, which means that although they are thermodynamically possible they do not necessarily take place; in order for them to take place a certain overpotential is required; while these diagrams may show definitely that a reaction cannot take place, they do not show definitely whether or not a thermodynamically possible reaction *will* take place.

In spite of these limitations, the equilibrium diagrams (Figs. 4 and 5), and the "corrosion, immunity and passivation" diagrams derived from them, have proved to be useful and in good agreement with the facts. They have enabled us to specify, predict and control the conditions of cathodic protection of iron and non-alloyed steels in various surrounding media (waters, acid solutions, alkaline solutions, soils and concretes). Moreover, as Evans pointed out in his preface to the English translation of our Delft thesis, by enabling us to predetermine the theoretical conditions of the formation of oxide films, the diagrams have provided explanations of certain controversial phenomena connected with the passivation of metals by film formation; in particular they have enabled us to elucidate the conditions under which oxygen and other oxidizing agents act as activating or passivating substances.

Nevertheless, it should be realized that such equilibrium diagrams cannot, by themselves, provide the *complete* solution to any problem. They should be considered primarily as a tool which, in the hands of those who fully understand the meaning of electrode potentials, can assist in the understanding of facts, guide research and lead to the development of near-perfect techniques in fields involving electrochemistry, in particular concerning the protection of metals against corrosion. Such research must involve not only thermodynamic studies but also kinetic studies and chemical, microscopic and structural examination.

By way of an example we draw the reader's attention to Figs. 7*a* and *b*, which represent potential–current curves for the successive anodic and cathodic polarization of iron in a 0·1 M sodium bicarbonate solution, firstly using a galvanostatic method (Fig. 7*a*), and, secondly, using a potentiokinetic method (Fig. 7*b*). Diagrams such as that in Fig. 7*a* have enabled us to determine the passivation potentials and passivation current densities represented in Figs. 8 and also in Figs. 9*a* and *b* which are derived from them: these potentials and current densities are respectively the ordinates and abscissae of the points P, for which passivation appears.

The curves in Fig. 7 reveal that, contrary to a still widespread opinion, the passivation is, to all intents and purposes, reversible, at least in the case of bicarbonate solutions: just as "active" iron becomes passive if, by oxidation, its potential is raised above the passivation potential corresponding to the point P, so also "passivated" iron becomes active if, by reduction, its potential is lowered below this value. This gives a quantitative aspect to Evans' theory of the *reductive dissolution* of the passivation film formed on iron.

Recent work by de Zoubov [16] and Clerbois [17] working independently of each other, has shown that for sodium bicarbonate solutions, the passivation potential of iron is exactly that at which ferrous carbonate $FeCO_3$ is in thermodynamic equilibrium with an oxide of iron $Fe_2O_3$ or $Fe_3O_4$; these equilibrium conditions have been indicated in the construction of potential–pH equilibrium diagrams for the ternary system $Fe–CO_2–H_2O$ [18]. The passivation of iron therefore seems to be due to the formation of a film of $Fe_2O_3$ or $Fe_3O_4$ in contact with the metal in a solution saturated with $FeCO_3$, and this passivation would therefore appear when the solid substance formed by corrosion ceases to be non-protective ferrous carbonate and becomes protective oxide.

## 4. BIBLIOGRAPHY

[1] M. POURBAIX, *Thermodynamique des solutions aqueuses diluées. Représentation graphique du rôle du pH et du potentiel* (Thèse, Delft, 1945; Béranger, Paris and Liège). *Thermodynamics of Dilute Aqueous Solutions,* Arnold, London.

[2] B. SCHRAGER, *Chem. News.,* 138, 1929, p. 354.

[3] CH. D. HODGMANN, *Handbook of Chemistry and Physics,* 26, Chemical Rubber Publ. Co., Cleveland, 1936.

[4] G. CHARLOT, *L'analyse qualitative et les réactions en solution,* 4th ed., Masson, Paris, 1957, pp. 180–185.

[5] M. POURBAIX, *Corrosion, passivité et passivation du fer; le rôle du pH et du potentiel* [Thèse, Brussels, 1945; *Mémoires Soc. Roy. Belge Ingénieurs et Industriels,* No. 1, March 1951, pp. 1–40].

[6] M. POURBAIX, *Sur l'interprétation thermodynamique des courbes de polarisation* (Rapport technique RT.1 of CEBELCOR, 1952).

[7] M. POURBAIX, *Compte rendu d'une séance d'étude sur des recherches fondamentales en électrochimie et en corrosion* (Brussels, 15 July 1958) (Rapport technique RT.67 of CEBELCOR, 1958).

[8] M. POURBAIX, J. LAUREYS and L. NEELEMANS, *Méthode de prédétermination des circonstances de non corrosion et de corrosion des métaux et alliages* (Rapport CEFA/R.1 of the Commission des Études Fondamentales et Applications of CEBELCOR, 1958).

[9] U. R. EVANS, *Nature,* **126**, 130 (1930). See also U. R. EVANS and M. J. PRYOR, *J. Chem. Soc.,* 1949, p. 3330; 1950, pp. 1259, 1266 and 1274.

A more recent description of the method of isolation of the protective film and a discussion of the important phenomenon of "reductive dissolution" of the oxide can be found in U. R. EVANS, *The Corrosion and Oxidation of Metals,* pp. 222–8 (Ed. Arnold, London, 1960).

[10] J. E. O. MAYNE and M. J. PRYOR, The mechanism of inhibitors of corrosion of iron; I. by chromic acid and potassium chromate, *J. Chem. Soc.,* 1949, pp. 1831–5; II. by sodium hydroxide solution (in collaboration with J. W. MENTER), *J. Chem. Soc.,* 1950, p. 3229.

[11] M. POURBAIX, *Applications de diagrammes tension–pH relatifs au fer et à l'eau oxygénée. Expériences de démonstration* (Rapport technique RT.2 of CEBELCOR, 1954).

[12] M. POURBAIX, *Leçons sur la corrosion électrochimique* (1er fascicule) (Rapport technique RT.57 of CEBELCOR, 1957).

[13] M. POURBAIX, Deux expériences de cours en thermodynamique électrochimique, *C. R. 2e Réunion du CITCE,* Milan, 1950, Tamburini, Milan, 1951.

[14] J. FERON and M. POURBAIX, Potentiels de passivation et d'activation du fer. Corrosion cathodique du fer en présence d'oxygène, *C.R. 3e Réunion du CITCE,* Berne, 1951; Manfredi, Milan, 1952.

[15] U. R. EVANS, *J. Inst. Metals,* **30**, 267 (1923).

[16] N. DE ZOUBOV, *Sur le comportement électrochimique du fer en solution bicarbonique.* Lecture delivered in Brussels on 30 August 1960 at the reunion of Commission 5 "corrosion" of the Comité International de Thermodynamique et de Cinétique Électrochimiques CITCE.

[17] F. CLERBOIS, *Contribution à l'étude du comportement anodique des métaux en milieu aqueux,* Grenoble Thesis, 1960.

[18] E. DELTOMBE and M. POURBAIX, *Comportement électrochimique du fer en solution carbonique. Diagrammes d'équilibres tension–pH du système* $Fe–CO_2–H_2O$, at 25°C (Rapport technique RT.8 of CEBELCOR, 1954).

SECTION 18.3

# ARSENIC(¹)

J. VAN MUYLDER and M. POURBAIX

SUMMARY

1. *Substances considered and substances not considered.*
2. *Reactions and equilibrium formulae.*
   2.1. Two dissolved substances.
      2.1.1. Relative stability of the dissolved substances.
      2.1.2. Limits of the domains of relative predominance of the dissolved substances.
   2.2. Two solid substances.
      Limits of the domains of relative stability of the solid substances.
   2.3. One solid substance and one dissolved substance.
      Solubility of the solid substances.
   2.4. One solid substance and one gaseous substance.
      Limits of the domains of relative stability of As and $AsH_3$.
3. *Equilibrium diagram and its interpretation.*
   3.1. Establishment of the diagram.
   3.2. Stability of arsenic.
   3.3. Stability of arsenious anhydride and the arsenites.
   3.4. Stability of arsenic anhydride and the arsenates.
   3.5. Stability of arsine.
   3.6. Passivating action of arsenic compounds.
   3.7. Arsenic electrodes.
4. *Bibliography.*

---

(¹) Shortened and adapted version of the Rapport technique RT.46 of CEBELCOR (February 1957) [1].

## 1. SUBSTANCES CONSIDERED AND SUBSTANCES NOT CONSIDERED

| | Oxidation number (Z) | Considered | Not considered | $\mu^0$(cal.) | Name, colour, crystalline system |
|---|---|---|---|---|---|
| Solid substances | $-1$ | – | $\mathbf{As_2H_2}$ | – | Diarsenic dihydride, brown |
| | $-0.5$ | – | $\mathbf{As_4H_2}$ | – | Tetra-arsenic dihydride, red–brown |
| | 0 | $\mathbf{As}$ | – | 0 | Arsenic, steel grey, rhomb. |
| | $+1$ | – | $\mathbf{As_2O}$ | – | Arsenic sub-oxide |
| | $+3$ | $\mathbf{As_2O_3}$ | – | —137 680 | Arsenious anhydride, white, cub. |
| | » | – | $\mathbf{As_2O_3}$ | – | Arsenious anhydride, colourless, monocl. |
| | $+4$ | – | $\mathbf{As_2O_4}$ | – | Arsenic peroxide |
| | $+5$ | $\mathbf{As_2O_5}$ | – | —184 600 | Arsenic anhydride, white, amorphous |
| Dissolved substances | $+3$ | $AsO^+$ | – | — 39 100 | Arsenyl ion, colourless |
| | » | $HAsO_2$ | – | — 96 250 | Meta-arsenious acid, colourless |
| | » | $AsO_2^-$ | – | — 83 700 | Meta-arsenite ion, colourless |
| | » | $H_3AsO_3$ | – | —152 940 | Ortho-arsenious acid |
| | » | $H_2AsO_3^-$ | – | —140 400 | Mono-ortho-arsenite ion, colourless |
| | $+5$ | $H_3AsO_4$ | – | —183 800 | Ortho-arsenic acid, colourless |
| | » | $H_2AsO_4^-$ | – | —178 900 | Mono-ortho-arsenate ion, colourless |
| | » | $HAsO_4^{--}$ | – | —169 000 | Di-ortho-arsenate ion, colourless |
| | » | $AsO_4^{---}$ | – | —152 000 | Tri-ortho-arsenate ion, colourless |
| | » | – | $AsO_2^+$ | – | Arsenyl ion |
| | $+7$ | – | $AsO_3^+$ | – | Perarsenyl ion |
| Gaseous substance | $-3$ | $AsH_3$ | – | 42 000 | Arsine, colourless |

## 2. REACTIONS AND EQUILIBRIUM FORMULAE

### 2.1. TWO DISSOLVED SUBSTANCES

### 2.1.1. *Relative stability of the dissolved substances*

$Z = +3$

1. $AsO^+ + H_2O = HAsO_2 + H^+$ $\qquad \log\frac{(HAsO_2)}{(AsO^+)} = 0.34 + pH$

2. $HAsO_2 = AsO_2^- + H^+$ $\qquad \log\frac{(AsO_2^-)}{(HAsO_2)} = -9.21 + pH$

$Z = +5$

3. $H_3AsO_4 = H_2AsO_4^- + H^+$ $\qquad \log\frac{(H_2AsO_4^-)}{(H_3AsO_4)} = -3.60 + pH$

4. $H_2AsO_4^- = HAsO_4^{--} + H^+$ $\qquad \log\frac{(HAsO_4^{--})}{(H_2AsO_4^-)} = -7.26 + pH$

5. $HAsO_4^{--} = AsO_4^{---} + H^+$ $\qquad \log\frac{(AsO_4^{---})}{(HAsO_4^{--})} = -12.47 + pH$

$+3 \rightarrow +5$

6. $AsO^+ + 3H_2O = H_3AsO_4 + 3H^+ + 2e^-$ $\qquad E_0 = 0.550 - 0.0887\,pH + 0.0295\log\frac{(H_3AsO_4)}{(AsO^+)}$

7. $HAsO_2 + 2H_2O = H_3AsO_4 + 2H^+ + 2e^-$ $\qquad E_0 = 0.560 - 0.0591\,pH + 0.0295\log\frac{(H_3AsO_4)}{(HAsO_2)}$

8. $HAsO_2 + 2H_2O = H_2AsO_4^- + 3H^+ + 2e^-$ $\qquad E_0 = 0.666 - 0.0887\,pH + 0.0295\log\frac{(H_2AsO_4^-)}{(HAsO_2)}$

9. $HAsO_2 + 2H_2O = HAsO_4^{--} + 4H^+ + 2e^-$ $\qquad E_0 = 0.881 - 0.1182\,pH + 0.0295\log\frac{(HAsO_4^{--})}{(HAsO_2)}$

10. $AsO_2^- + 2H_2O = HAsO_4^{--} + 3H^+ + 2e^-$ $\qquad E_0 = 0.609 - 0.0887\,pH + 0.0295\log\frac{(HAsO_4^{--})}{(AsO_2^-)}$

11. $AsO_2^- + 2H_2O = AsO_4^{---} + 4H^+ + 2e^-$ $\qquad E_0 = 0.977 - 0.1182\,pH + 0.0295\log\frac{(AsO_4^{---})}{(AsO_2^-)}$

### 2.1.2. *Limits of the domains of relative predominance of the dissolved substances*

1'. $AsO^+ / HAsO_2$ $pH = -0.34$
2'. $HAsO_2 / AsO_2^-$ $pH = 9.21$
3'. $H_3AsO_4 / H_2AsO_4^-$ $pH = 3.60$
4'. $H_2AsO_4^- / HAsO_4^{--}$ $pH = 7.26$
5'. $HAsO_4^{--} / AsO_4^{---}$ $pH = 12.47$

6'. $AsO^+ / H_3AsO_4$ $E_0 = 0.550 - 0.0887\,pH$
7'. $HAsO_2 / H_3AsO_4$ $E_0 = 0.560 - 0.0591\,pH$
8'. $HAsO_2 / H_2AsO_4^-$ $E_0 = 0.666 - 0.0887\,pH$
9'. $HAsO_2 / HAsO_4^{--}$ $E_0 = 0.881 - 0.1182\,pH$
10'. $AsO_2^- / HAsO_4^{--}$ $E_0 = 0.609 - 0.0887\,pH$
11'. $AsO_2^- / AsO_4^{---}$ $E_0 = 0.977 - 0.1182\,pH$

## 2.2. TWO SOLID SUBSTANCES

*Limits of the domains of relative stability of the solid substances*

$0 \rightarrow +3$
12. $2\,\mathbf{As} + 3H_2O = \mathbf{As_2O_3} + 6H^+ + 6e^-$ $E_0 = 0.234 - 0.0591\,pH$

$0 \rightarrow +5$
13. $2\,\mathbf{As} + 5H_2O = \mathbf{As_2O_5} + 10H^+ + 10e^-$ $E_0 = 0.429 - 0.0591\,pH$

$+3 \rightarrow +5$
14. $\mathbf{As_2O_3} + 2H_2O = \mathbf{As_2O_5} + 4H^+ + 4e^-$ $E_0 = 0.721 - 0.0591\,pH$

## 2.3. ONE DISSOLVED SUBSTANCE AND ONE SOLID SUBSTANCE

*Solubility of the solid substances*

$Z = +3$
15. $2AsO^+ + H_2O = \mathbf{As_2O_3} + 2H^+$ $\log(AsO^+) = -1.02 - pH$
16. $\mathbf{As_2O_3} + H_2O = 2HAsO_2$ $\log(HAsO_2) = -0.68$
17. $\mathbf{As_2O_3} + H_2O = 2AsO_2^- + 2H^+$ $\log(AsO_2^-) = -9.89 + pH$

$Z = +5$
18. $\mathbf{As_2O_5} + 3H_2O = 2H_3AsO_4$ $\log(H_3AsO_4) = 4.74$
19. $\mathbf{As_2O_5} + 3H_2O = 2H_2AsO_4^- + 2H^+$ $\log(H_2AsO_4^-) = 1.15 + pH$
20. $\mathbf{As_2O_5} + 3H_2O = 2HAsO_4^{--} + 4H^+$ $\log(HAsO_4^{--}) = -6.12 + 2\,pH$
21. $\mathbf{As_2O_5} + 3H_2O = 2AsO_4^{---} + 6H^+$ $\log(AsO_4^{---}) = -18.59 + 3\,pH$

$0 \rightarrow +3$
22. $\mathbf{As} + H_2O = AsO^+ + 2H^+ + 3e^-$ $E_0 = 0.254 - 0.0394\,pH + 0.0197\log(AsO^+)$
23. $\mathbf{As} + 2H_2O = HAsO_2 + 3H^+ + 3e^-$ $E_0 = 0.248 - 0.0591\,pH + 0.0197\log(HAsO_2)$
24. $\mathbf{As} + 2H_2O = AsO_2^- + 4H^+ + 3e^-$ $E_0 = 0.429 - 0.0788\,pH + 0.0197\log(AsO_2^-)$

$0 \rightarrow +5$
25. $\mathbf{As} + 4H_2O = AsO_4^{---} + 8H^+ + 5e^-$ $E_0 = 0.648 - 0.0946\,pH + 0.0118\log(AsO_4^{---})$

$+3 \rightarrow +5$
26. $\mathbf{As_2O_3} + 5H_2O = 2H_3AsO_4 + 4H^+ + 4e^-$ $E_0 = 0.580 - 0.0591\,pH + 0.0295\log(H_3AsO_4)$
27. $\mathbf{As_2O_3} + 5H_2O = 2H_2AsO_4^- + 6H^+ + 4e^-$ $E_0 = 0.687 - 0.0887\,pH + 0.0295\log(H_2AsO_4^-)$
28. $\mathbf{As_2O_3} + 5H_2O = 2HAsO_4^{--} + 8H^+ + 4e^-$ $E_0 = 0.901 - 0.1182\,pH + 0.0295\log(HAsO_4^{--})$
29. $\mathbf{As_2O_3} + 5H_2O = 2AsO_4^{---} + 10H^+ + 4e^-$ $E_0 = 1.270 - 0.1477\,pH + 0.0295\log(AsO_4^{---})$

## 2.4. ONE SOLID SUBSTANCE AND ONE GASEOUS SUBSTANCE

*Limits of the domains of relative stability of* **As** *and* $AsH_3$

$-3 \rightarrow 0$
30. $AsH_3 = \mathbf{As} + 3H^+ + 3e^-$ $E_0 = -0.608 - 0.0591\,pH - 0.0197\log p_{AsH_3}$

## 3. EQUILIBRIUM DIAGRAM AND ITS INTERPRETATION

### 3.1. ESTABLISHMENT OF THE DIAGRAM

Using formulae (1)–(30), we have constructed Fig. 1 (potential–pH equilibrium diagram for the system arsenic–water) and Fig. 2 (influence of pH on the solubility of arsenious anhydride).

These figures are valid only in the absence of substances with which arsenic can form soluble complexes or insoluble salts. According to Charlot [2], the tartrates, molybdates and tungstates form complexes with arsenic. The alkali metal arsenites and arsenates are very soluble; the other arsenites and arsenates are soluble only in acid solutions. We point out, in particular, the following two sparingly soluble arsenates: triargentic arsenate $Ag_3AsO_4$ (brick red), and magnesium ammonium arsenate $MgNH_4AsO_4$ (white), analogous to magnesium ammonium phosphate.

### 3.2. STABILITY OF ARSENIC

According to Fig. 1, elementary arsenic is a fairly noble element, as a considerable portion of its stability domain overlaps that of water. It is therefore an element which is stable in the presence of water and aqueous solutions of all pH's free from oxidizing agents.

Arsenic is not therefore affected by water free from air, and remains perfectly shiny in it; in aerated water arsenic is slowly attacked to give the very soluble arsenious anhydride $As_2O_3$; if a stream of air is passed through the water, the oxidation becomes fairly rapid [3].

When exposed to dry air arsenic is not oxidized at all, but on contact with moist air it undergoes a reaction at its surface and becomes covered with a black oxidation product, which can be removed by means of chlorine water or bleaching-water (oxidation to soluble arsenic acid $H_3AsO_4$).

At room temperature, dilute acids such as HCl, $HNO_3$, $H_2SO_4$ and $H_3PO_4$, when free from air, do not affect arsenic; on the other hand, it dissolves in concentrated hydrochloric acid, and hot concentrated sulphuric and nitric acids oxidize it to arsenic acid $H_3AsO_4$. According to Palit and Dhar, quoted by Gmelin [4], fairly dilute solutions of nitric acid (2 to 5 M) can attack arsenic at room temperature through the formation of nitrous acid $HNO_2$, which oxidizes arsenic to arsenious anhydride $As_2O_3$; the addition of reducing agents such as hydrazine $N_2H_4$ or sodium nitride $N_3Na$, which destroy the nitrous acid, prevents this attack; however, according to Millon [4], the capacity of nitric acid to react with arsenic is not increased by the presence of nitrous acid. Caustic soda solutions maintained in an atmosphere of inert gas react only slightly with arsenic; in the presence of air they oxidize arsenic to arsenite [4].

The nobility of arsenic is also confirmed by the fact that this element can be found in the natural state. It can be reduced to arsenic hydride in the presence of acid, neutral and alkaline aqueous solutions; depending on the circumstances, the reduction of arsenic can lead to the formation of arsine $AsH_3$, one of the solid hydrides $As_2H_2$ or $As_4H_2$, or more than one of these compounds simultaneously. $AsH_3$ can be obtained by the electrolysis of an acetic solution of sodium acetate using a platinum anode and an arsenic cathode; the electrolysis of aqueous solutions of HCl, $H_2SO_4$, $H_2CrO_4$, KOH and NaOH of various concentrations leads to the formation of arsine $AsH_3$ and diarsenic dihydride $As_2H_2$.

Depending on the pH and the concentration, arsenic can be oxidized to the "arsenyl" cation $AsO^+$, arsenious acid $HAsO_2$, arsenious anhydride $As_2O_3$ or arsenite $AsO_2^-$; further oxidation converts it into arsenic acid $H_3AsO_4$ or arsenates $H_2AsO_4^-$, $HAsO_4^{--}$, depending on the pH of the solution. Oxygen oxidizes arsenic to $As_2O_3$; oxidizing acids, such as concentrated sulphuric and nitric acids, and aqua regia, oxidize arsenic to arsenic acid $H_3AsO_4$; ozone, hydrogen peroxide, potassium permanganate, etc., convert arsenic to arsenates; perchloric acid, at a concentration of 60–70 per cent and at room temperature, oxidizes arsenic to the trivalent state, i.e. the anhydride $As_2O_3$; when heated, perchloric acid oxidizes it to the pentavalent state, i.e. arsenic acid.

Arsenic can be prepared either by the reduction of arsenites and arsenates, or by the limited oxidation of the arsenic hydrides; we give examples of these reactions in paragraphs 3.3, 3.4 and 3.5.

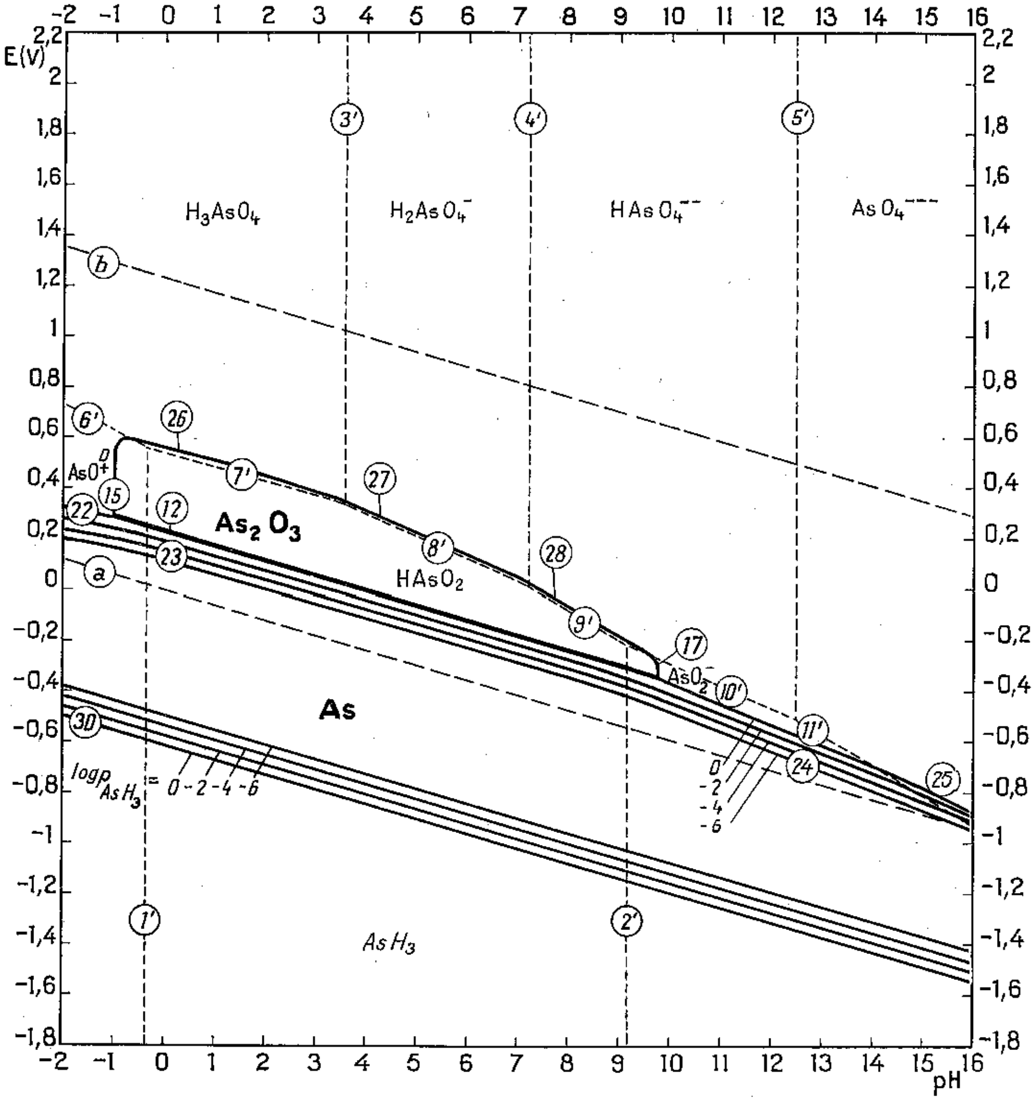


FIG. 1. Potential–pH equilibrium diagram for the system arsenic–water, at 25°C.

### 3.3. STABILITY OF ARSENIOUS ANHYDRIDE AND THE ARSENITES

Arsenious anhydride $As_2O_3$ is formed by the limited oxidation of arsenic by oxygen or perchloric acid, in the cold.

The position of its domain of stability in the equilibrium diagram (Fig. 1) shows it to be soluble, thermodynamically stable in the presence of water and acid, neutral and slightly alkaline solutions free from oxidizing agents.

According to Fig. 2, which represents the influence of pH on its solubility in solutions free from complexing substances [as given by formulae (15), (16) and (17)], $As_2O_3$ is an amphoteric oxide which dissolves in water and in solutions of pH between 1 and 8 with the formation of undissociated arsenious acid $HAsO_2$; the solubility is constant in this pH range and is equal to $10^{-0.68}$ g-at As/l (i.e. 0·21 g-at/l, or 21 g $As_2O_3$/l, which agrees with a result obtained by Anderson and Story [5]); it increases at pH's below 1 with the formation of "arsenyl" ions $AsO^+$, and at pH's above 8 with the formation of arsenite ions $AsO_2^-$.

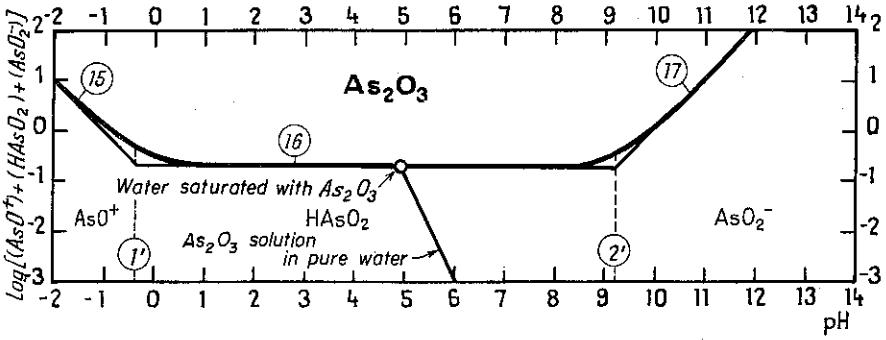


FIG. 2. Influence of pH on the solubility of arsenious anhydride, at 25°C.

It follows from Fig. 2 that, in solutions obtained by dissolving $As_2O_3$ in pure water of pH = 7, arsenic will exist mainly as undissociated $HAsO_2$, with a small proportion of $AsO_2^-$. This $AsO_2^-$ will be produced according to the reaction $As_2O_3 + H_2O \rightarrow 2AsO_2^- + 2H^+$, i.e. with the formation of equal amounts of $H^+$ and $AsO_2^-$ ions. As stated in an account published elsewhere ([6], pp. 19–27), the $AsO_2^-$ and $HAsO_2$ concentrations in $As_2O_3$ solutions will depend on the pH according to the relations

$$(AsO_2^-) = (H^+) - 10^{-7.00} \quad \text{and} \quad \log(HAsO_2) = \log(AsO_2^-) + 9.21 - \text{pH}.$$

These relations enable us to represent the pH's of $As_2O_3$ solutions of various concentrations by a line of slope −2, in Fig. 2.

The characteristics of the solution obtained by saturating pure water with $As_2O_3$ will be given by the point of intersection of this line of gradient −2 with the heavy line indicating the solubility of $As_2O_3$; the pH coordinate of this point is 5·0, a value which has been confirmed experimentally.

This pH can also be determined by calculation, taking into account the fact that the concentrations of $H^+$ and $AsO_2^-$ ions are practically equal, by putting $\log(AsO_2^-) = -\text{pH}$ in the relation $\log(AsO_2^-) = -9.89 + \text{pH}$ (17) referring to the equilibrium $As_2O_3/AsO_2^-$; the pH value so obtained is 4·94.

According to Fig. 1, $As_2O_3$ and arsenious solutions can be oxidized to arsenates and can be reduced to elementary arsenic and arsenic hydride.

The *oxidation of the arsenites* to arsenates is clearly irreversible: although theoretically possible as soon as the potential exceeds the values indicated by lines (6'), (7'), (8'), (9'), (10') and (11') in Fig. 1, it takes place in actual fact only at considerably higher potentials, and on condition that there is an appreciable overpotential: although the arsenates are the thermodynamically stable form of arsenic in the presence of oxygen, they can be obtained by the action of oxygen on arsenite solutions only in the presence of catalysts, such as the system iodine–iodide, for example, (Charlot [2]). In the absence of catalysts the oxidation of arsenites to arsenates requires a more powerful oxidizing agent, such as a halogen or one of its oxygen compounds, chromic acid, nitric acid, hydrogen peroxide or permanganate; this oxidation can also be brought about electrolytically, using a platinum anode.

The *reduction of the arsenites* to arsenic or arsenic hydride can be brought about chemically or electrolytically at potentials below those indicated by the family of lines (22)–(24) (for As) and the family of lines (30) (for $AsH_3$).

*Chemically:* stannous chloride $SnCl_2$ and hypophosphorous acid $H_3PO_2$ in hydrochloric solution reduce arsenious solutions to brown colloidal arsenic; under similar conditions, copper reduces these solutions to copper arsenide $Cu_3As_2$, which covers the metal with an iron grey coating. Metals which produce an evolution of "nascent hydrogen" at low electrode potentials, such as zinc in hydrochloric or sulphuric acid solution, reduce arsenious solutions with the formation of gaseous arsine $AsH_3$; this reaction is the basis of the classical process for the toxicological detection of arsenic in forensic medicine.

*Electrolytically:* arsenious solutions can be cathodically reduced, using a platinum or copper cathode, for instance. Depending on the nature of the solution, the metal used as the cathode, and the value of the current density, it is possible to obtain either arsenic alone (shiny, mat, spongy, adherent, non-adherent, etc.) or arsenic simultaneously with arsenic hydrides (mainly $AsH_3$ and $As_2H_2$).

### 3.4. STABILITY OF ARSENIC ANHYDRIDE AND THE ARSENATES

Arsenic anhydride $As_2O_5$ is the form of arsenic oxide which is thermodynamically stable in the presence of oxygen. It is very hygroscopic and very soluble in water to form arsenic acid $H_3AsO_4$ and arsenates $H_2AsO_4^-$, $HAsO_4^{--}$ and $AsO_4^{---}$; on account of its great solubility it does not appear in the equilibrium diagram (Fig. 1), which shows that arsenate solutions are thermodynamically stable in the absence of reducing agents.

The arsenates can be reduced to arsenites, to arsenic and to arsenic hydride; however, like the oxidation of arsenites to arsenates, the reduction of arsenates to arsenites is clearly irreversible: although theoretically possible as soon as the potential is below the values indicated by lines (6′), (7′), (8′), (9′), (10′) and (11′) of Fig. 1, the reaction takes place in general only at considerably lower potentials, with an appreciable overpotential: this reduction usually occurs at an appreciable rate only in very acid solutions; in alkaline solutions it is infinitely slow (Charlot [2]). Warm sulphurous acid leads to the formation of arsenious acid $HAsO_2$; hypophosphorous acid $H_3PO_2$ and stannous chloride form arsenic As; "nascent hydrogen" forms arsine $AsH_3$. The electrolytic reduction of the arsenates in acid solution is more difficult to bring about than that of the arsenites; depending on the operating conditions, it can lead to arsenic or arsine.

### 3.5. STABILITY OF ARSINE $AsH_3$

From Fig. 1 it can be seen that arsenic can be reduced to the gaseous trihydride of arsenic $AsH_3$ or arsine, at potentials below those indicated by the family of lines (30). As stated in paragraphs 3.2, 3.3 and 3.4, this reduction can be brought about chemically or electrolytically.

In view of the fact that its stability domain lies at very low potentials, arsine appears to be a reducing substance which is thermodynamically unstable.

Arsine is actually oxidized to arsenious acid by chloric acid $HClO_3$, and to arsenic acid or arsenates by the halogens, hot concentrated sulphuric acid, nitric acid, permanganate or ferrocyanide.

Although it tends thermodynamically to decompose into arsenic and hydrogen, arsine is practically stable in the presence of distilled water free from oxygen, at room temperature; aerated water causes the slow formation of a brown precipitate, which seems to be either arsenic or a solid lower hydride; according to Moser and Brukl [7], it is $As_2H_2$. When dry and pure, arsine can be kept for a long time without undergoing any change, but it readily decomposes on being warmed.

### 3.6. PASSIVATING ACTION OF ARSENIC COMPOUNDS

When iron or an ordinary steel corrodes in an acid, such as sulphuric acid, its electrode potential is generally around $-0{\cdot}2$ to $-0{\cdot}4$ volt. Under these conditions it is the elementary arsenic which is the stable form of system As–$H_2O$; the arsenious and arsenic compounds tend to be reduced by the iron with the formation of an arsenic cement.

It is well known that, other things being equal, the steel containers used for storing sulphuric acid are corroded less when they contain lead chamber acid than when the acid is prepared by the contact process. It is probable that this difference in behaviour is due to the fact that chamber acid contains arsenic compounds, which contact acid does not contain, and that these compounds form a deposit of arsenic on the steel which is partially protective and imperfectly passivates the metal.

### 3.7. ARSENIC ELECTRODES

Sometimes arsenic is used in measuring the pH of aqueous solutions and in potentiometric estimations.

The operation of the arsenic electrode in determining pH depends most probably on the equilibrium of the As/$As_2O_3$ system, whose electrode potential varies linearly with pH from 0 to 9, according to the relation:

$$E = 0{\cdot}234 - 0{\cdot}0591 \text{ pH} \qquad (12)$$

with the reservation, however, that the equilibrium solubility of the arsenic is very large (15 g As/l).

These deductions made from Fig. 1 correspond well with the results obtained by Tourky and Mousa [8], according to which, in the absence of air, the potential of an arsenic electrode (solid or powder) varies as indicated by relation (12) for pH's between 3 and 10.

The fact that arsenic can be used as an electrode for the measurement of pH makes possible its application on the potentiometric titration of bases and acids, especially the estimation of NaOH, HCl, $HNO_3$ and $H_2C_2O_4$ (Gmelin [4]).

## 4. BIBLIOGRAPHY

[1] J. VAN MUYLDER and M. POURBAIX, *Comportement électrochimique de l'arsenic. Diagramme d'équilibres tension*–pH *du système* As–$H_2O$, *à 25°C* (Rapport technique RT.46 of CEBELCOR, February 1957).

[2] G. CHARLOT, *Théorie et méthode nouvelles d'analyse qualitative,* 3rd ed., Masson, Paris, 1949, p. 214.

[3] P. PASCAL, *Traité de Chimie minérale*, Vol. III, Masson, Paris, 1932.

[4] *Gmelins Handbuch der anorganischen Chemie, Arsen,* S.N.17, 1952, Verlag Chemie, G.m.b.H., Weinheim, Bergstrasse.

[5] E. ANDERSON and LER. G. STORY, Studies on certain physical properties of $As_2O_3$ in water solution, *J. Amer. Chem. Soc.* **45**, 1102 (1923).

[6] M. POURBAIX, *Leçons sur la corrosion électrochimique*, 2ᵉ fascicule (Rapport technique RT.30 of CEBELCOR, 1956).

[7] L. MOSER and A. BRUKL, Zur Kenntnis der festen Arsenhydride, *Monatsh.* **45**, 25 (1924).

[8] A. R. TOURKY and A. A. MOUSA, Studies on some metal electrodes. Part VI. The arsenic electrode as a metal–metal oxide–oxygen electrode, *J. Chem. Soc.* II, 1297 (1949).