THERMODYNAMICS OF DILUTE AQUEOUS SOLUTIONS

With applications to
ELECTROCHEMISTRY AND CORROSION

BY

M. J. N. POURBAIX

AGRÉGÉ DE L'ENSEIGNEMENT SUPÉRIEUR
DOCTOR IN DE TECHNISCHE WETENSCHAP, DELFT
INGÉNIEUR CIVIL A.I.Br.

TRANSLATED BY
J. N. AGAR, M.A., Ph.D.

WITH A FOREWORD BY
U. R. EVANS, M.A., Sc.D., F.R.S.
READER IN THE SCIENCE OF METALLIC CORROSION,
UNIVERSITY OF CAMBRIDGE

LONDON
EDWARD ARNOLD & CO.

First published in 1949

Printed in Great Britain by Jarrold and Sons, Ltd., Norwich

FOREWORD

By Dr. U. R. Evans

(*Reader in the Science of Metallic Corrosion, Cambridge*)

During the last decade, Dr. Marcel Pourbaix of Brussels has developed a graphical method, based on generalized thermodynamical equations, for the solution of many different kinds of scientific problems, involving numerous types of heterogeneous or homogeneous reactions and equilibria. In particular, Dr. Pourbaix has applied his method to the discussion of the passage between the metallic and combined states, and to the changes commonly known as "corrosion reactions"—a somewhat unfortunate description which, by emphasizing the undoubted technical importance of the subject, has tended to obscure its scientific interest.

Some of these problems have long been treated from the aspect of thermodynamics; the thermodynamical discussion of electrode potentials, for instance, reached an advanced stage through the classical work of the schools of Nernst in Germany and of G. N. Lewis in America. The application of thermodynamics to typical corrosion reactions is a much newer development. Indeed, many of those working on the subject still hold that thermodynamics can here give little guidance, although the fruitful work of J. C. Warner at Pittsburgh, and that of Gatty and Spooner in this country, should have made evident how helpful the thermodynamical line of approach may be.

Dr. Pourbaix, however, has introduced a number of original features into his treatment of corrosion changes. By plotting the lines representing thermodynamical equations on paper, he has obtained diagrams embodying a vast amount of pertinent information in a small space. In particular, the diagrams in which equilibrium potential is plotted against pH show domains representing "corrosion", "*passivité*" and "passivation" respectively. The first represents those conditions where metal suffers attack. The domain of *passivité* (which includes what in this country is called "cathodic protection") represents conditions where the potential is depressed too far for passage into the combined state, so that corrosion is avoided. The domain of passivation, on the other hand, represents those conditions of elevated potential where the metal escapes attack, usually through the formation of some film which isolates it from the liquid.

The recognition accorded in the diagrams to the domain of passivation really answers the objection so often raised against the thermodynamic treatment of corrosion problems, by those who point out that many hypothetical corrosion reactions, which should be possible in the sense that they involve a considerable diminution of free energy, do not in practice occur, because the attack stifles itself by the formation of an obstructive film. Since, however, it is possible to distinguish graphically the conditions under which solid films can exist from those under which their appearance is impossible, both types of immunity can receive due recognition on the diagrams, and the anomaly is removed.

It might, on the other hand, be objected that in several cases where the reaction between metal and solution would lead to a solid substance at the interface, no continuous protective film is in practice formed, so that the reaction is not—in point of fact—stifled. For instance, when the nucleation number governing the formation of the solid substance is low, we may expect, instead of a continuous protective film consisting of a vast number of little crystals, a few isolated crystals or an open interlacing network, which can hardly be protective. Interesting examples of the formation of solid films at an interface, which are not always protective, are found in the extensive work of Feitknecht at Bern, who has studied the various forms of the oxides, hydroxides or basic salts produced on corroding zinc specimens. Of the numerous forms of hydroxide, some are more protective than others, and it is noteworthy that under some conditions, the most stable (i.e. the least soluble) form does not appear at all; possibly its nucleation rate is too low. Crystal-habit is also of importance; Feitknecht finds that the ε-hydroxide, when it occurs, assumes a flaky form, and attributes thereto its protective properties. It is fairly certain that a full treatment of passivity from the thermodynamical standpoint will have to include considerations of nucleation rate and crystal-habit. But this, far from limiting the importance of energy considerations, makes it increasingly desirable to utilize them to the full; in crystallography and metallurgy, the theoretical treatment of nucleation from the standpoint of energy increment is already making progress, and the distinction between films capable of passivation and those which are incapable may well receive thermodynamical discussion in the near future.

Another objection raised against a thermodynamical treatment of corrosion is that the corrosion student is more concerned with reaction velocity than equilibrium. A velocity, however, can be represented in terms of a driving force and a resistance. In many reactions, e.g. the oxidation of metals, the driving force can be expressed in volts as an E.M.F., whilst the resistance can be represented in ohms, being the electrical resistance opposing the transport of ions and electrons through the oxide film. The work of Wagner at Darmstadt on this subject is of the greatest importance. Now the derivation of the expression for the E.M.F. is essentially thermodynamical, whilst the conductivity of the film substance depends on the presence of lattice defects, the number and mobility of which is also obtained by statistical methods which—even if not universally regarded as appertaining to thermodynamics—are closely related to that subject. The modern treatment of reaction velocities, developed by Eyring and others, makes extensive use of thermodynamical concepts. It would be an over-simplification of the position to suggest that no other considerations need be taken into account; but it is surely correct to claim that even for those who are interested solely in reaction velocity, thermodynamic considerations are helpful, and probably essential, to understanding.

If this is true, the great value of Dr. Pourbaix's method of treatment becomes evident, since it offers a common elucidation of numerous problems which are to-day regarded as quite distinct, and concentrates a vast mass of pertinent data in diagrams which, to those who have gained familiarity with his system, are remarkably simple. Students sometimes regard thermodynamical treatment as something complicated and formidable, and possibly the methods of exposition adopted to-day in some quarters may justify repugnance to the subject. But Dr. Pourbaix, in an admirable lecture which he delivered at Cambridge on 23 April 1946, emphasized, not the complexity, but rather the simplicity of thermodynamical treatment, which offers a unified method for the discussion of so many diverse problems.

This lecture was the first occasion on which Dr. Pourbaix's views were explained to a British audience, although they had long been known in Belgium and the neighbouring countries. The writer first made Dr. Pourbaix's acquaintance at a congress in Paris a few years before the war, and friendly correspondence was already passing between Brussels and Cambridge when, in 1939, the blow fell which put an end to discussions on pure science almost everywhere, and particularly between those working on different sides of the Channel. When peace was restored, arrangements were soon made for Dr. Pourbaix to visit Great Britain, and his visits to British laboratories where corrosion research was in progress have already established his reputation as a scientist, besides leading to the formation of links of personal friendship. It had already become obvious, however, that a translation of Dr. Pourbaix's writings into the English language was a matter of urgency. Dr. J. N. Agar, whose experience of electrochemical reactions involving metals particularly fits him for the task, has kindly undertaken to prepare an English version of Dr. Pourbaix's *Thermodynamique des Solutions Aqueuses Diluées*, originally presented as a thesis at Delft, where the author was awarded his doctorate.

Dr. Pourbaix, who is of Belgian nationality, has already formed contacts with many countries. After having studied in the University of Brussels, he worked in the Research Department of the Union

Chimique Belge, in close touch with Dr. J. Guillissen, who helped him with information regarding industrial problems and encouraged his study of applied thermodynamics. In 1934, Dr. Pourbaix returned to Brussels University, as assistant to Professor Dony and Professor Erculisse, and several times visited Delft, where he received much encouragement from Professor Scheffer, in whose laboratory the idea of the present book came to him. In 1937 he travelled in France and discussed the use of thermodynamics in the study of corrosion problems with Professor Chaudron, whose experimental work on corrosion is well known in Great Britain.

In his introductory note, after acknowledging the close collaboration with Professor Scheffer and Professor Burgers of Delft, Dr. Pourbaix expresses his thanks to Professor Chaudron, to Professor De Donder of Brussels, whose distinguished thermodynamical studies have provided a sound theoretical basis on which Dr. Pourbaix has built his original treatment of the problem under discussion, as well as to other eminent Belgian scientists, including Professors Erculisse and Flamache. It is likely that the Research Group at the Université Libre de Bruxelles, which Dr. Pourbaix is now organizing, will come to be one of the world's centres for the experimental and theoretical development of the numerous subjects on which he is working; its development will be watched with sympathy and interest by Dr. Pourbaix's friends in many different countries.

U. R. Evans

Cambridge University

PREFACE

In this monograph a general method is developed for the calculation of equilibrium conditions in reactions in dilute aqueous solutions; methods whereby such equilibria can be represented graphically are also explained, and examples of their application are given.

The method employed to calculate equilibrium conditions is based on the ideas of "chemical potential" and "affinity", and conveniently summarizes the majority of the laws of chemical and electrochemical equilibrium.* This approach shows the importance of "potential" in chemical and electrochemical oxidation-reduction processes, a fact which Haber[46, 47] emphasized as long ago as 1898 in connexion with certain electrochemical reactions. The usual notions of "equilibrium potential" and "overpotential" may, in fact, be generalised (pp. 30 and 44), and provide a useful criterion relating the direction of all types of electrochemical reactions to the sign of their overpotential (p. 45). It is thus possible to predict the conditions under which such reactions are energetically possible or impossible.

Some of the methods of graphical representation subsequently developed are well known, or are closely related to known methods—in particular, to those worked out by Michaelis[83] (1922) and by Huybrechts[58] (1932). Michaelis gives curves showing the effect of pH on dissociation, which suggested the layout of our fig. 1*b*, while Huybrechts developed a diagram rather similar to fig. 7 to demonstrate the relations between pH, redox potential, rO and rH. Logarithmic scales are widely used in these graphs; they make the diagrams simpler, but demand some effort on the part of readers not accustomed to them. The idea of "domains of thermodynamic stability", introduced on p. 40, helps to clarify and simplify the complicated equilibria that so frequently arise in practice.

Finally, some applications of the theoretical principles and of the graphical representation are discussed. I have tried to show that the absolutely general thermodynamic treatment of phenomena has important practical applications, especially in electrochemistry. It is frequently possible to understand, and, indeed, to predict, experimental results by bearing in mind the fundamental principle that any transformation is impossible except when it tends to the realization of a state of thermodynamic equilibrium. Several examples are given in the discussion of derivatives of copper (pp. 61 ff.), iron (pp. 87 ff.) and nitrogen (pp. 112 ff.). In the discussion of copper and iron the thermodynamical theory underlying corrosion processes, immunity and

---

* More or less similar treatments have been given by Wohl,[128] Jolibois[59] and others.

passivation is developed (pp. 47–51, 78–80, 90–96); it is closely related to several well-known theories of corrosion and passivation, arising mainly from the work of Nernst, Palmaer,[91] U. R. Evans,[32] E. Müller[85] and W. J. Müller.[88] In many cases it shows the conditions under which the various theories are applicable, and indicates the experimental techniques that should prove most fruitful.

In the course of the book it becomes clear how important it is to measure both pH and potential in the study of chemical and electrochemical oxidation-reduction phenomena in general; this point can hardly be emphasized too much. Many research workers have, of course, already realized this, and have made their experiments accordingly—in particular Clark[13] (studies of redox indicators and other substances), Michaelis[84] and Wurmser[129, 130] (biochemical systems). A similar point of view has been adopted in corrosion experiments (see p. 52) by several authors, and by Travers[119] and his school (Colombier[15] and Thiesse[116]) in the investigation of passivation and inorganic redox systems. The last-mentioned have empirically established a "theory of characteristic areas", with the object of predicting the possible reactions. The work of Déribéré[21] on industrial applications may also be mentioned.

The field covered by this book—the study of reactions in aqueous solutions—is wide and complex, with ramifications extending into many branches of science. There are thus many points of contact with the work of others, both on the theoretical and on the experimental side. A fairly extensive list of references is given, but I realize that it is far from complete. There is much published work with which I am unaquainted, and during the war I was able to consult only the Dutch, French and Belgian publications. I shall be grateful if readers will indicate omissions in this connexion.

The most important parts of the book were communicated in two lectures, on 11 June 1938 and 19 October 1938, under the auspices of the Association des Ingénieurs sortis de l'École Polytechnique de Bruxelles (A.I.Br.) and of the Société Chimique de Belgique. A short summary of these lectures was published in November 1938.[96] The applications to corrosion first appeared in a paper presented at the *Journées de la Lutte contre la Corrosion* at Paris in November 1938.[97, 98] Publication has been greatly retarded by the war; the work was written in 1939 and revised in 1943, in close collaboration with Professors F. E. C. Scheffer and W. G. Burgers, of the Technical High School at Delft. I am especially glad to have this opportunity of acknowledging my debt to them for their encouragement, advice and constructive criticism on many occasions. Since the appearance of the first (French) edition of this work, some further developments have been published in several recent papers.[131, 137]

A point of view rather close to that expressed in part of the present book is contained in three papers on the thermodynamics of electrodes by Lange and Nagel[67, 68, 69] (November 1938); their work is to some extent parallel to mine, but is quite independent of it. An important paper by Wagner and Traud,[125] dealing with the use of polarization curves in the study of corrosion phenomena, has been of great assistance. I have also been aided by helpful discussions or criticisms; for these, I am especially indebted to Professor G. Chaudron, of the University of Paris (on corrosion), to Professor Th. De Donder of the Université Libre de Bruxelles (theoretical basis); to Professor P. Erculisse, also of the Université Libre de Bruxelles (classification of reactions and role of pH in analytical chemistry); to M. L. Flamache, Maître de Conférences de l'Université Libre de Bruxelles (methods of graphical presentation) and to M. J. Guillissen, Directeur des Services de Recherches de l'Union Chimique Belge. The responsibility for the opinions expressed, however, rests on me alone. I would also thank M. L. Braekman, my collaborator at the Université Libre de Bruxelles, for his loyal and constant help.

TRANSLATOR'S NOTE

The translation is based on the second impression of Dr. Pourbaix's book, published in 1946. No major alterations have been made in the text.

The terms "*passif*" and "*passivité*", which have come to have a meaning somewhat different from the English "passive" and "passivity", have, after discussion with Dr. U. R. Evans, been translated as "immune" and "immunity".

CONTENTS

CHAPTER IV

POTENTIAL-pH DIAGRAMS

Figs. 9–27 refer to certain chemical systems in which the independent components are the constituents of water (H and O) and a third substance of simple type; the majority of them refer to equilibria between the various condensed (i.e. solid or liquid) derivatives of this third substance, and between the various solutes derived from it. Some of the remaining diagrams show the conditions under which the solutes are in equilibrium with certain condensed or gaseous phases. In this chapter the construction, properties and uses of these diagrams will be described in detail.

A. ACID AND ALKALINE, AND OXIDIZING AND REDUCING MEDIA

Just as a solution can be considered acid or alkaline according as its pH is below or above 7, so it can be considered oxidizing or reducing according as its rH is above or below 27·6. In fact, water may be split up into its acid and basic components, H^+ and OH^-, or into its oxidized and reduced components, O_2 and H_2

$$H_2O = H^+ + OH^-,$$

and

$$2H_2O = 2H_2 + O_2.$$

The equilibrium conditions at 25°C. are respectively

$$(H^+)(OH^-) = 10^{-14{\cdot}0},$$

and $$(p_{H_2})^2(p_{O_2}) = 10^{-82{\cdot}99} \quad \text{or} \quad 2\text{rH} + \text{rO} = 82{\cdot}99.^*$$

---

* The standard chemical potentials of H_2, O_2 and gaseous H_2O are

$$\mu^0_{H_2} = 0; \quad \mu^0_{O_2} = 0; \quad \mu^0_{H_2O\,(g.)} = -\ 54{,}510 \text{ cal.};$$

and we thus obtain the dissociation constant of water vapour, $2H_2O = 2H_2 + O_2$, at 25° C. from equation [6], which here leads to the usual mass-action constant:

$$\log \frac{(p_{H_2})^2\, p_{O_2}}{(p_{H_2O})^2} = -\ \frac{2\mu^0_{H_2} + \mu^0_{O_2} - 2\mu^0_{H_2O}}{1363} = -\ 79{\cdot}977.$$

But at 25°C. the pressure of water vapour in presence of pure liquid water, or of a very dilute aqueous solution, is 23·756 mm. Hg, i.e. 0·0313 atm.; hence,

$$\log p_{H_2O} = -\ 1{\cdot}505.$$

For water vapour at this pressure, the above equilibrium condition becomes

$$\log\,[(p_{H_2})^2(p_{O_2})] = -\ 79{\cdot}977 + 2 \log p_{H_2O} = -\ 82{\cdot}987.$$

Huybrechts[58] has discussed three conventions which have been proposed in connexion with the idea of neutrality as regards oxidation. The first of these conventions assumes that neutrality exists when the pressure of hydrogen is equal to the pressure of oxygen (rH = rO). The second convention, which we have adopted here, assumes that neutrality exists when the pressure of hydrogen is double the pressure of oxygen (rH = rO − 0·30). The third convention defines as neutral those solutions in which rH is equal to half the rH corresponding to a reversible oxygen electrode working at an oxygen pressure of 1 atm. Huybrechts has calculated the rH's corresponding to these three hypotheses, and finds respectively 27·3, 27·2 and 20·5. The difference between Huybrechts's value 27·2 and our value 27·56 is the result of slight differences in the values used for the standard potential of the oxygen electrode and for the coefficients of the terms log p_{H_2} and log p_{O_2} in the formulae giving the electrode potentials.

A solution may be said to be neutral as regards acidity or as regards oxidation when the concentrations (activities) or pressures (fugacities) of the substances into which the water splits up have values that correspond stoichiometrically to the decomposition of H_2O; the neutrality conditions are thus:

for acidity: $(H^+) = (OH^-)$,
corresponding to $\text{pH} = 7{\cdot}0$;
for oxidation: $p_{H_2} = 2p_{O_2}$,
or $\text{rH} = \text{rO} - 0{\cdot}30$,
which is equivalent to $\text{rH} = 27{\cdot}56$,
$\text{rO} = 27{\cdot}86$.

According to the above convention the conditions of "absolute" neutrality in an aqueous solution at 25°C. are thus substantially

$$\text{pH} = 7{\cdot}0, \qquad \text{rH} = 27{\cdot}6,$$

which corresponds to a potential $E = +\ 0{\cdot}40$ V.

Four regions may thus be distinguished in fig. 8*a*:

top left:	oxidizing and acid media,
bottom left:	reducing and acid media,
top right:	oxidizing and alkaline media,
bottom right:	reducing and alkaline media.

B. CONDITIONS OF THERMODYNAMIC EQUILIBRIUM IN COMPLEX SYSTEMS

The potential and pH of any medium may be represented by a point on a potential-pH diagram, and the thermodynamic equilibria of all the reactions in which the various constituents present can take part may be determined by projecting this point on to appropriate scales, or by noting the "levels" of reference lines that pass through it.

EXAMPLE. Consider a solution of $CuSO_4$ at pH 2, in which a metal is immersed, having a potential of $+\,0{\cdot}286$ V. with respect to the standard hydrogen electrode. Assuming that the system is in thermodynamic equilibrium the solution has the following characteristics:

$$\mathrm{pH} = 2{\cdot}0,$$

$$E = +\,0{\cdot}286\ \mathrm{V.},$$

$$\log \frac{(\mathrm{Cu^{++}})}{(\mathrm{Cu^{+}})} = 2{\cdot}0 \text{ (equilibrium } \mathrm{Cu^{++}} + e^- = \mathrm{Cu^+}\text{, see fig. 4}a\text{)},$$

$$\mathrm{rH} = 13{\cdot}5 \text{ (equilibrium } 2\mathrm{H^+} + 2e^- = \mathrm{H_2}\text{, see fig. 7)},$$

$$\mathrm{rO} = 56{\cdot}0 \text{ (equilibrium } \mathrm{O_2} + 4\mathrm{H^+} + e^- = 2\mathrm{H_2O}\text{; this value}$$

is given by $2\mathrm{rH} + \mathrm{rO} = 83{\cdot}0$).

When the metal under consideration is copper, a state of equilibrium requires in addition a certain concentration of cupric ions, determined by the equilibrium

$$\mathrm{Cu^{++}} + 2e^- = \mathrm{Cu},$$

which gives $\log (\mathrm{Cu^{++}}) = -\,2{\cdot}00$ (i.e. 0·63 g. $\mathrm{Cu^{++}}$ per litre; see fig. 5). In consequence, an ideal solution of pH 2·0 in equilibrium with metallic copper at $+0{\cdot}286$ V. will contain 0·63 g. per litre copper as cupric ions and 0·0063 g. per litre as cuprous ions; its rH will be 13·5 and its rO, 56·0.

C. DOMAINS OF THERMODYNAMIC STABILITY

Any solid, liquid, gaseous or dissolved substance, having a definite chemical potential, is thermodynamically stable in presence of an aqueous solution only under conditions of potential and pH corresponding to certain definite domains in the potential-pH diagram. The limits of the domains depend on the concentrations (activities) and pressures (fugacities) of the substances present.

EXAMPLE:

(1) According to fig. 7, water under a pressure of 1 atm. is stable only in the domain lying between the lines rH = 0 and rO = 0. Outside this domain water tends to decompose with liberation of hydrogen or oxygen.

(2) Fig. 10 (p. 58) shows the conditions under which copper and its oxides are thermodynamically stable in presence of an aqueous copper solution; there are three domains, in each of which a certain solid (indicated in the figure) can exist in equilibrium with the solution. The domains are separated from one another by lines; points on these lines represent conditions under which two solids can coexist in equilibrium with the solution.

(3) In fig. 9 (p. 57) there are four domains, separated from one another by thick lines; these are "predominance domains". Within each of them the greater part of the dissolved copper exists in one and the same ionic form, as indicated in the diagram. The lines separating these domains show the conditions under which the concentrations of two ionic species are equal to one another.

For certain solids, and particularly for metallic oxides and hydroxides, the conditions of stability may depend markedly on factors such as mode of formation, state of division, age, etc. Thus, hydrated aluminium oxide becomes less soluble as it "ages", and the hydrated iron oxide formed in electrochemical passivation of iron is less soluble than that obtained by precipitating ferric chloride solution with ammonia. In such cases there is no rigid and fixed "domain of stability", but rather an "elastic" domain, the limits of which are more or less mobile and become further separated from one another if the oxide becomes more stable (i.e. if its chemical potential diminishes). In the case of substances which can exist in several distinct forms of different stabilities there exists a definite domain of stability for each form, and this domain expands or contracts in all directions as the chemical potential of the form diminishes or increases.

D. SCALES USED IN THE DIAGRAMS

In the diagrams we frequently make use of subsidiary scales showing the concentrations of the various substances present in solution; as an example, we have drawn several scales in fig. 9 giving the ratios of the concentrations of two ions in the solution. It will be seen that it is only in the immediate neighbourhood of the five lines shown that a solution contains two ionic species in comparable amounts; within each domain the amount of other ions is generally negligible in comparison with that which prevails in the domain as a whole. It follows that the concentration scales need occupy only a small part of the diagrams.

CHAPTER V

UTILITY OF POTENTIAL AND pH

Before dealing with various examples of binary and ternary systems in greater detail, we would emphasize the usefulness of the graphical method not only in the study of equilibria, but also in the study of the possibility of chemical or electrochemical changes under arbitrarily chosen conditions. With this object, we now discuss some general thermodynamic propositions relating to potential and pH.

A. CHARACTERISTICS OF MEDIA IN THERMODYNAMIC EQUILIBRIUM

1. Potentials of Conductors in Equilibrium with a Solution

If a conducting substance is in thermodynamic equilibrium with a solution containing an oxidizing or a reducing agent, its potential is equal to the redox potential of the solution;

and conversely:

If a conducting substance has a potential equal to the redox potential of the solution in which it is immersed, the substance is in thermodynamic equilibrium with the solutions; hence no reaction can take place at its surface.

It follows, in particular, that any conductor that does not react with a solution containing an oxidizing and a reducing agent in equilibrium can be used to measure the redox potential of the solution.

EXAMPLE. If electrodes of Pt, Au and Ag, which do not react with the solution, are immersed in an acidified and de-aerated solution of cupric and cuprous sulphates, the three electrodes take up the same potential, i.e. the redox potential.

If a copper electrode, which can react with cupric ions to form cuprous ions in accordance with the equation $Cu + Cu^{++} \leftrightharpoons 2Cu^+$, is also immersed in this solution, it is found that its potential differs from that common to the former three electrodes. If dissolution of copper is allowed to proceed until a state of equilibrium is realized, the two potentials progressively approach one another and finally become steady at identical values.[137]

2. Potentials of Conductors in Equilibrium with any System of Reactants

The preceding principle, which refers particularly to oxidizing and reducing agents which are both in solution (e.g. Cu^+ and Cu^{++} ions),

remains valid when the oxidizing or reducing agent is in a different state (gaseous, solid, liquid); it can be generalized as follows:

If a conductor is in equilibrium with any electrochemical system of reactants, its potential is equal to the equilibrium potential of this system;

and conversely:

If a conductor has a potential equal to the equilibrium potential of a given electrochemical system of reactants, the conductor is in thermodynamic equilibrium with the system; no reaction between the constituents of the system can occur at the surface of the conductor.

EXAMPLE. Wagner and Traud[125] have recently shown that the reducing action of hydrogen on various oxidizing agents in presence of platinized platinum is suppressed if the potential of the platinized platinum is artificially kept at a value equal to the equilibrium potential of the reaction

$$H_2 = 2H^+ + 2e^-.$$

For this purpose, Wagner and Traud immersed a platinized platinum electrode in a solution of fixed H^+ ion concentration (0·5 M. Na_2SO_4 + 0·1 M. HCl, i.e. a HSO_4^-/SO_4^{--} buffer); the solution was saturated with hydrogen at 25° C. and the equilibrium potential of the hydrogen electrode determined. An oxidizing agent (persulphate, nitrobenzene or As_2O_5) was then added to the solution. Hydrogen was used up by reaction with the oxidizing agent, catalyzed by the platinized platinum; at the same time, the potential of the platinized platinum electrode was observed to rise, in conformity with the thermodynamic principle stated on p. 45, i.e. electro-chemical oxidation of hydrogen, $H_2 \rightarrow 2H^+ + e^-$, is only possible at an electrode having a potential higher than the equilibrium potential of the reaction.

Wagner and Traud then lowered the potential of the hydrogen electrode by cathodic polarization, using an external source of current and an auxiliary anode, and thus superposed a second reducing action of an electrolytic nature on the reducing action of hydrogen. They found that the progressive lowering of the cathode potential, although it necessarily involved an increase in the total quantity of oxidizing agent reduced, decreased the amount of reduction due to hydrogen; the consumption of hydrogen diminished as the cathode potential was lowered, and became zero when the potential attained the value which it had at the beginning of the experiment, when no oxidizing agent was present and when the potential was that of a reversible hydrogen electrode. This result is in agreement with the thermodynamical principle under discussion, i.e. it is impossible for the reaction $H_2 \rightarrow 2H^+ + 2e^-$ or $2H^+ + 2e^- \rightarrow H_2$ to take place at any electrode with a potential equal to the equilibrium potential of the reaction $H_2 = 2H^+ + 2e^-$.

It follows from the above principle that every elementary redox reaction, homogeneous or heterogeneous, has a corresponding equilibrium potential which depends only on the chemical potentials μ^0 of the reactants, i.e. on temperature, concentration (activity) of dissolved reactants and, where applicable, pressure (fugacity) of gaseous reactants. At this potential, the reaction has zero electrochemical affinity, and is therefore thermodynamically impossible.

EXAMPLE:

(1) For the reaction

$$H_2 = 2H^+ + 2e^- \text{ (or } 2H^+ - H_2 + 2e^- = 0)$$

the equilibrium potential at 25°C. is

$$E = -\,0{\cdot}0591\text{pH} - 0{\cdot}0295 \log p_{H_2} \text{ V.,}$$

e.g. for pH = 4 and $pH_2 = 1$ atm., $E = -\,0{\cdot}24$ V.

(2) For the reaction

$$Fe = Fe^{++} + 2e^- \text{ (or } Fe^{++} - Fe + 2e^- = 0)$$

the equilibrium potential at 25°C. is

$$E = -\,0{\cdot}44 + 0{\cdot}0295 \log (Fe^{++}) \text{ V.,}$$

e.g. for $(Fe^{++}) = 10^{-2}$ M., $E = -\,0{\cdot}50$ V.

It follows that

(1) In presence of hydrogen at 1 atm. and in a solution of pH 4, the change $H_2 = 2H^+ + 2e^-$ cannot take place in either direction at an electrode having a potential of $-0{\cdot}24$ V.

(2) In a solution containing 0·56 g. Fe^{++} per litre, for which $(Fe^{++}) = 10^{-2}$ M., the change $Fe = Fe^{++} + 2e^-$ cannot take place in either direction at an electrode having a potential of $-0{\cdot}50$ V.

B. CHARACTERISTICS OF REACTING MEDIA

1. Electrochemical Affinity—Overpotential

If the substances taking part in an electrochemical reaction are in contact with an electrode whose potential, E',* differs from the equilibrium potential E, the electrochemical affinity is no longer zero and has the value

$$\bar{A} = -\sum_\gamma \nu_\gamma \mu_\gamma + 23{,}060nE' \quad \text{(cal.).}$$

Since the equilibrium potential E is defined by the relation

$$-\sum_\gamma \nu_\gamma \mu_\gamma + 23{,}060nE = 0, \qquad \ldots [2]$$

the electrochemical affinity thus becomes

$$\bar{A} = 23{,}060n(E' - E) \quad \text{(cal.),}$$

or

$$\bar{A} = n(E' - E) \quad \text{(V.).}$$

---

* The "reaction" potential E' is the potential of a metallic surface on which the reaction under consideration takes place; like the "equilibrium" potential E, it is measured with reference to a standard hydrogen electrode. Measurement of the reaction potential is more difficult than that of the equilibrium potential, because it is necessary (as Haber pointed out as long ago as 1900[47]) for the connecting tube from the reference electrode to open into the reacting solution in the *immediate* neighbourhood of the surface under examination. In collaboration with H. Luggin, Haber developed the use of a capillary connexion, which has since become common practice.

The electrochemical affinity of a reaction can thus be measured by the difference between the "reaction" potential E' and the "equilibrium" potential E,[136] when both potentials refer to the same values of the chemical potentials of the reactants i.e. to the same temperature, the same concentratio nof dissolved reactants and, where applicable, to the same pressure of gaseous reactants. It amounts in general to $n(E'—E)$ volt-faradays per g. mol. for a change involving n faradays.

We shall use the term "overpotential" to denote the difference $\Delta E = E' - E$; overpotential (which is here defined as an electrochemical affinity) provides a measure of the irreversibility of the reaction under consideration and is a generalization of the more usual notion of overpotential (see, e.g. Meunier[80]).

EXAMPLE:

(1) If a metallic electrode in a solution of pH 4 and in contact with hydrogen at 1 atm. has a potential of $-0{\cdot}42$ V., the reaction $H_2 = 2H^+ + 2e^-$ (equilibrium potential $-0{\cdot}24$ V.) has an overpotential of $-0{\cdot}42 + 0{\cdot}24 = -0{\cdot}18$ V. at the surface of the electrode. The affinity of the reaction is $-0{\cdot}18$ volt-faradays per g.-ion of hydrogen.

(2) If an iron electrode in a solution containing 10^{-2} g.-ions Fe^{++} per litre has a potential of $-0{\cdot}42$ V., the reaction $Fe = Fe^{++} + 2e^-$ (equilibrium potential $-0{\cdot}50$ V.) has an overpotential of $-0{\cdot}42 + 0{\cdot}50 = +\,0{\cdot}08$ V. The affinity of this reaction is $+\,0{\cdot}08 \times 2 = +0{\cdot}16$ volt-faradays per g.-atom of iron.

(3) If a platinum electrode in a solution of pH = 0 containing permanganate and manganous ions in equal quantities has a potential of $+\,1{\cdot}00$ V.l the reaction $Mn^{++} + 4H_2O = MnO_4^- + 8H^+ + 5e^-$ (equilibrium potentia, $+\,1{\cdot}52$ V.) has an overpotential of $1{\cdot}00 - 1{\cdot}52 = -\,0{\cdot}52$ V. The affinity of the reaction is $-0{\cdot}52 \times 5 = -\,2{\cdot}60$ volt-faradays per g.-ion of permanganate.

2. Direction of Oxidation and Reduction Reactions

Consider an electrochemical reaction,

$$\sum_\gamma \nu_\gamma M_\gamma + ne^- = 0 \qquad \ldots [1]$$

(e.g. $-\,H_2 + 2H^+ + 2e^- = 0$). It can readily be shown* that the direction of a reaction is related to the sign of the overpotential in the following way:

Oxidation takes place if the reaction potential is higher than the equilibrium potential (i.e. if the overpotential is positive);

Reduction takes place if the reaction potential is lower than the equilibrium potential (i.e. if the overpotential is negative);

and conversely:

In an oxidation, the reaction potential is higher than the equilibrium potential; in a reduction, it is lower.

---

* De Donder's concept of the "driving force" of a reacting system[19,20] leads to the required result.

When the reaction potential E' and the equilibrium potential E of a given reaction are known, its direction may thus be predicted. This enables us to state the conditions under which a given oxidation or reduction reaction is possible, which is sometimes useful when considering possible reaction mechanisms for a given overall transformation.*

EXAMPLE:

(1) If a metallic electrode, in a solution of pH 4 and in contact with gaseous hydrogen at 1 atm. pressure, has a potential of $-0{\cdot}42$ V., the reaction $H_2 = 2H^+ + 2e^-$ (equilibrium potential $-0{\cdot}24$ V.) has a negative overpotential ($-0{\cdot}18$ V.) and can only take place in the reduction direction, i.e.

$$2H^+ + 2e^- \rightarrow H_2.$$

(2) If an iron electrode in a solution containing 10^{-2} g.-ion Fe^{++} per litre has a potential of $-0{\cdot}42$ V., the reaction $Fe = Fe^{++} + 2e^-$ (equilibrium potential $-0{\cdot}50$ V.) has a positive overpotential ($+0{\cdot}08$ V.) and can only occur in the oxidation direction, i.e.

$$Fe \rightarrow Fe^{++} + 2e^-.$$

(3) If an iron electrode in a solution of pH 4 containing 10^{-2} g.-ion Fe^{++} per litre is in contact with gaseous hydrogen at 1 atm., the directions of the two reactions that can occur at this electrode,

$$H_2 = 2H^+ + 2e^- \qquad \text{and} \qquad Fe = Fe^{++} + 2e^-,$$

depend on the values of the electrode potential relative to the two equilibrium potentials ($-0{\cdot}24$ and $-0{\cdot}50$ V.).

If $E' > -0{\cdot}24$ V.,

we have $H_2 \rightarrow 2H^+ + 2e^-$

and $Fe \rightarrow Fe^{++} + 2e^-$,

which can be realized experimentally by using an iron electrode as anode at a sufficiently high potential, and bubbling a stream of hydrogen around the electrode. Both hydrogen and iron are oxidized, the pH of the solution falls and iron is dissolved; the current required is equal to the sum of the separate reaction currents (both counted positive).

If $-0{\cdot}24 > E' > -0{\cdot}50$ V.,

we have $2H^+ + 2e^- \rightarrow H_2$

and $Fe \rightarrow Fe^{++} + 2e^-$,

---

* In his investigation of the reduction of nitrobenzene, Haber[46] emphasized the fact that "the phenomena of electrochemical oxidation and reduction depend, in the first instance, on the potential of the electrode at which they take place", and expressed the view that "current density, duration of current flow and the nature of the electrode material have no effect except in so far as they determine the electrode potential and its changes during the electrolysis".

Later, in a controversy with Löb, Haber states[47] that "it is the potential that matters; the current density is only a means of controlling this potential—a means whose efficacy, from this point of view, is limited by the concentration of depolarizer in solution, by the properties of the electrode material and by additions of acid or alkali".

The importance of the reaction potential E', which seems to have been first recognized by Haber, arises from the fact that the difference $(E' - E)$ between a reaction potential and the various equilibrium potentials relating to the reactions under consideration, determines the possibility, and, in large measure, the velocity of these reactions; whatever the factor may be which brings about a fall of E' at a cathode (current density, duration of current flow, nature of electrode), this cathode will have greater reducing power as the potential becomes lower.

which occurs in practice in the corrosion of iron by acids. H^+ ions are reduced and iron is oxidized, with liberation of hydrogen, increase of pH of the solution and dissolution of iron. The *current* is positive, zero or negative according as the oxidation occurs at a rate greater than, equal to or less than that of the reduction.

If $E' < 0{\cdot}50$ V.,

we have $2H^+ + 2e^- \rightarrow H_2$

and $Fe^{++} + 2e^- \rightarrow Fe$,

which can be experimentally realized at a cathode at a sufficiently low potential in a ferrous solution; Fe^{++} and H^+ ions are both reduced, with liberation of hydrogen, increase of pH and deposition of metallic iron on the electrode. The current is equal to the sum of the two separate reaction currents (both counted negative).

3. Potentials of Conductors in Reacting Systems

Any electrically neutral oxidation-reduction reaction* can be split into two elementary reactions, one of which is an oxidation and the other a reduction.

It follows from paragraph 2 above, that *if a reaction between an oxidizing and a reducing agent takes place at the surface of a conductor, the potential must lie between the equilibrium potential of the system which is oxidized and that of the system which is reduced.*

EXAMPLE. Suppose iron is corroding with evolution of hydrogen according to the overall reaction

$$Fe + 2H^+ \rightarrow Fe^{++} + H_2$$

in a solution of pH 4 containing 10^{-2} g.-ions Fe^{++} per litre. The reaction can be split into the two elementary reactions

$$Fe \rightarrow Fe^{++} + 2e^-$$

and

$$2H^+ + 2e^- \rightarrow H_2,$$

with equilibrium potentials $-0{\cdot}50$ and $-0{\cdot}24$ V. respectively. It belongs to the third group of reactions considered in paragraph 2—actually a special case where the total current is zero and the velocity of the oxidation reaction is equal to the velocity of the reduction reaction. It follows from the discussion above that the potential of the corroding iron must lie between $-0{\cdot}24$ and $-0{\cdot}50$ V.

Experimentally, it has been observed that iron (piano wire) corroding with liberation of hydrogen in a de-aerated solution of pH 4 containing 10^{-2} g.-ions Fe^{++} per litre has a potential of $-0{\cdot}42$ V., which lies between the limits imposed by thermodynamics.

4. Corrosion

The principles developed below follow directly from the foregoing discussion:

---

* A reaction between an oxidizing and a reducing agent is called an "oxidation-reduction" reaction.

(a) General Criterion of Corrosion

A metallic surface can be corroded by an aqueous solution only if its potential lies above the potential characteristic of equilibrium between the metal and its ions, for such concentration of ions as exists in the solution.

This follows from the fact that the primary step in corrosion is the oxidation of the metal (e.g. $Fe \rightarrow Fe^{++} + 2e^-$), which is only possible at potentials above the equilibrium potential.

(b) Corrosion Potential

Corrosion, and the rise of the potential of the metal above its inherent equilibrium potential, can occur only if the electrons liberated in the reaction are absorbed by a system having a still higher potential.* This system may be either an electrolytic anode (electrolytic corrosion), or a chemical oxidizing system (electrochemical or chemical corrosion).

It follows that *the potential of a metallic surface corroding under the action of an oxidizing agent must lie between the equilibrium potential of the metal and the equilibrium potential of the oxidizing agent.*†

EXAMPLE. When a metal corrodes in an aqueous solution with liberation of hydrogen under a given pressure, its potential lies between its own equilibrium potential (which is often the same as the Nernst "solution potential") and the potential of a reversible hydrogen electrode at this pressure. Unpublished experiments by the writer have confirmed this conclusion for the case of iron in various solutions at 25° C.[133–136]

If the corrosive solution contains no oxidizing agents, so that the metal can corrode only by liberation of hydrogen, the above principle leads to a very simple criterion for the occurrence of corrosion; it is sufficient to measure the difference of potential between a specimen of the metal and a reversible hydrogen electrode, both being in the solution under investigation. Corrosion occurs if the potential of the metal is below the potential of the hydrogen electrode; corrosion does not occur if the metal has a potential above that of the hydrogen electrode.

Like all other thermodynamical laws, this principle is valid whatever the temperature, pressure of hydrogen or composition of solution. It has been verified experimentally for several metals in de-aerated caustic soda solutions at different temperatures (20° to 110°C.) and with different concentrations of NaOH (2 to 660 g. per litre). For zinc, which corrodes in all cases, the potential is always lower than the reversible hydrogen potential; for iron, which does or does not corrode, depending on temperature, concentration and surface condition, the potential is lower or higher than the hydrogen potential when corrosion occurs and higher when it does not; for copper, stainless steel (V2A), nickel, silver and platinum, which do not corrode, the potential is always higher.

---

* See Erculisse.[24]

† This principle is in accord with the treatment of corrosion potentials by W. J. Müller[89] (assuming the existence of a porous film) and by T. P. Hoar[53] (based on anodic and cathodic polarization curves), and with Gatty and Spooner's discussion[38] of the "steady state" in corrosion.

(c) Increase of Corrosion Velocity*

Any factor which brings about an increase of the potential of the metal or lowers its equilibrium potential, without changing the condition of its surface, tends to increase the corrosion velocity.

This follows at once from the fact that such a factor increases the difference, $(E' - E)$, between the reaction potential and the equilibrium potential of the corrosion reaction; the "affinity" (or overpotential) of the corrosion reaction, $\Delta E = E' - E$ is thus increased. If all other conditions remain constant, the result must be an increase of corrosion velocity.

Increase of corrosion velocity by raising the potential of the metal may arise from "anodic polarization", as when the metal is the anode in an electrolytic circuit, or from the action of an oxidizing agent in the solution. The rise of potential must, however, take place without changing the surface condition of the metal (e.g. without forming a passivating film). For a metal, such as zinc, which corrodes with liberation of hydrogen, a similar increase of corrosion velocity by raising the potential may result from contact with another, more noble, metal of low hydrogen overpotential, e.g. platinum.

Increase of corrosion velocity by lowering the equilibrium potential may occur when a substance which forms a soluble complex with the metallic ions is added to the solution.

EXAMPLE. Suppose that metallic copper is immersed in a de-aerated solution of $CuSO_4$. As the Cu/Cu^{++} equilibrium potential lies above the H_2/H^+ potential, there can be no corrosion of the copper, which will take up the Cu/Cu^{++} equilibrium potential (e.g. +0·30 V.).

If oxygen is bubbled through the solution, the potential of the copper rises, owing to the reaction

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O,$$

and the metal corrodes in accordance with the overall reaction

$$2Cu + O_2 + 4H^+ \rightarrow 2Cu^{++} + 2H_2O.$$

Instead of bubbling oxygen, one may add cyanides to the solution in sufficient amount to transform the Cu^+ and Cu^{++} ions into complex cuprocyanide ions, $Cu(CN)_2^-$, and in such manner as to bring the equilibrium potential of these ions against metallic copper below the H_2/H^+ potential.

---

* See also ref. 98.

(d) Retardation and Inhibition of Corrosion

Any factor which lowers the potential of the metal or changes its surface so that it becomes covered with a thermodynamically stable film, may diminish or suppress corrosive action.

Protection of iron and other metals by lowering the potential is realized practically in "cathodic protection", "electrical drainage" or contact with a less "noble" metal, which is itself corroded ("zinc protectors").

Passivation of iron and other metals by a thermodynamically stable film occurs in certain cases of "anodic passivation", and in passivation by oxidizing agents, such as air or chromates.

Changes in corrosion velocity will be considered in greater detail in the course of the subsequent discussion of copper and iron.

(e) Domains of Corrosion and Domains of Non-corrosion

It has been mentioned above that "domains of thermodynamic stability" for the various solid compounds of a given metal, e.g. Cu, Cu_2O, CuO and $Cu(OH)_2$, can be depicted on a potential-pH diagram and that the conditions under which these compounds have a given solubility can also be indicated on the diagram.

If we assume that a metal does not corrode unless the substance forming its surface has a solubility in excess of some specified value, e.g. 10^{-6} M., the line representing this solubility on the potential-pH diagram divides the diagram into two regions—a "domain" in which corrosion is thermodynamically possible and a "domain" in which corrosion is thermodynamically impossible. Two examples of such domains are given in figs. 18 and 19, which relate to copper and iron respectively, and which will be discussed more fully on pp. 78 and 90. It is evident that it is not possible to fix the position of such "domains of corrosion" and "domains of non-corrosion" with accuracy unless the nature and equilibrium chracteristics of the metal, its oxides and other substances that may cover its surface, are known. For example, the limits thermodynamically predicted for the domain of non-corrosion of iron vary greatly according to the assumptions made about the composition of the protective film (Fe_2O_3, Fe_3O_4 or other compound); it is obvious that they also depend on the value taken for the solubility of the film-forming substance. The theoretical diagrams given must therefore be regarded only as rough approximations, and the conclusions to which they lead must be accepted with reserve; they do, however, provide an interpretation of observed facts sufficiently accurate for many purposes, and they indicate profitable lines for further experiment.

It is important that the concept of domains of corrosion and non-corrosion should not be used without due regard to the hypotheses on which it is based. In practice, there may be corrosion within what we have called the "domain of non-corrosion", and conversely, there may sometimes be no corrosion in the "domain of corrosion". In particular, it has been supposed that the metal cannot corrode if the solubility of the substance which covers its surface is less than 10^{-6} g.-atm. per litre; this only implies absence of corrosion if the substance forms an adherent and non-porous film. Again, the limit of 10^{-6}, which we have adopted to fix our ideas, is somewhat arbitrary. In certain cases where the operating conditions require a higher metal content in the solution, the limit must clearly be modified; this situation arises in the anodic passivation of metals.

(f) Immune and Passivated Metals; Domains of Immunity and Domains of Passivation

In the "domains of non-corrosion" just defined, one may, following Chaudron,[10] distinguish those cases where the surface of the metallic specimen really consists of the metal and those where it consists of an oxide or salt (carbonate, phosphate, etc.).

In the first case the surface of the metal is *bare*; it will be called *immune*, and the corresponding domain, an *immunity domain.* Within this domain corrosion of the metal is thermodynamically impossible. This situation arises generally for noble metals (e.g. platinum), for copper in many non-aerated acid solutions and for copper and iron when used as electrolytic cathodes. If the metal is electrically insulated, its potential is equal to the redox potential of the solution; if the solution is oxidized or reduced so that the redox potential rises or falls, while remaining within the "domain of stability" of the metal, the latter will undergo no change, and will act in these oxidations and reductions only as a reservoir of electrons, although it may show specific catalytic properties.

In the second case, the metal is *covered with a deposit of oxide or salt*; it will be called *passivated*—the usual case for iron, chromium, zinc, aluminium, magnesium, etc. The corresponding domain is a *passivation domain*; as we have just remarked, passivation does not imply absence of corrosion unless the substance covering the metal forms a perfect, non-porous film, completely screening the metal from contact with the solution. If this film is conducting, the potential follows laws analogous to those that determine the potential of a bare metal; if the film is a perfect insulator and covers the metal completely, it is meaningless to talk about the potential of the latter.

C. *USE OF POTENTIAL-pH DIAGRAMS*

We have already seen that these diagrams show the conditions under which the occurrence of given oxidation and reduction reactions is possible from the energetic standpoint; such diagrams thus enable us to predict and to interpret experimental observations.

It is unfortunate that very little of the extensive published work in the field to which these diagrams relate includes determinations of pH and potential; in consequence, the data necessary for the thermodynamic interpretation of experimental facts are often lacking. Nevertheless, some measurements of the required type have been carried out. We may note particularly the work of Travers and Thiesse[116, 119] on inorganic oxidation and reduction reactions; of McAulay and White,[76] Meunier and Bihet[81] and more recently Reiller[102, 103] on the corrosion of iron; of Gatty and Spooner[38] on copper; and Whitby,[127] and Evans and Hoar[31] on magnesium. Attention should also be directed to an investigation by Hoar[54] on the corrosion of tin, which was carried out in accordance with these principles and which solved the problem posed in a very elegant manner. Gatty and Spooner[38] have made a number of experiments on similar lines and have given a comprehensive review of the literature for several metals; their work is an important contribution to the theoretical and experimental investigation of corrosion.

A recent dissertation by Mlle Denise Bézier[3a] (Faculté des Sciences de l'Université de Paris, 21 March 1945), on the electrochemical investigation of the ferric ion and some of its complexes, illustrates the use of "potential-pH" diagrams in the discussion of experimental results, and also contains a treatment of the redox potentials of *irreversible* systems. Two recent works by G. Charlot[9a, 9b] also demonstrate the application of such diagrams to general and analytical chemistry.

CHAPTER VI

EXAMPLES

A. *THE SYSTEM* $Cu\text{-}H_2O$

The manner in which the $Cu\text{-}H_2O$ equilibrium diagram is derived from data to be found in the literature is explained below. A general account is then given of the stability of various copper compounds, the electrolysis of solutions of copper salts and the potential of copper electrodes, in terms of the diagram thus obtained. The equilibrium diagram of the ternary system $Cu\text{-}Cl\text{-}H_2O$ is established in a similar manner.

Fig. 11 (p. 59) shows the approximate conditions of thermodynamic stability of copper and some of its compounds in contact with a dilute aqueous solution at 25°C.[*]

1. Derivation of Fig. 11

The following values are adopted for the standard chemical potentials μ^0 of the various substances concerned:

Solvent and solutes		Solids	
$\mu^0_{H_2O}$	$= -\ 56{,}560$ cal.[75]		
$\mu^0_{H^+}$	$=$ 0 cal.		
$\mu^0_{OH^-}$	$= -\ 37{,}455$ cal.[121]	μ^0_{Cu}	$=$ 0 cal.
$\mu^0_{Cu^+}$	$= +\ 12{,}050$ cal.[34]	$\mu^0_{Cu_2O}$	$= -\ 34{,}990$ cal.[101]
$\mu^0_{Cu^{++}}$	$= +\ 15{,}912$ cal.[75]	μ^0_{CuO}	$= -\ 30{,}300$ cal.[101]
$\mu^0_{CuO_2H^-}$	$= -\ 60{,}960$ cal.	$\mu^0_{Cu(OH)_2}$	$= -\ 84{,}900$ cal.
$\mu^0_{CuO_2^{--}}$	$= -\ 43{,}100$ cal.		

The μ^0 values for CuO_2H^-, CuO_2^{--} and $Cu(OH)_2$ have been calculated as follows:

CuO_2H^-. McDowell and Johnston's[78] value of the solubility constant of CuO in alkalis has been used:

$$(CuO_2H^-)/(OH^-) = 1{\cdot}03 \times 10^{-5}.$$

CuO_2^{--}. Following McDowell and Johnston[78] we adopt the value $(CuO_2^{--})(H^+)/(CuO_2H^-) = 7{\cdot}9 \times 10^{-14}$ for the dissociation constant of CuO_2H^- in the equilibrium $CuO_2H^- = H^+ + CuO_2^{--}$.

---

[*] We have neglected polymerized cuprous ions, Cu_2^{++}, cuprous hydroxide Cu(OH) and derivatives of trivalent copper, as there exists no adequate information as to their thermodynamic properties. It is also assumed, as a first approximation, that the various solid phases do not form solid solutions with one another.

$Cu(OH)_2$. The solubility product of $Cu(OH)_2$ for the reaction $Cu(OH)_2 = Cu^{++} + 2OH^-$ is taken to be $(Cu^{++})(OH^-)^2 = 10^{-19}$, as given by Fricke and Hüttig.[36]

See also Ulich.[121]

The equilibrium conditions for the reactions under consideration may now be formulated.* They are tabulated below, the potentials being expressed in volts on the normal hydrogen scale.

1. *Homogeneous reactions*

(*a*) *Without oxidation*

(1) $CuO_2H^- - Cu^{++} - 2H_2O + 3H^+ = 0$:

$$\log \frac{(CuO_2H^-)}{(Cu^{++})} = -26\cdot 59 + 3\text{pH}.$$

(2) $CuO_2^{--} - Cu^{++} - 2H_2O + 4H^+ = 0$:

$$\log \frac{(CuO_2^{--})}{(Cu^{++})} = -39\cdot 69 + 4\text{pH}.$$

(3) $CuO_2^{--} - CuO_2H^- + H^+ = 0$:

$$\log \frac{(CuO_2^{--})}{(CuO_2H^-)} = -13\cdot 10 + \text{pH}.$$

---

* The following relations are used (cf. pp. 8 and 9):

Reactions without oxidation, type $aA + bB + cH_2O + mH^+ = 0$;

$$a \log (A) + b \log (B) = \log K + m\text{pH},$$

where the equilibrium constant K is given by

$$\log K = -\frac{\Sigma \nu\mu^0}{1363}, \qquad \ldots [6]$$

or

$$\log K = -\frac{a\mu^0{}_A + b\mu^0{}_B + c\mu^0{}_{H_2O} + m\mu^0{}_{H^+}}{1363}. \qquad \ldots [6']$$

Reactions with oxidation, type $aA + bB + cH_2O + mH^+ + ne^- = 0$;

$$E = E^0 - \frac{0\cdot 0591m}{n}\text{pH} + \frac{0\cdot 0591}{n}[a \log (A) + b \log (B)], \qquad \ldots [9]$$

where the standard potential E^0 is given by

$$E^0 = \frac{\Sigma \nu\mu^0}{23{,}060n} \quad \text{or} \quad E^0 = \frac{a\mu^0{}_A + b\mu^0{}_B + c\mu^0{}_{H_2O} + m\mu^0{}_{H^+}}{23{,}060n}. \qquad \ldots [7']$$

All reactions expressed in the general form, as above, are written according to the following rules:

For reactions without oxidation ($n = 0$), the coefficients a and m are taken positive. The substance A, which appears first in each equation, is thus the more basic of the substances under consideration.

For reactions with oxidation ($n \neq 0$) the coefficients a and n are taken positive. The compound A is thus the more highly oxidized of the substances under consideration.

Example.
In reaction (1), CuO_2H^- is more basic than Cu^{++}.
In reaction (24), CuO_2H^- is more oxidized than Cu_2O.

(*b*) *With oxidation*

(4) $Cu^{++} - Cu^+ + e^- = 0$:

$$E = 0\cdot 168 + 0\cdot 0591 \log \frac{(Cu^{++})}{(Cu^+)}.$$

(5) $CuO_2H^- - Cu^+ - 2H_2O + 3H^+ + e^- = 0$:

$$E = 1\cdot 739 - 0\cdot 1773\text{pH} + 0\cdot 0591 \log \frac{(CuO_2H^-)}{(Cu^+)}.$$

(6) $CuO_2^{--} - Cu^+ - 2H_2O + 4H^+ + e^- = 0$:

$$E = 2\cdot 513 - 0\cdot 2364\text{pH} + 0\cdot 0591 \log \frac{(CuO_2^{--})}{(Cu^+)}.$$

2. *Heterogeneous reactions involving two solid phases*

(7) $Cu_2O - 2Cu - H_2O + 2H^+ + 2e^- = 0$:

$$E = 0\cdot 468 - 0\cdot 0591\text{pH}.$$

(8) $CuO - Cu - H_2O + 2H^+ + 2e^- = 0$:

$$E = 0\cdot 569 - 0\cdot 0591\text{pH}.$$

(9) $Cu(OH)_2 - Cu - 2H_2O + 2H^+ + 2e^- = 0$:

$$E = 0\cdot 612 - 0\cdot 0591\text{pH}.$$

(10) $2CuO - Cu_2O - H_2O + 2H^+ + 2e^- = 0$:

$$E = 0\cdot 671 - 0\cdot 0591\text{pH}.$$

(11) $2Cu(OH)_2 - Cu_2O - 3H_2O + 2H^+ + 2e^- = 0$:

$$E = 0\cdot 756 - 0\cdot 0591\text{pH}.$$

3. *Heterogeneous reactions involving one solid phase*

(*a*) *Without oxidation*

(12) $Cu_2O - 2Cu^+ - H_2O + H^+ = 0$:

$$\log (Cu^+) = -0\cdot 93 - \text{pH}.$$

(13) $CuO - Cu^{++} - H_2O + 2H^+ = 0$:

$$\log (Cu^{++}) = 7\cdot 59 - 2\text{pH}.$$

(14) $CuO_2H^- - CuO - H_2O + H^+ = 0$:

$$\log (CuO_2H^-) = -19\cdot 00 + \text{pH}.$$

(15) $CuO_2^{--} - CuO - H_2O + 2H^+ = 0$:

$$\log (CuO_2^{--}) = -32\cdot 10 + 2\text{pH}.$$

(16) $Cu(OH)_2 - Cu^{++} - 2H_2O + 2H^+ = 0$:

$$\log (Cu^{++}) = 9\cdot 02 - 2\text{pH}.$$

(17) $CuO_2H^- - Cu(OH)_2 + H^+ = 0$:

$$\log (CuO_2H^-) = -17\cdot 56 + \text{pH}.$$

(18) $CuO_2^{--} - Cu(OH)_2 + 2H^+ = 0$:

$$\log (CuO_2^{--}) = -30\cdot 66 + 2\text{pH}.$$

(*b*) *With oxidation*

(19) $Cu^+ - Cu + e^- = 0$:

$$E = 0{\cdot}523 + 0{\cdot}0591 \log (Cu^+).$$

(20) $Cu^{++} - Cu + 2e^- = 0$:

$$E = 0{\cdot}345 + 0{\cdot}0295 \log (Cu^{++}).$$

(21) $CuO_2H^- - Cu - 2H_2O + 3H^+ + 2e^- = 0$:

$$E = 1{\cdot}130 - 0{\cdot}0886\text{pH} + 0{\cdot}0295 \log (CuO_2H^-).$$

(22) $CuO_2^{--} - Cu - 2H_2O + 4H^+ + 2e^- = 0$:

$$E = 1{\cdot}518 - 0{\cdot}1182\text{pH} + 0{\cdot}0295 \log (CuO_2^{--}).$$

(23) $2Cu^{++} - Cu_2O + H_2O - 2H^+ + 2e^- = 0$:

$$E = 0{\cdot}222 + 0{\cdot}0591\text{pH} + 0{\cdot}0591 \log (Cu^{++}).$$

(24) $2CuO_2H^- - Cu_2O - 3H_2O + 4H^+ + 2e^- = 0$:

$$E = 1{\cdot}794 - 0{\cdot}1182\text{pH} + 0{\cdot}0591 \log (CuO_2H^-).$$

(25) $2CuO_2^{--} - Cu_2O - 3H_2O + 6H^+ + 2e^- = 0$:

$$E = 2{\cdot}568 - 0{\cdot}1773\text{pH} + 0{\cdot}0591 \log (CuO_2^{--}).$$

(26) $CuO - Cu^+ - H_2O + 2H^+ + e^- = 0$:

$$E = 0{\cdot}616 - 0{\cdot}1182\text{pH} - 0{\cdot}0591 \log (Cu^+).$$

These equilibrium conditions are shown graphically in figs. 9, 10, 11 and 14.

Homogeneous equilibria. In fig. 9, the heavy lines show the loci of points for which the activities (or in ideal solutions, the concentrations) of two copper compounds, simultaneously present in the solution, are equal to one another. The five lines of this type refer to the reactions (1), (3), (4), (5) and (6). The equation of each line is obtained from the corresponding equilibrium condition by making the logarithmic term zero.

EXAMPLE. The locus of points at which the activities of Cu^+ and CuO_2H^- are equal (reaction (5)) is the line $E = 1{\cdot}739 - 0{\cdot}1773\text{pH}$ (V.); the slope is $-177{\cdot}3$ mV. per pH unit.

The three lines (1), (4) and (5) intersect at the same point ($E = 0{\cdot}168$ V., pH $= 8{\cdot}86$), at which the activities of the three different ionic forms of copper coexisting in the solution, Cu^+, Cu^{++} and CuO_2H^-, are equal. The lines (3), (5) and (6) also intersect at a single point, ($E = 0{\cdot}584$ V., pH $= 13{\cdot}10$), at which the activities of the ions Cu^+, CuO_2H^- and CuO_2^{--} are all equal. These five lines divide the field of the diagram into four domains, each corresponding to the predominance of a particular solute species.

The finer lines, which also appear in fig. 9, refer to the reactions just considered, and show the conditions under which the logarithms of the activity ratios of various pairs of copper derivatives have values of 3, 2, 1, 0, −1, −2, −3, (i.e. the ratios of activities are respectively 1000, 100, 10, 1, 0·1, 0·01, and 0·001). To simplify the diagram, each of these lines is terminated when it meets another line referring to the same relative activity of the predominant solute. The families of lines are analogous to map contours, and from them one can determine the ratio of the activities of two solutes at any point on the diagram. It is only necessary to find the "level" of the line of the appropriate family passing through the point; the "level" is equal to the logarithm of the desired ratio. Extrapolation or interpolation may be required in some cases.

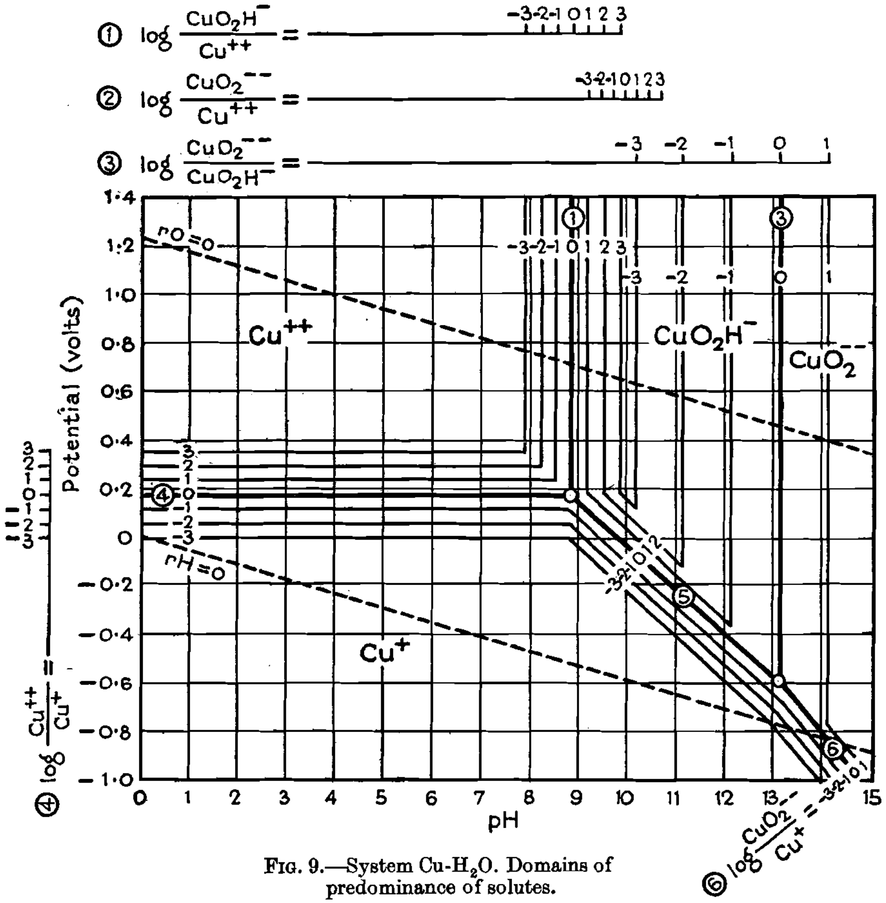


FIG. 9.—System Cu-H₂O. Domains of predominance of solutes.

EXAMPLE. The point $E = 0{\cdot}050$ V., pH $= 8{\cdot}86$, lies in the domain of predominance of Cu^+, and the levels of the lines (1), (3), (4) and (5) are respectively 0, $-4{\cdot}24$, -2 and -2 We thus have

$$\frac{(CuO_2H^-)}{(Cu^{++})}=1,\quad \frac{(CuO_2^{--})}{(CuO_2H^-)}=10^{-4\cdot24},\quad \frac{(Cu^{++})}{(Cu^+)}=10^{-2}\ \text{and}\ \frac{(CuO_2H^-)}{(Cu^+)}=10^{-2}.$$

Thus, if the solution contains 1 part of Cu^+, it will also contain 10^{-2} parts Cu^{++}, 10^{-2} parts CuO_2H^-, and $10^{-6\cdot24}$ parts CuO_2^{--}.

Heterogeneous equilibria involving two solids. The two full lines of fig. 10 refer to reactions (7) and (10) and the three broken lines correspond to reactions (8), (9) and (11). Each of these lines has a slope of $-59{\cdot}1$ mV. per pH unit.

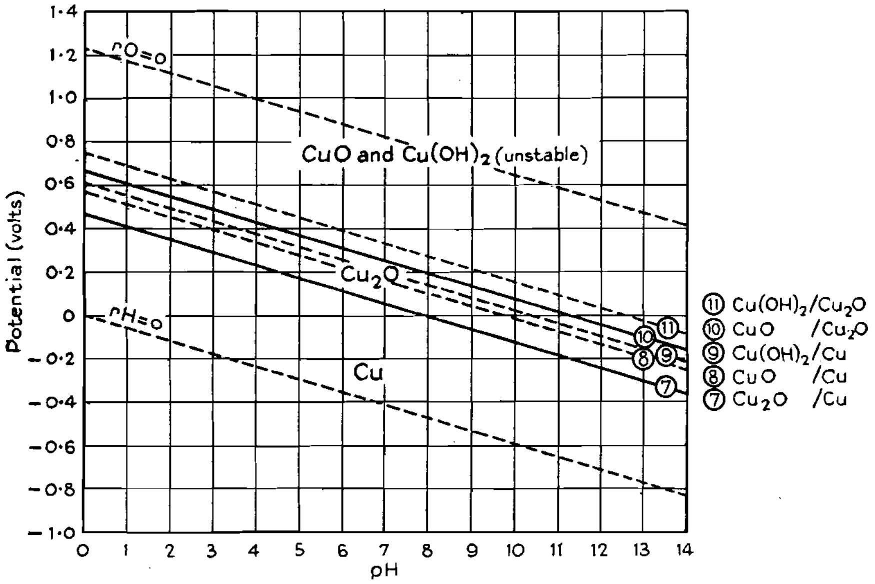


FIG. 10.—System Cu-H_2O. Domains of stability of solid phases.

The two full lines form the boundaries of three domains, within which metallic Cu, Cu_2O or CuO is absolutely stable. In addition, each of the three broken lines separates two domains, in each of which one of two solid substances is stable with respect to the other. Relative stability of one substance with respect to another does not always imply that this substance is stable with respect to a third; for example, CuO is stable towards Cu in the domain lying above line (8), but it is stable towards Cu_2O only above line (10). Between the two lines (8) and (10) CuO is only metastable, and tends to undergo a reaction producing Cu_2O.

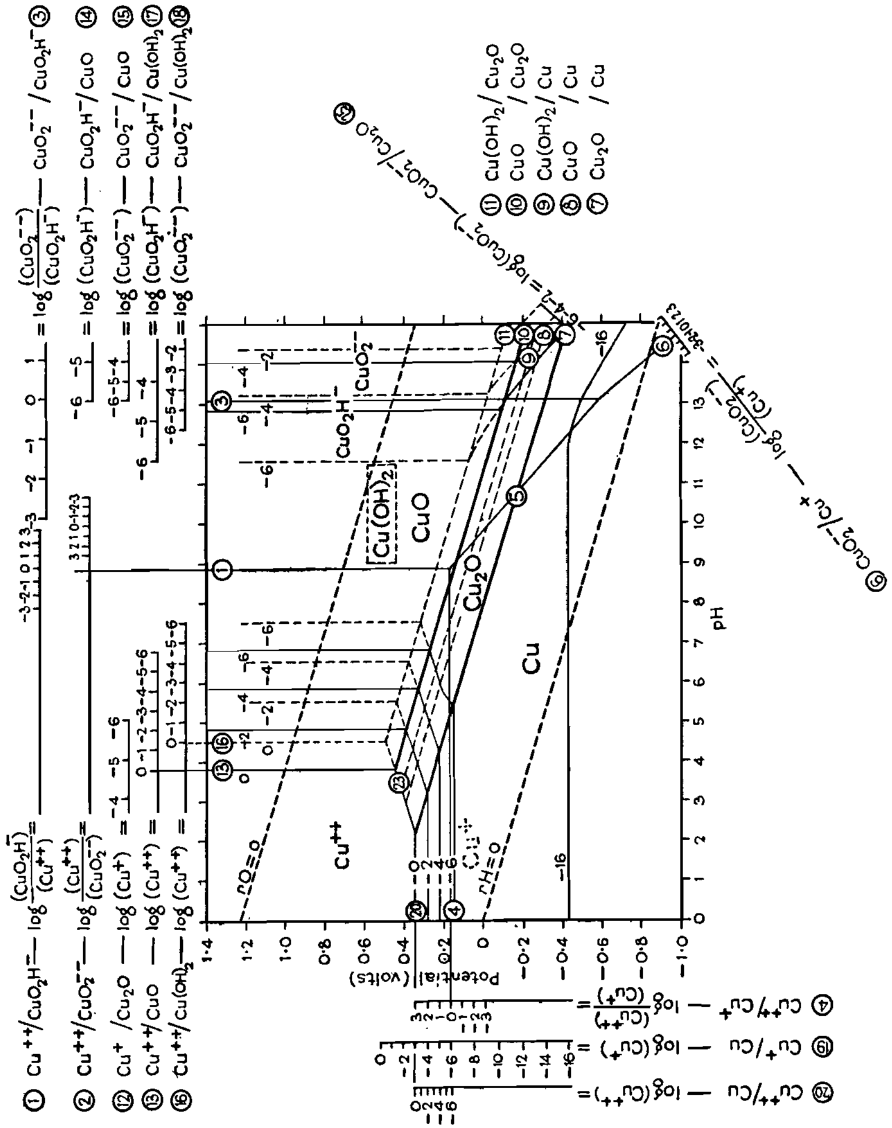


FIG. 11.—System Cu-H_2O. Combined diagram.

Two forms of the oxide of bivalent copper have been considered; they are $Cu(OH)_2$, for which solubilities have been calculated from the data of Fricke and Hüttig,[36] and an anhydrous oxide, CuO, which, according to Von Euler,[124] is one of the products of ageing of $Cu(OH)_2$. Examination of fig. 10 shows, as might have been foreseen, that $Cu(OH)_2$ possesses no domain of absolute stability, and is thermodynamically unstable in the whole of the CuO stability domain.

Heterogeneous equilibria involving one solid. The combined diagram, fig. 11,* shows

(*a*) The lines (1), (3), (4), (5) and (6), which separate the domains of predominance of the solutes, and the lines (7), (8), (9), (10) and (11), which separate the domains of relative stability of the appropriate solids.

(*b*) The loci of points where the activity of dissolved copper in a particular form has certain given values, namely 10^0, 10^{-2}, 10^{-4} and 10^{-6} g.-ion per litre; the logarithm is shown by an index. The equations of these lines are obtained by making the logarithmic term of the corresponding equilibrium condition equal to 0, -2, -4 and -6 respectively.

EXAMPLE. By equation (25), the locus of points at which Cu_2O is in equilibrium with a solution having a cuprite ion (CuO_2^{--}) activity of 10^{-6} M. (i.e. 0·06 mg. Cu per litre), is the line

$$E = 2{\cdot}568 - 0{\cdot}1773\text{pH} - 0{\cdot}354, \quad \text{or} \quad E = 2{\cdot}214 - 0{\cdot}1773\text{pH}.$$

The locus of points at which the *total* activity of dissolved copper, in all the four forms considered (Cu^+, Cu^{++}, CuO_2H^- and CuO_2^{--}), has a given, constant value, is a curve which roughly follows the polygonal outline formed by the separate lines of the same index; the curve practically coincides with one of these lines whenever one of the four ionic species is greatly predominant, i.e. outside the regions occupied by the families of straight lines in fig. 9. Conversely, the curve diverges from the polygonal shape in the neighbourhood of the latter lines.

EXAMPLE. It will be clear from fig. 11 and from fig. 14, which reproduces a part of fig. 11 on a larger scale, that the line of index -6 (i.e. total dissolved copper content of 10^{-6} g.-atom per litre) in the stability domain of Cu_2O and in acid solutions curves inwards at potentials around 0·168V., at which potential the solution contains equal amounts of Cu^+ and Cu^{++}. In the stability domain of metallic copper this same line of index -6 lies *below* the two lines corresponding to concentrations of Cu^+ and Cu^{++} separately equal to 10^{-6}. In the stability domain of Cu_2O in alkaline solutions, the -6 line curves inwards at pH's around 13·10 (where the solution contains equal amounts of CuO_2H^- and CuO_2^{--}); in the stability domain of CuO, the line lies to the *left* of the two lines which separately denote concentrations of 10^{-6} M. in CuO_2H^- and CuO_2^{--}.

---

* An approximation to this diagram has been published previously.[97, 98]

The curves showing total solubility can readily be plotted by a method explained below in connexion with figs. 15 and 16 (p. 74).

2. Discussion of Fig. 11

Fig. 11 is a graphical summary of the thermodynamical equilibrium data for the various copper compounds (solid and in solution) mentioned. Before dealing with the applications of this diagram, it is desirable to consider the concept of "potential" more closely; to this end some particular cases, introducing various features of the diagram, will now be discussed.

(a) The Concept of Potential[137]

(1) *Behaviour of electrically insulated Platinum, Gold and Copper*

Consider a solution of pH 2 containing Cu^+ and Cu^{++} in thermodynamic equilibrium, e.g. a solution of cuprous and cupric sulphates in dilute sulphuric acid. Such a solution has a well-defined "equilibrium potential", which, assuming the solution to be ideal, depends only on the ratio of the Cu^+ and Cu^{++} concentrations. This potential can be calculated from equation (4) or from the "level" on scale (4) in figs. 11 or 14, which is equivalent to equation (4). The potential may be measured by introducing into the solution a metal whose presence has no effect on the Cu^+ and Cu^{++} concentrations.

If an electrically insulated platinum or gold wire is dipped into such a solution, the platinum or gold, neither of which affect the Cu^+ or Cu^{++} concentrations, will take up a potential equal to the redox potential of the solution and therefore determined uniquely by the Cu^{++}/Cu^+ concentration ratio. For example, if this ratio is 10^6, the potential will be $+0{\cdot}522$ V., by equation (4).

On the other hand, if a *copper* wire is immersed in the solution, a completely different potential will be observed; the redox system which we now have to consider contains not only Cu^{++} and Cu^+ ions, but also metallic Cu. In addition to the equilibrium $Cu^+ = Cu^{++} + e^-$ (with an equilibrium potential of 0·522 V. in the present case), we have also to take account of the reactions

$$Cu = Cu^{++} + 2e^- \qquad \text{and} \qquad Cu = Cu^+ + e^-$$

with equilibrium potentials in general lower than the Cu^{++}/Cu^+ potential. The potential of the metal is thus no longer an *equilibrium* redox potential, but a *reaction potential* determined by the fact that copper tends to dissolve ($Cu^{++} + Cu \rightarrow 2Cu^+$), in order to establish equilibrium in the $Cu^{++}/Cu^+/Cu$ system. One may consider this overall reaction as made up of two elementary reactions:

$$Cu \rightarrow Cu^+ + e^- \text{ (oxidation)} \quad \text{and} \quad Cu^{++} + e^- \rightarrow Cu^+ \text{ (reduction)}.$$

The potential of the copper will therefore lie between the Cu^{++}/Cu^{+} redox potential and the Cu/Cu^{+} solution potential, as shown on p. 47. In practice, the potential of the copper lies close to the Cu/Cu^{++} equilibrium potential and thus depends mainly on the cupric ion concentration in the solution; it is around + 0·286 V. when this concentration is 10^{-2} g.-atom Cu per litre.

If three electrodes, of gold, platinum and copper, are immersed in a solution containing 10^{-2} g.-ion Cu^{++} and 10^{-8} g.-ion Cu^{+} per litre, the potential of both gold and platinum will thus be +0·522 V., while that of the copper will be around +0·286 V. In absence of oxidizing agents other than Cu^{++}, the copper will dissolve according to the reaction $Cu + Cu^{++} \rightarrow 2Cu^{+}$, whereby the concentration of Cu^{+} increases from the initial value of 10^{-8} M. to a final value of about 10^{-4} M., which is the value appropriate to Cu/Cu^{+} equilibrium at +0·286 V. As the Cu^{+} ions thus formed diffuse into the bulk of the solution, the potentials of the platinum and gold will fall, and will finally attain the same stable value when the concentration of Cu^{+} ions has become uniform throughout the solution and the copper has ceased to dissolve. The $Cu/Cu^{+}/Cu^{++}$ system has then reached a state of thermodynamic equilibrium, and the redox and solution potentials have one and the same value—the equilibrium potential of the system.

(2) *Behaviour of Platinum and Gold when not electrically insulated*

We now consider what happens when we take a solution of Cu^{++} and Cu^{+} ions (at pH 2, and containing 10^{-2} g.-ion Cu^{++} and 10^{-8} g.-ion Cu^{+} per litre as above) and introduce a platinum or gold wire which is not insulated and which acts as an electrolytic anode or cathode. Since the potential of the *insulated* metal is the redox potential of the solution (+0·522 V.), it must have a higher value when it acts as anode, and a lower value when it acts as cathode.

If the noble metal is used as *anode*, and has a potential of, e.g. +0·759 V., the redox potential will tend to increase from +0·522 to +0·759 V.; in other words, Cu^{+} ions are oxidized ($Cu^{+} \rightarrow Cu^{++} + e^{-}$) until the concentration ratio $(Cu^{++})/(Cu^{+})$ has increased from 10^{6} to 10^{10}, which corresponds to the potential +0·759 V., by equation (4).

On the other hand, if the gold or platinum is made a *cathode*, and has a potential of, say, +0·345 V., which lies between the redox potential (+0·522 V.) and the solution potential corresponding to the concentration of Cu^{++} ions present (+0·286 V.), then the redox potential will tend to fall from +0·522 to +0·345 V.; in other words, Cu^{++} is reduced to Cu^{+} ($Cu^{++} + e^{-} \rightarrow Cu^{+}$) until the concentration ratio $(Cu^{++})/(Cu^{+})$ has fallen from 10^{6} to 10^{3}, corresponding to 0·345 V.

Finally, if the gold or platinum acts as *cathode*, and has a potential of, say, 0·168 V., which lies below the redox potential (+0·522 V.) and below the solution potential (+0·286 V.), the action of the cathode will tend to reduce the redox potential from +0·522 to +0·168 V. and to reduce the solution potential from +0·286 to +0·168 V. Reduction of Cu^{++} to Cu^{+} and reduction of Cu^{+} to metallic Cu will thus both occur, until the $(Cu^{++})/(Cu^{+})$ ratio has fallen from 10^{6} to 1 (corresponding to +0·168 V.), and the Cu^{++} concentration has fallen to 10^{-6} M. (which again corresponds to +0·168 V.). A deposit of copper is formed on the electrode.

(3) *Behaviour of Copper when not electrically insulated*

If a copper electrode is introduced into the solution of Cu^{++} and Cu^{+} ions considered above, its potential will lie above or below the solution potential according as the metal is made anodic or cathodic.

If the copper functions as *anode* and has a potential above the redox potential and above the solution potential, its action on the solution will not only tend to increase the redox potential (as with the noble metal anodes just considered), but will also cause the solution potential to increase. It will thus bring about the reactions

$$Cu^{+} \rightarrow Cu^{++} + e^{-},\ Cu \rightarrow Cu^{+} + e^{-} \quad \text{and} \quad Cu \rightarrow Cu^{++} + 2e^{-},$$

simultaneously.

If the copper functions as *anode* and has a potential lying between the redox and solution potentials, the metal will dissolve according to the reactions $Cu \rightarrow Cu^{+} + e^{-}$ and $Cu \rightarrow Cu^{++} + 2e^{-}$, the relative rates being such that the redox potential of the solution falls, i.e. the concentration ratio $(Cu^{++})/(Cu^{+})$ falls.

Finally, if the copper is a *cathode*, the situation is the same as that considered above for a gold or platinum cathode covered with copper and at a potential below the redox and solution potentials. Cu^{++} ions are reduced, forming both Cu^{+} ions and metallic copper, which is deposited on the cathode.

(4) *Behaviour of Copper covered with Cu_2O*

Consider the case of a copper specimen covered with Cu_2O, which is immersed in a solution of pH2 containing 10^{-2} g.-ion Cu^{++} per litre. Figs. 11 and 14 show that Cu_2O is not stable with respect to Cu^{++} ion at this pH, and that metallic copper is stable only if its potential does not exceed +0·286 V. The Cu_2O thus tends to dissolve, forming Cu^{++} ions

$$(23) \qquad Cu_2O + 2H^{+} \rightarrow 2Cu^{++} + H_2O + 2e^{-}.$$

This is an oxidation, and it can occur only if it is associated with a reduction. If the solution contains no other substances capable of being reduced, the reduction can take place only at the expense of the Cu_2O itself, i.e.

$$(7) \qquad Cu_2O + 2H^+ + 2e^- \rightarrow 2Cu + H_2O.$$

It follows that Cu_2O under these conditions is decomposed according to the overall reaction $Cu_2O + 2H^+ \rightarrow Cu^{++} + Cu + H_2O$, resulting from the combination of reactions (23) and (7). Cu^{++} ions and metallic copper are formed and the pH of the solution rises. The potential of the metal must be below that of the line (7) in figs. 11 and 14 and above that of line (23) of index —2, which refer respectively to the equilibria Cu/Cu_2O and Cu^{++}/Cu_2O for $(Cu^{++}) = 10^{-2}$ M. It can easily be shown that these limiting values are respectively $+0{\cdot}350$ and $+0{\cdot}222$ V. at pH 2; in practice, the potential of the metal will be near the Cu/Cu^{++} equilibrium potential, i.e. $+0{\cdot}286$ V. in this case.

(b) Stability of Copper Derivatives

(1) *Stability of Copper Sulphate Solutions*

A solution containing sulphuric acid and copper sulphate with a total activity of copper, as Cu^+ and Cu^{++}, of 0·01 g.-ion per litre, is thermodynamically stable only in the domain lying above and to the left of the line of index —2, i.e. in media sufficiently oxidizing and acid. Inside this domain the solution has no tendency to precipitate any of the four solid substances considered in fig. 11 (Cu, Cu_2O, CuO and $Cu(OH)_2$). As far as the concentrations of cuprous and cupric ions are concerned, its composition is defined by equation (4), and is shown by the scales marked (4), which are plotted in figs. 9, 4 and 14. For each value of the redox potential, the ratio of the Cu^{++} and Cu^+ concentrations has a fixed value; for example, it is 100 at $+0{\cdot}286$ V. and 10,000 at $+0{\cdot}404$ V.

Theoretically, no solution of $CuSO_4$ can be completely free from all trace of cuprous ions; solutions which are practically free from cuprous ions can be obtained, but all such solutions have in principle a potential determined by the $(Cu^{++})/(Cu^+)$ ratio—for example, $+0{\cdot}522$ V. in a solution containing one million times less cuprous ions than cupric. A small addition of cuprous ions to such a solution, just as "saturating" it with metallic copper, i.e. leaving it in contact with the metal until equilibrium is established, brings about a sharp fall in potential; in a solution containing 0·01 g.-ion Cu^{++} per litre, the potential falls to $+0{\cdot}286$ V. if the proportion of cuprous ions is raised to 1% or if the solution is "saturated" with metallic copper. On the other hand, aeration of such solutions oxidizes cuprous ions, and brings about a rise of potential, towards the value characteristic of a reversible oxygen electrode.

Along the curve of index —2, the solution of the sulphates of copper at total concentration 10^{-2} M., which we have considered above, is in equilibrium with a solid phase (Cu, Cu_2O, CuO or $Cu(OH)_2$). Any of these solids can be precipitated from the solution by making changes in it which push the "representative point" into the stability domain of the solid in question. Thus, if the pH is below 3·3, reduction by an electrolytic cathode, or by a metal having a potential below $+0{\cdot}286$ V. (such as iron or zinc), leads to the separation of metallic copper; if the pH is above 3·3, a similar reducing action gives rise to Cu_2O, and not the metal. Addition of alkali to the solution can cause precipitation of Cu_2O or of CuO, according as the redox potential of the solution lies below or above approximately $+0{\cdot}38$ V. If the precipitate is $Cu(OH)_2$, the corresponding figure is *ca.* $+0{\cdot}43$ V.

(2) *Solubility of CuO and $Cu(OH)_2$*

If a representative point in the stability domain of CuO (or $Cu(OH)_2$) in fig. 11 is moved along a line of constant rH or rO (e.g. the line rO = 0), the equilibrium concentrations of Cu^{++} and CuO_2H^- ions will vary in opposite senses. These concentrations may be read off scales (13) and (14) for CuO, and (16) and (17) for $Cu(OH)_2$. For example, when the point moves from left to right, the Cu^{++} concentration decreases and the CuO_2H^- concentration increases; at the point of intersection with line (1) (pH = 8·86, $E = +0{\cdot}704$ V.) the two concentrations are equal, and are $10^{-10{\cdot}13}$ M. in presence of CuO, and $10^{-8{\cdot}70}$ M. in presence of $Cu(OH)_2$. The *total* concentration of Cu^{++} and CuO_2H^- ions at this point is almost minimal, and is $10^{-9{\cdot}83}$ M. in presence of CuO and $10^{-8{\cdot}40}$ M. in presence of $Cu(OH)_2$; in other words, $0{\cdot}94 \times 10^{-5}$ and $25{\cdot}2 \times 10^{-5}$ mg. of Cu per litre. At this point, also, the concentration of Cu^+ ions is much less than the concentrations of Cu^{++} and CuO_2H^- ions (in fact, $(Cu^+)/(Cu^{++}) = 10^{-9{\cdot}07}$), but it increases as one moves downwards along line (1). At the point where lines (1), (4) and (5) meet, the concentrations of Cu^+, Cu^{++} and CuO_2H^- become equal, and are $10^{-10{\cdot}13}$ M. in presence of CuO or $10^{-8{\cdot}70}$ M. in presence of $Cu(OH)_2$; the *total* concentration of these three ions together is thus $10^{-9{\cdot}65}$ M. in presence of CuO or $10^{-8{\cdot}22}$ M. in presence of $Cu(OH)_2$, corresponding to $1{\cdot}4 \times 10^{-5}$ and $38{\cdot}0 \times 10^{-5}$ mg. Cu per litre.

It can be shown that the total copper in a solution in contact with CuO or $Cu(OH)_2$ is a minimum at pH 8·96, with values $10^{-9{\cdot}85}$ M. or $10^{-8{\cdot}42}$ M.; lines that refer to total solubilities less than this have only a single branch and not *two* branches, as have the lines of index 0 to —6 in fig. 11 (cf. the line of index —16 in fig. 11).

(3) *Ageing of $Cu(OH)_2$*

According to fig. 11, a suspension of freshly precipitated $Cu(OH)_2$ in a solution of pH 13·2 contains dissolved copper, as CuO_2H^- and CuO_2^{--}, to the extent of 10^{-4} M. (i.e. 6·3 mg. Cu per litre); if the $Cu(OH)_2$ is allowed to "age", so that it changes into the less soluble CuO, the copper content of the solution will fall,

$$CuO_2H^- + H^+ \rightarrow CuO + H_2O$$

and

$$CuO_2^{--} + 2H^+ \rightarrow CuO + H_2O,$$

and the pH will in consequence rise.

If the ageing of $Cu(OH)_2$ takes place in presence of cuprous oxide, the redox potential will fall, so that we pass from some point on line (11) to a point on line (10), which is lower by 0·085 V. at any given pH. These lines refer respectively to the $Cu(OH)_2/Cu_2O$ and CuO/Cu_2O equilibria.

(4) *Influence of Substances which form Soluble Complexes with Cu^+, Cu^{++}, CuO_2H^- or CuO_2^{--} ions*

If a substance which forms a soluble complex with any of the four ions considered is added to the solutions discussed above, equations (1) to (26) of pp. 54–6, and the corresponding lines in figs. 9 and 11, no longer represent the equilibria of the system completely; additional equations, determining the stability of the soluble complex, must be taken into consideration. New lines giving the solubility of the complex must appear in fig. 11; all the lines previously drawn remain valid except for those referring to *total* solubility, since the number of component solubilities which make up the total is now five, instead of four.

Influence of Cyanides. As an example, consider the case of cyanides, which react with cuprous ions according to the equation

$$Cu^+ + CN^- = CuCN,$$

forming the white cuprous cyanide, which is soluble in excess of CN^- ions:

$$(27) \qquad CuCN + CN^- = Cu(CN)_2^-,$$

$$(28) \qquad CuCN + 3CN^- = Cu(CN)_4^{---}.$$

As a first approximation, we assume that only $Cu(CN)_2^-$ ions are formed when CuCN dissolves (reaction (27)), and we take the dissociation constant of $Cu(CN)_2^-$,

$$(29) \qquad Cu(CN)_2^- = Cu^+ + 2CN^-,$$

to be approximately $\dfrac{(Cu^+)(CN^-)^2}{(Cu(CN)_2^-)} = 1 \times 10^{-16}.$

This estimate was made by Latimer,[71] from data obtained by Spitzer.[112]

Eliminating the (Cu^+) term between this relation and (19), which refers to the Cu/Cu^+ equilibrium, we obtain the following for the $Cu/Cu(CN)_2^-$ equilibrium:

$$(30) \quad Cu(CN)_2^- - Cu - 2CN^- + e^- = 0;$$

$$E = -0{\cdot}423 + 0{\cdot}0591 \log \frac{(Cu(CN)_2^-)}{(CN^-)^2}.$$

In a solution molar with respect to CN^- the solubility of copper as $Cu(CN)_2^-$ will thus be 1 g.-atom per litre at a potential near to $-0{\cdot}423$ V.,* which is represented in fig. 11 by a horizontal line. In absence of cyanide, the corresponding total solubility is 10^{-16} M. (as cuprous ions). Hence the stability domain of a solution containing 1 g.-atom of copper per litre is now limited not by the line of index zero in fig. 11, but by the horizontal line forming the left-hand part of the curve of index -16; the copper in such a solution cannot be precipitated as hydroxide or oxide by adding alkali, and a reducing agent having a potential lower than $+0{\cdot}35$ V. no longer suffices to deposit metallic copper. A potential below $-0{\cdot}43$ V. is now needed. Another example of the formation of complex cuprous ions is given in the discussion of the Cu-Cl-H_2O system.

(5) *Influence of Substances which form Insoluble Salts with Cu^+, Cu^{++}, CuO_2H^- or CuO_2^{--} ions*

When substances are present that can form an insoluble salt with any one of these ions, a stability domain for this salt must appear in fig. 10; the salt must replace Cu, Cu_2O or CuO in part of the stability domains previously devoted to them.

The same modification must be introduced into figs. 11 and 14, where the solubility lines will also be changed in the stability domain of the salt; in fact, in this domain it is the solubility of the salt which has to be considered and not that of the metal or one of its oxides.

With Cu^{++} ions, carbonates form solid cupric carbonate but do not give rise to any known soluble complexes with the ions Cu^+, Cu^{++}, CuO_2H^- or CuO_2^{--}. The ternary system Cu-CO_2-H_2O illustrates what has just been said, and shows that Cu_2O and CuO can be supplanted by cupric carbonate in part of their stability domain, in agreement with the well-known formation of basic carbonates. For reasons of space this system will not be considered further, but it may be discussed on lines similar to those used in connexion with the more complex ternary system, Cu-Cl-H_2O.

---

* **Provided that no other reaction, such as formation of solid CuCN, occurs.**

(c) The System Cu-Cl-H$_2$O

The presence of chlorides in acid solutions of cuprous and cupric salts has two effects on equilibria in these solutions: it may give rise to (i) sparingly soluble solid CuCl, or to (ii) various complex ions, such as $CuCl_2^-$ and $CuCl_3^{--}$.

In the following discussion of equilibria in this system we shall use the values of the standard chemical potentials given on p. 53, and shall adopt in addition the following values for the ions Cl$^-$ and $CuCl_2^-$ and solid CuCl.

$\mu^0 Cl^-$ = — 31,345 cal. (Randall and Young[100]).
$\mu^0 CuCl_2^-$ = — 58,222 cal.
$\mu^0 CuCl$ = — 28,490 cal. (Wanatabe[126]).

The value for $CuCl_2^-$ has been calculated on the assumption that the equilibrium constant of the reaction

$$CuCl + Cl^- = CuCl_2^-$$

is

$$(CuCl_2^-)/(Cl^-) = 6{\cdot}5 \times 10^{-2},$$

as given by Noyes and Chow.[90]

As there are no data available regarding their stability, we shall not consider other compounds of Cu and Cl, such as the cuprous complex $CuCl_3^{--}$ and the possible cupric complex ions; for simplicity, we shall also omit any further consideration of cupric hydroxide $Cu(OH)_2$.

The following conditions of equilibrium are derived by applying equations [6], [7], [9] and [10] and relate to the various possible reactions between CuCl, $CuCl_2^-$ and some of the copper compounds already discussed.

1. *Homogeneous Reactions*

(*a*) *Without oxidation*

(31) $Cu^+ - CuCl_2^- + 2Cl^- = 0$:
$$\log (CuCl_2^-) = 5{\cdot}55 + \log (Cu^+) + 2 \log (Cl^-).$$

(*b*) *With oxidation*

(32) $Cu^{++} - CuCl_2^- + 2Cl^- + e^- = 0$:
$$E = 0{\cdot}495 + 0{\cdot}0591 \log \frac{(Cu^{++})(Cl^-)^2}{(CuCl_2^-)}.$$

(33) $CuO_2H^- - CuCl_2^- + 2Cl^- - 2H_2O + 3H^+ + e^- = 0$:
$$E = 2{\cdot}067 - 0{\cdot}0173pH + 0{\cdot}0591 \log \frac{(CuO_2H^-)(Cl^-)^2}{(CuCl_2^-)}.$$

(34) $CuO_2^{--} - CuCl_2^- + 2Cl^- - 2H_2O + 4H^+ + e^- = 0$:
$$E = 2{\cdot}842 - 0{\cdot}2364pH + 0{\cdot}0591 \log \frac{(CuO_2^{--})_2(Cl^-)^2}{(CuCl_2^-)}.$$

2. *Heterogeneous Reactions involving two solid phases*

(*a*) *Without oxidation*

(35) $Cu_2O - 2CuCl + 2Cl^- - H_2O + 2H^+ = 0$:
$$\log (Cl^-) = - 5{\cdot}82 + pH.$$

(*b*) *With oxidation*

(36) $CuCl - Cu - Cl^- + e^- = 0$:
$$E = 0{\cdot}124 - 0{\cdot}0591 \log (Cl^-).$$

(37) $CuO - CuCl + Cl^- - H_2O + 2H^+ + e^- = 0$:
$$E = 1{\cdot}016 - 0{\cdot}1182pH + 0{\cdot}0591 \log (Cl^-).$$

3. *Heterogeneous Reactions involving one solid phase*

(*a*) *Without oxidation*

(38) $CuCl - Cu^+ - Cl^- = 0$:
$$\log (Cu^+) = - 6{\cdot}74 - \log (Cl^-).$$

(39) $CuCl - CuCl_2^- + Cl^- = 0$:
$$\log (CuCl_2^-) = - 1{\cdot}19 + \log (Cl^-).$$

(40) $Cu_2O - 2CuCl_2^- + 4Cl^- - H_2O + 2H^+ = 0$:
$$\log (CuCl_2^-) = 4{\cdot}63 + 2 \log (Cl^-) - pH.$$

(*b*) *With oxidation*

(41) $CuCl_2^- - Cu - 2Cl^- + e^- = 0$:
$$E = 0{\cdot}194 + 0{\cdot}0591 \log \frac{(CuCl_2^-)}{(Cl^-)^2}.$$

(42) $CuO - CuCl_2^- + 2Cl^- - H_2O + 2H^+ + e^- = 0$:
$$E = 0{\cdot}944 - 0{\cdot}1182pH + 0{\cdot}0591 \log \frac{(Cl^-)^2}{(CuCl_2^-)}.$$

(43) $Cu^{++} - CuCl + Cl^- + e^- = 0$:
$$E = 0{\cdot}566 + 0{\cdot}0591 \log (Cu^{++})(Cl^-).$$

(44) $CuO_2H^- - CuCl + Cl^- - 2H_2O + 3H^+ + e^- = 0$:
$$E = 2{\cdot}139 - 0{\cdot}1773pH + 0{\cdot}0591 \log (CuO_2H^-)(Cl^-).$$

(45) $CuO_2^{--} - CuCl + Cl^- - 2H_2O + 4H^+ + e^- = 0$:
$$E = 2{\cdot}914 - 0{\cdot}2364pH + 0{\cdot}0591 \log (CuO_2^{--})(Cl^-).$$

Figs. 12, 13 and 15 show the equilibria in the Cu-Cl-H$_2$O system; the derivation of these figures is as follows:

Homogeneous Equilibria. For a given activity of the Cl$^-$ ions, it is possible to set up a diagram analogous to fig. 9, showing the domains of predominance of the various ionic species, Cu$^+$ and/or $CuCl_2^-$,

CuO_2H^- and CuO_2^{--}. Taking the Cl^- activity to be 10^{-2} M., equations (31) to (34) become respectively:

(31′) $Cu^+/CuCl_2^-$ equilibrium: $\log \frac{(CuCl_2^-)}{(Cu^+)} = 1{\cdot}55.$

(32′) $Cu^{++}/CuCl_2^-$ equilibrium: $E = 0{\cdot}259 + 0{\cdot}0591 \log \frac{(Cu^{++})}{(CuCl_2^-)}.$

(33′) $CuO_2H^-/CuCl_2^-$ equilibrium: $E = 1{\cdot}831 - 0{\cdot}1773\text{pH} + 0{\cdot}0591 \log \frac{(CuO_2H^-)}{(CuCl_2^-)}.$

(34′) $CuO_2^{--}/CuCl_2^-$ equilibrium: $E = 2{\cdot}606 - 0{\cdot}2364\text{pH} + 0{\cdot}0591 \log \frac{(CuO_2^{--})}{(CuCl_2^-)}.$

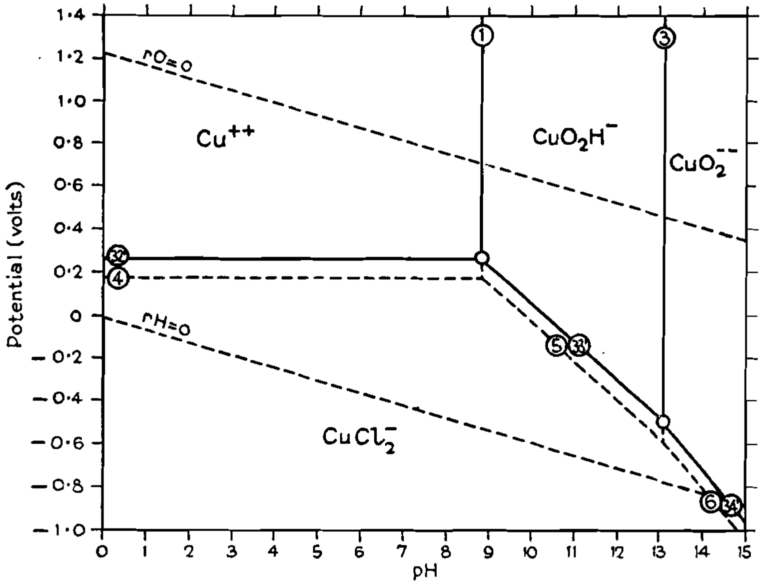


FIG. 12.—System Cu-Cl-H_2O. Domains of predominance of solutes when Cl^- activity in the solution is 0·01 M.

Fig. 12 is based on these equations, together with (1) to (6) of p. 54–5, and shows the domains of predominance of the various solutes under consideration; the limits of the corresponding domains in a solution free from chlorides, already plotted in fig. 9, are also shown (broken lines).

It will be seen that the Cu^+ ion is nowhere the predominant copper derivative in an 0·01 M. chloride solution; in fact, (31′) shows that the concentration of $CuCl_2^-$ is always seventy-four times greater than that of Cu^+. $CuCl_2^-$ has become the predominant ion in the whole of what was formerly the domain of predominance of Cu^+, and the new domain of $CuCl_2^-$ extends beyond the limits of the old Cu^+ domain, into regions in which other ions were previously predominant.

Heterogeneous Equilibria involving two solid phases. The stability

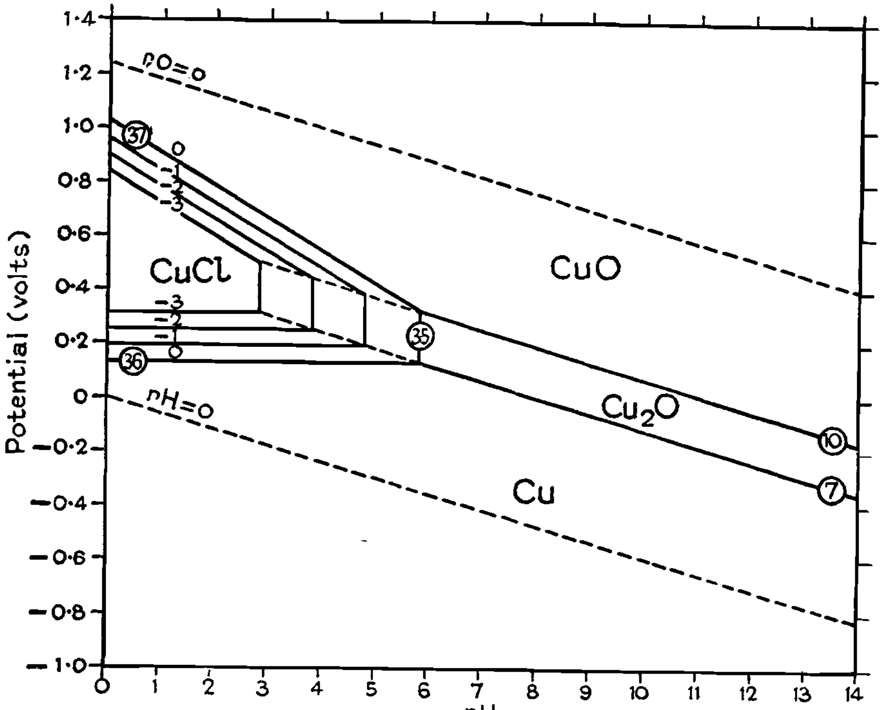


FIG. 13.—System Cu-Cl-H_2O. Domains of stability of solid phases when Cl^- activity in the solution is 1, 10^{-1}, 10^{-2} and 10^{-3} M.

domains of the various solids at different Cl^- activities can be shown in diagrams analogous to fig. 10, which refers to zero chloride activity.

Fig. 13, based on equations (7), (8), (35) and (37), shows the domains of stability of Cu, Cu_2O, CuO and CuCl at chloride activities equal to 1, 10^{-1}, 10^{-2} and 10^{-3} M. It will be recalled that $Cu(OH)_2$ has been omitted for the sake of simplicity; in addition the diagram takes no account of basic chlorides. Such compounds may possess domains of stability in the neighbourhood of the lines separating the CuCl domain from the Cu_2O and CuO domains.

At all chloride concentrations there is a domain, with the shape of a truncated triangle, where CuCl is the stable condensed phase. Below this domain, CuCl is reduced to metallic Cu,

$$\mathrm{CuCl} + e^- \rightarrow \mathrm{Cu} + \mathrm{Cl}^-;$$

above it, CuCl is oxidized with formation of CuO,

$$\mathrm{CuCl} + \mathrm{H_2O} \rightarrow \mathrm{CuO} + 2\mathrm{H}^+ + e^-;$$

and to the right, CuCl is transformed into cuprous oxide,

$$2\mathrm{CuCl} + \mathrm{H_2O} \rightarrow \mathrm{Cu_2O} + 2\mathrm{H}^+ + 2\mathrm{Cl}^-.$$

Heterogeneous Equilibria involving one solid phase. A combined diagram similar to fig. 11, showing, *inter alia*, the solubilities of the various solids, can be developed in the manner already described. Considering a solution in which the Cl^- activity is 10^{-2} M., equations (38) to (45) become

(38′) $\mathrm{CuCl/Cu^+}$ equilibrium:

$$\log(\mathrm{Cu^+}) = -4{\cdot}74.$$

(39′) $\mathrm{CuCl/CuCl_2^-}$ equilibrium:

$$\log(\mathrm{CuCl_2^-}) = -3{\cdot}19.$$

(40′) $\mathrm{Cu_2O/CuCl_2^-}$ equilibrium:

$$\log(\mathrm{CuCl_2^-}) = 0{\cdot}26 - \mathrm{pH}.$$

(41′) $\mathrm{Cu/CuCl_2^-}$ equilibrium:

$$E = 0{\cdot}430 + 0{\cdot}0591 \log(\mathrm{CuCl_2^-}).$$

(42′) $\mathrm{CuO/CuCl_2^-}$ equilibrium:

$$E = 0{\cdot}708 - 0{\cdot}1182\mathrm{pH} - 0{\cdot}0591 \log(\mathrm{CuCl_2^-}).$$

(43′) $\mathrm{CuCl/Cu^{++}}$ equilibrium:

$$E = 0{\cdot}448 + 0{\cdot}0591 \log(\mathrm{Cu^{++}}).$$

(44′) $\mathrm{CuCl/CuO_2H^-}$ equilibrium:

$$E = 2{\cdot}021 - 0{\cdot}1773\mathrm{pH} + 0{\cdot}0591 \log(\mathrm{CuO_2H^-}).$$

(45′) $\mathrm{CuCl/CuO_2^{--}}$ equilibrium:

$$E = 2{\cdot}796 - 0{\cdot}2364\mathrm{pH} + 0{\cdot}0591 \log(\mathrm{CuO_2^{--}}).$$

These expressions, in conjunction with those given previously, make it possible to plot fig. 15, which is an equilibrium diagram of the ternary system Cu-Cl-$\mathrm{H_2O}$ for a chloride ion activity of 10^{-2} M. Fig. 14, which refers to a solution containing no chloride, has been plotted on the same scale as fig. 15, so that the influence of the chloride ion can be more readily appreciated.

To simplify the interpretation of the curves of *total* solubility, ($\mathrm{Cu^+} + \mathrm{Cu^{++}} + \mathrm{CuCl_2^-}$), the effect of potential on the *separate* solubilities, as $\mathrm{Cu^+}$, $\mathrm{Cu^{++}}$ and $\mathrm{CuCl_2^-}$, in presence of Cu and of CuCl, is shown in fig. 16. The straight lines (19) and (20), which give the solubility of metallic copper as $\mathrm{Cu^+}$ ions and $\mathrm{Cu^{++}}$ ions respectively, intersect at a point of ordinate $+0{\cdot}168$ V.; this is the standard potential for the $\mathrm{Cu^{++}/Cu^+}$ equilibrium, at which the concentrations of $\mathrm{Cu^+}$ and $\mathrm{Cu^{++}}$ ions are equal, amounting in this case to 10^{-6} g.-ion per litre. The total solubility of copper in absence of chlorides is shown by a broken curve inscribed within the lines (19) and (20); from this curve one may readily read off the potentials at which the total solubility as $\mathrm{Cu^+} + \mathrm{Cu^{++}}$ has a given value.

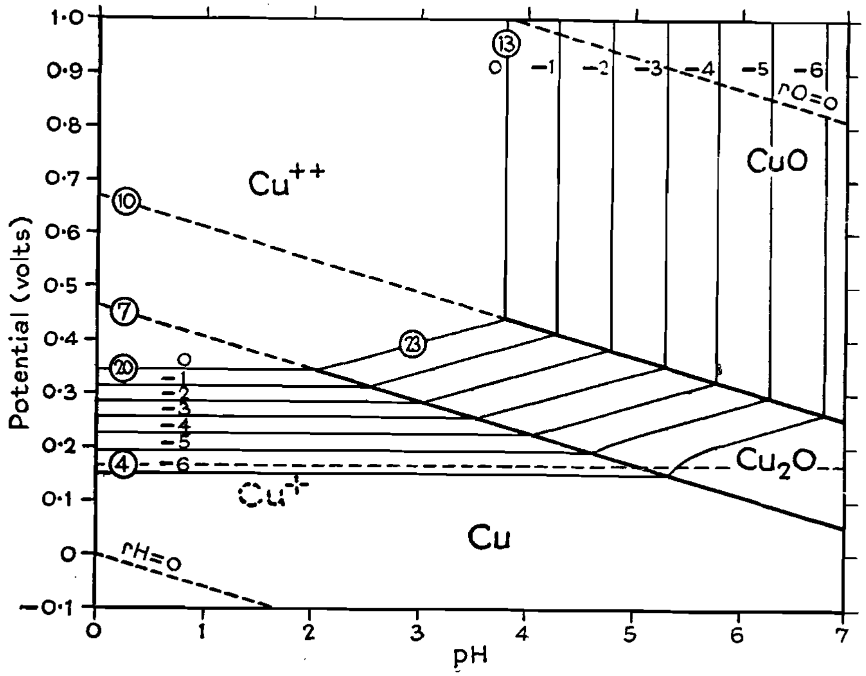


Fig. 14.—System Cu-$\mathrm{H_2O}$. Combined diagram (detail).

The solubility of metallic copper as the complex ion $\mathrm{CuCl_2^-}$ is shown by line (41′), which intersects line (20) at $+0{\cdot}259$ V., at which potential the concentrations of $\mathrm{Cu^{++}}$ and $\mathrm{CuCl_2^-}$ are equal. The solubilities of CuCl as $\mathrm{Cu^+}$, $\mathrm{Cu^{++}}$ and $\mathrm{CuCl_2^-}$ ions are represented by the lines (38′), (43′) and (39′), which cut the lines (19), (20) and (41′) respectively at $+0{\cdot}242$ V. The latter three lines refer to the equilibrium between metallic copper and the three ions; Cu and CuCl are in equilibrium with one another at this potential.

The total solubilities of metallic copper and of CuCl in the three forms $\mathrm{Cu^+}$, $\mathrm{Cu^{++}}$ and $\mathrm{CuCl_2^-}$ together, can readily be derived from the lines mentioned; it is, in fact, only necessary to read off the values of log (Cu^+), log (Cu^{++}) and log $(CuCl_2^-)$ at various potentials, from which the separate activities (Cu^+), (Cu^{++}) and $(CuCl_2^-)$, their sum and its logarithm, log $((Cu^+) + (Cu^{++}) + (CuCl_2^-))$ may be calculated. For ideal solutions, the activities are, of course, equal to the concentrations. The two curves obtained in this way, with Cu and CuCl as solid phases, intersect at +0·242 V.; the stable solid is CuCl or Cu according as the potential is above or below this value, and the required solubility curve, plotted as a thick line in fig. 16, thus has two branches, referring to CuCl and to Cu, or to potentials above and below +0·242 V.

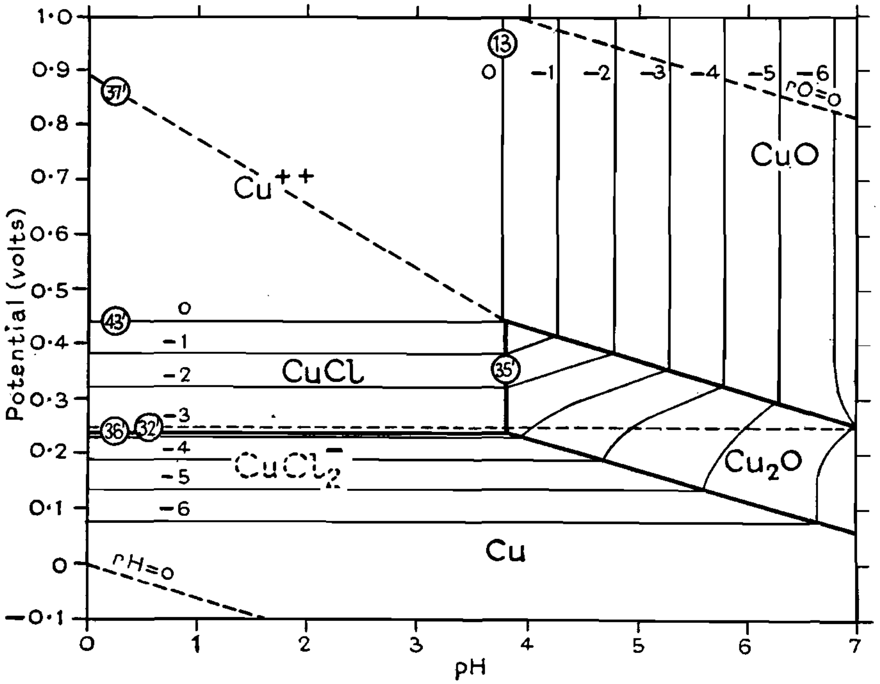


FIG. 15.—System Cu-Cl-H_2O. Combined diagram (detail) when Cl^- activity in the solution is 0·01 M.

At potentials lower than +0·260 V., the presence of 0·01 g.-ion of Cl^- per litre causes an increase of the quantity of copper dissolved, owing to formation of $CuCl_2^-$, as may be seen by comparing the thick, continuous curve with the broken curve; above +0·260 V., on the other hand, and on the hypothesis that no soluble complex other than $CuCl_2^-$ is formed (which is probably not strictly true), the presence of chloride *may* diminish the amount of copper in solution, owing to the formation of a film of CuCl on the metal.

The following table, which is derived from fig. 16, shows the potentials (in volts) at which the solubilities of metallic copper as $(Cu^+ + Cu^{++})$, and of CuCl and Cu as $(Cu^+ + Cu^{++} + CuCl_2^-)$, have certain predetermined values:

Total solubility (g.-ion per litre)	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
Potential in absence of chloride.							
Solid phase: Cu	0·345	0·315	0·286	0·256	0·227	0·192	0·150
Potential in presence of chloride, $(Cl^-) = 10^{-2}$ M.							
Solid phase: CuCl	0·448	0·389	0·325	—	—	—	—
Cu	—	—	—	0·230	0·188	0·135	0·076

The lines of constant solubility in figs. 14 and 15 may be plotted by using these values.

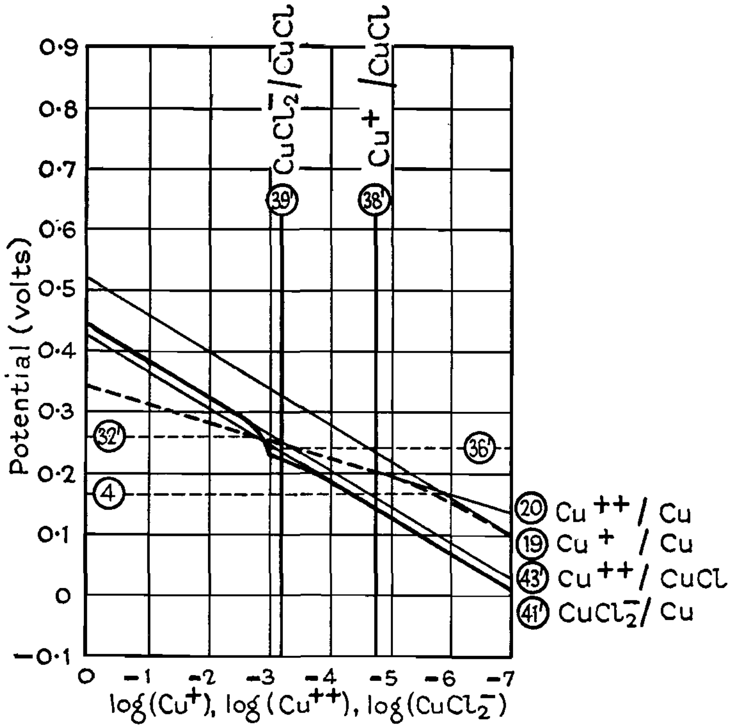


FIG. 16.—Influence of potential on (Cu^+), (Cu^{++}), $(CuCl_2^-)$ and on $(Cu^+)+(Cu^{++})+(CuCl_2^-)$, in contact with Cu metal and with CuCl. (Cl^-)=0·01 M.

The curves in fig. 15 showing the total solubilities of Cu_2O and CuO can be obtained by drawing the lines for which the partial solubilities as Cu^{++} and as $CuCl_2^-$ have given values, using equations (23), (13), (40′) and (42′); it is then a simple matter to find the points at which the total solubility as $Cu^{++} + CuCl_2^-$ has the same value.

It can be seen from fig. 15 that CuCl is stable in contact with solutions with Cl^- activity equal to 10^{-2} M. only if the total copper in solution as $Cu^+ + Cu^{++} + CuCl_2^-$ equals or exceeds 10^{-3} M., and if the potential is not less than +0·242 V. It will also be noticed that the lines for constant solubility in presence of Cu_2O are curved at potentials around +0·259 V., where the activities of Cu^{++} and $CuCl_2^-$ are equal; a similar feature of figs. 11 and 14 is mentioned on p. 60.

(d) The Electrolysis of Copper Solutions

A short discussion is given below of the electrolysis of solutions containing copper, in presence of sulphuric acid and of cyanides at 25°C.

Sulphuric acid solutions

If two insulated copper electrodes are immersed in an acid $CuSO_4$ solution containing 1 g.-atom of copper per litre, they will take up a potential of approximately +0·35 V. (point *A*, fig. 17). If a difference of potential is applied to the electrodes, the anode, *B*, having a representative point in the stability domain of the Cu^{++} ion, will dissolve ($Cu \rightarrow Cu^{++} + 2e^-$); a deposit of copper will form on the cathode *C*, whose representative point lies in the stability domain of metallic copper ($Cu^{++} + 2e^- \rightarrow Cu$).

This situation arises in the electrolytic refining of copper, in copper-plating from an acid bath, and in the copper voltameter. Investigations of the copper voltameter have shown that the cathodic current efficiency is less than unity and that Cu_2O may be formed at both electrodes; the latter effect has been studied by Meyer[82] and by Dony-Hénault.[22]

If the cathodic current efficiency is to be unity, metallic copper alone must be formed by reduction at the cathode; the potential, E_C, of the point *C*, must therefore have a value that is not lower than $(E_{C'} + s)$, where $E_{C'}$ is the potential of a reversible hydrogen electrode at the pH of the catholyte and *s* is the overpotential of hydrogen on the copper deposit. If E_C is lower than $(E_{C'} + s)$, liberation of hydrogen at the cathode becomes appreciable.

It thus appears that the current density must not be too high if the cathodic deposition of copper is to be quantitative, especially in strongly acid solutions. An increase of current density lowers the cathode potential; moreover, the domain in which point *C* may lie, situated between the lines $E = +0{\cdot}30$ and $E = E_{C'} + s$, becomes narrower as the pH is reduced. It will be recalled that the overpotential here has a negative value, in accordance with the definition given on p. 45; the potential $E_{C'} + s$ is lower than $E_{C'}$.

On the other hand, if the solution of $CuSO_4$ is only very slightly acid (pH higher than approximately 3), the cathodic point *c* may lie in the stability domain of Cu_2O (see fig. 17); in this case, Cu_2O may be formed at the cathode. Moreover, if the cathodic potential falls below the line rH = 0, hydrogen may be evolved and the solution become more alkaline, whereby the representative points for all parts of the solution are displaced to the right. It is important to note that this displacement applies to all parts of the solution—in particular, to the anodic point, *b*—and not only to the catholyte; the anodic point, *b*, may thus be moved into the stability domain of Cu_2O or CuO.

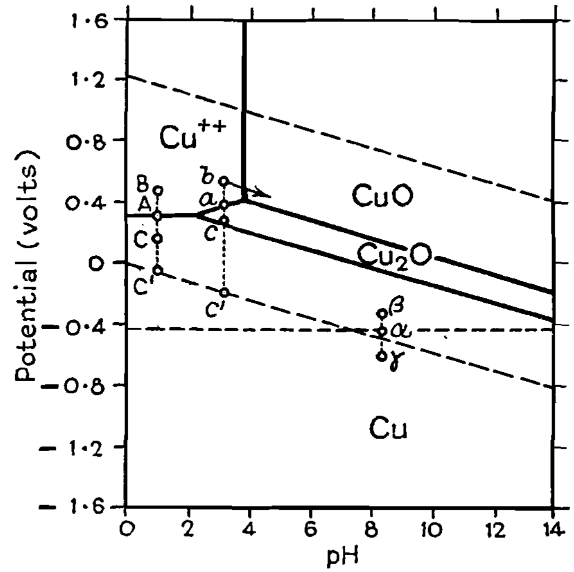


FIG. 17.—Electrolysis of copper solutions.

This is possibly an explanation of the formation of Cu_2O at ***both*** electrodes of a voltameter, as observed by Meyer and Dony-Hénault; further experimental work on the subject would be useful. An analogous mechanism may also account for the formation of $Cu(OH)_2$ in electrolysis by an electric discharge, as demonstrated by Jolibois.[60]

Cyanide Solutions

In cyanide solutions we have to deal with a system in which the Cu^+ and Cu^{++} ions are locked up in a complex such as $Cu(CN)_2^-$, and have practically no existence in the free state; we thus obtain a solution in which the blue colour of the Cu^{++} ion has vanished and which possesses a considerably enlarged stability domain (see p. 67).

Two insulated copper electrodes immersed in a cyanide solution, such as that considered on p. 67, will take up a potential of approximately $-0{\cdot}43$ V. (point *a* in fig. 17). If a difference of potential is applied to these electrodes, the anode, with a representative point in the stability domain of $Cu(CN)_2^-$, will dissolve. The representative point of the cathode lies in the stability domain of metallic copper, and possibly in that of gaseous hydrogen, so that copper is deposited and hydrogen may be liberated at the cathode; reduction products of the cyanide, such as NH_3, may also be formed.

It is well known that copper can be electro-deposited from an alkaline bath under these conditions—iron may thus be copper-plated. For satisfactory operation, the ratio of the concentrations of CN^- and $Cu(CN)_2^-$ ions in the bath (in other words, the copper/cyanide ratio) must be carefully controlled; in fact, this ratio controls the equilibrium potential of the copper, which is fundamentally important in determining the cathodic reactions.

(e) "Corrosion Domains" of Copper

Following the discussion given on p. 50, it will be assumed as a first approximation that copper does not corrode when the solution is incapable of dissolving more than 10^{-6} g.-atom per litre (i.e. 0·06 mg. Cu per litre). With the help of the data given in fig. 11, the potential-pH diagram may be divided into a "domain of corrosion" and a "domain of non-corrosion", the two domains being separated by the line of index -6. In accordance with Chaudron's suggestion (see p. 51), the metal will be considered "immune" in that part of the domain of non-corrosion where metallic copper is the stable solid phase, and "passivated" in those parts where the stable solid is Cu_2O, CuO or $Cu(OH)_2$. The two conditions of the metal are termed "immunity" and "passivation".

The domains of corrosion, immunity and passivation of copper are shown in fig. 18; in plotting this diagram, it has been assumed that passivation in oxidizing media results from the formation of a film of hydroxide $Cu(OH)_2$, with a solubility product $(Cu^{++})(OH)^2 = 10^{-19{\cdot}00}$. This assumption requires experimental verification; the passivation domain will be larger in all directions than the domain shown if the hydroxide responsible for it is more stable than that considered, and vice versa.

Fig. 18 shows that the corrosion domain consists of two regions, which refer respectively to acid and neutral media, and to alkaline media. In acid media, with pH's below *c.* 5·4, the boundary of the corrosion domain is a horizontal straight line at a potential of $+0{\cdot}15$ V. approximately (see the line of index -6 in fig. 14 for greater accuracy), and refers to a truly metallic copper surface. When the pH is above 5·4, the boundary line changes in direction; after a short curved portion, it takes up an oblique but substantially linear course, and in this region the metal is covered with Cu_2O, which completely shields it from the action of the solution and protects it from destruction, *provided an adherent and non-porous layer is formed.* In such a case, passivation entails complete absence of corrosion, but if the Cu_2O occurs in a granular form or as a cracked film, the metal may change continuously into Cu_2O, provided the conditions of potential and pH in the cracks and fissures are suitable; corrosion of the metal may now take place, although the quantity of copper in solution always remains extremely small. At a pH in the neighbourhood of 7·5 (for $Cu(OH)_2$) or 6·8 (for CuO), the boundary of the corrosion domain intersects the line (11) or (10) of fig. 11; beyond these points, which correspond to rH values of 25·6 or 22·7, Cu_2O can change into $Cu(OH)_2$ or CuO, and the boundary of the corrosion domain takes up a vertical position. The metal is thus covered by successive layers of Cu_2O, and $Cu(OH)_2$ or CuO.

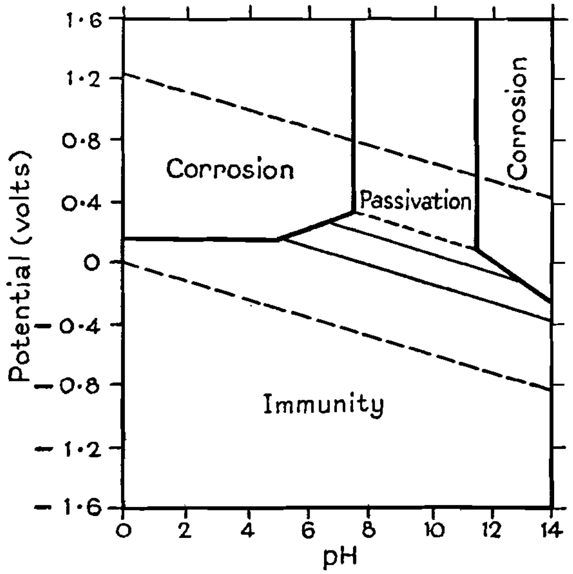


FIG. 18.—Domains of corrosion, immunity and passivation for copper.

In very alkaline media, at pH's in the region of 11·6 to 12·8, $Cu(OH)_2$ and CuO are no longer stable and tend to dissolve; a second "corrosion domain" thus makes its appearance, with an oblique line as its lower boundary. Along this line, the stable solid is Cu_2O, and the metal may become covered by this substance.

It is evident that this representation of the domains of corrosion, immunity and passivation is no longer valid when the copper exists in solution as ionic species other than those considered—namely, Cu^+, Cu^{++}, CuO_2H^- and CuO_2^-. If the solution contains substances capable of forming soluble complexes with these ions (e.g. bromides, iodides or cyanides) the extent of the corrosion domain may be considerably increased; conversely, if the solution contains substances which react with the ions to form an adherent solid precipitate on the metal, the extent of the domain may be reduced. Some substances can exercise both actions simultaneously; among these, as pointed out above, are chlorides, which form the complex ions $CuCl_2^-$ and the sparingly soluble CuCl, and in such cases the corrosion domain will be increased in some regions and may be diminished in others.

The writer has carried out experiments on the behaviour of copper under the conditions to which fig. 18 relates, and has observed that corrosion does in fact occur when the potential lies in one or other of the two corrosion domains shown in this figure, and that the metal is immune or passivated when the potential lies in the corresponding domains.

(f) The Potential of Electrically Insulated Copper

The classical law of Nernst, expressed by equations [19] and [20], enables one to calculate the equilibrium potential of copper as a function of the amounts of Cu^+ and Cu^{++} ions in the solution—at least, for ideal solutions. It is, however, valid only when the surface of the metal is really metallic; it does not hold, for example, when the metal is covered by a layer of some other substance, such as Cu_2O. Nernst's law is thus only applicable within the stability domain of metallic copper, i.e. below line (7) in fig. 11; in a solution containing 10^{-4} g.-atom of copper per litre as $Cu^+ + Cu^{++}$ and no complex forming constituents, the law is thus valid only at pH's below 4·2.

At higher pH's, the law no longer holds. In media which are actually alkaline, where the copper exists mainly as the ions CuO_2H^- and CuO_2^{--} rather than Cu^+ and Cu^{++}, the potential is given by equations such as [24] and [25], which refer to the CuO_2H^-/Cu_2O and CuO_2^{--}/Cu_2O equilibria, and it is shown in fig. 11 by lines having slopes between −118·2 and −177·3 mV. per pH unit. These curves differ completely from the horizontal straight lines on the left of the diagram, which represent Nernst's law.

In an investigation of the potentials of copper specimens in NaOH solutions (unstirred and not de-aerated) of different concentrations, the following values were observed:

pH	11·3	11·6	11·9	12·1	12·4	12·8	13·3
Potentials (volts):							
	−0·006	+0·128	+0·108	+0·088	+0·049	+0·008	−0·040
	−0·002	+0·133	+0·102	+0·078	+0·047	+0·011	−0·061

If these values are plotted in fig. 11, they are found to lie in the corrosion domain (as shown in fig. 18,) except for that at pH = 11·6, and they roughly follow the zone comprising solubilities between 10^{-5} and 10^{-4} M. This solubility is compatible with the corrosive action of the dissolved oxygen present in the solution.

Gatty and Spooner[38] state that one would expect the potential of copper in presence of oxygen to be as high in alkaline media as in acid, and they draw attention to the fall of potential which manifests itself in alkaline media. This is readily explained by fig. 11; in strongly alkaline media, the potential is controlled by the $CuO_2H^- + CuO_2^{--}/Cu_2O$ equilibrium, and not by the $Cu^+ + Cu^{++}/Cu$ equilibrium which determines the potential in acids.

B. THE SYSTEM Fe-H_2O

In the following discussion, data available in the literature are used to set up an equilibrium diagram of the Fe-H_2O system; the stability of iron compounds, the corrosion of iron, the potential behaviour of insulated iron specimens and the protection of iron against corrosion are then discussed on the basis of this diagram. Figs. *22a* and *22b* show the approximate* conditions of thermodynamic stability of iron and of some of its compounds, in the presence of a dilute aqueous solution at 25° C.

* Owing to the inadequacy of the available information as to the stability of certain derivatives of iron, we have had to neglect:

the hypoferrite ion, FeO_2^{--}, containing divalent iron and stable in strongly alkaline media (see Thiesse,[116]);
the ferrite ions FeO_2^- or $Fe_2O_4^{--}$, containing trivalent iron;
soluble derivatives of hexavalent iron other than the ferrate ion FeO_4^{--}; the value of μ^0 assumed for this ion is in any case only a very rough approximation;
solid oxides of greater oxygen content than Fe_2O_3.

Complex ions derived from iron are discussed by Grube and Gmelin.[44] Only one form of $Fe(OH)_2$ (solubility product $(Fe^{++})(OH^-)^2 = 10^{-14 \cdot 65}$) has been considered, and only two forms of $Fe_2O_3 . nH_2O$, one for each of the two figs. *22a* and *22b* (solubility products $(Fe^{+++}) . (OH^-)^3 = 10^{-38 \cdot 25}$ and $10^{-42 \cdot 00}$, respectively). These oxides can actually exist in several forms, possessing distinctly different thermodynamic properties; solubility products for Fe_2O_3 quoted in the literature range from 10^{-36} to $10^{-46 \cdot 2}$.

Finally, several clearly different ferrous ferrites can be formed under the conditions of pH and potential in which Fe_3O_4 appears as the stable solid phase (see Fricke and Hüttig[36]); in practice, the iron content and the Fe^{+++}/Fe^{++} ratio in "magnetite" vary with the method of preparation, and the compound thus possesses no characteristic potential.

The standard chemical potentials of $Fe(OH)_3$, $FeOH^{++}$, FeO_4^{--}, and FeO_2H^- have been calculated as follows:

$Fe(OH)_3$. We adopt two values for the solubility product $(Fe^{+++})(OH^-)^3$, pertaining to the reaction $Fe^{+++} + 3OH^- = Fe(OH)_3$, namely $10^{-38{\cdot}25}$ (Cooper[16]) and $10^{-42{\cdot}0}$; these are used to compute the values marked (*a*) and (*b*) respectively. We assume further that $\mu^0_{Fe^{+++}} = -\ 3120$ cal.

$Fe(OH)^{++}$. According to Bray and Hershey,[7] the equilibrium constant of the reaction $FeOH^{++} + H^+ = Fe^{+++} + H_2O$ is

$$K = \frac{(FeOH^{++})\,.\,(H^+)}{(Fe^{+++})} = 10^{-2{\cdot}22}.$$

We have used this value, together with $\mu^0_{Fe^{+++}} = -\ 3120$ cal.

FeO_4^{--}. As no better data exist, we have provisionally assumed that the standard potential for the equilibrium $Fe^{+++} + 4H_2O = FeO_4^{--} + 8H^+ + 3e^-$ is approximately $E^0 = +\ 1{\cdot}7$ V. This value is given by Latimer and Hildebrand;[56] as before, we assume $\mu^0_{Fe^{+++}} = -\ 3120$ cal. According to Van Bohnson and Robertson,[122] the free energy of formation (here identical with μ^0) of FeO_4^{--} should lie between —106,885 and —182,155 cal., and is probably in the neighbourhood of —140,000 cal., instead of —111,760 as we have assumed; it is likely that all these values are lower than the true value.

FeO_2H^-. We have taken the solubility product for the reaction $FeO_2H^- + H^+ = Fe(OH)_2$ to be

$$(FeO_2H^-)\,.\,(H^+) = 10^{-18{\cdot}3} \text{ (Schrager}^{110}\text{)}.$$

In addition, we take $\mu^0_{Fe(OH)_2}$ to be —115,200 cal.

References to literature on chemical potentials: Chipman and Murphy;[12] Lewis and Randall;[75] Randall and Frandsen;[99] Ulich.[121]

1. Derivation of Figs. 20a and 20b

The standard chemical potentials adopted for the various substances under consideration are given in the following table. Values marked ** are those calculated above.

Solvent and solutes			Solids		
$\mu^0_{H_2O}$	=	— 56,560 cal.[75]			
$\mu^0_{H^+}$	=	0 cal.			
$\mu^0_{OH^-}$	=	— 37,455 cal.[121]			
$\mu^0_{Fe^{++}}$	=	— 20,310 cal.[99]	μ^0_{Fe}	=	0 cal.
$\mu^0_{Fe^{+++}}$	=	— 3,120 cal.[75]	$\mu^0_{Fe(OH)_2}$	=	—115,220 cal.[99]
$\mu^0_{FeOH^{++}}$	=	— 56,650 cal.**	$\mu^0_{Fe(OH)_3}$	=	—167,640 cal. (*a*)**
$\mu^0_{FeO_4^{--}}$	=	—111,760 cal.**	$\mu^0_{Fe(OH)_3}$	=	—172,745 cal. (*b*)**
$\mu^0_{FeO_2H^-}$	=	— 90,250 cal.**	$\mu^0_{Fe_3O_4}$	=	—241,820 cal.[12]

The equilibrium conditions for the various possible reactions can now be obtained without difficulty, by the use of the equations summarized on p. 54. The results are tabulated below; as usual, E is expressed in volts with respect to the standard hydrogen electrode. Two values are given for all reactions involving $Fe(OH)_3$, corresponding to the two values, (*a*) and (*b*), of $\mu^0_{Fe(OH)_3}$.

1. *Homogeneous Reactions*

(*a*) *Without oxidation*

(1) $FeOH^{++} - Fe^{+++} - H_2O + H^+ = 0$:

$$\log \frac{(FeOH^{++})}{(Fe^{+++})} = -\ 2{\cdot}22 + pH.$$

(2) $FeO_2H^- - Fe^{++} - 2H_2O + 3H^+ = 0$:

$$\log \frac{(FeO_2H^-)}{(Fe^{++})} = -\ 31{\cdot}70 + 3pH.$$

(*b*) *With oxidation*

(3) $Fe^{+++} - Fe^{++} + e^- = 0$:

$$E = 0{\cdot}746 + 0{\cdot}0591 \log \frac{(Fe^{+++})}{(Fe^{++})}.$$

(4) $FeOH^{++} - Fe^{++} - H_2O + H^+ + e^- = 0$:

$$E = 0{\cdot}877 - 0{\cdot}0591pH + 0{\cdot}0591 \log \frac{(FeOH^{++})}{(Fe^{++})}.$$

(5) $FeO_4^{--} - Fe^{++} - 4H_2O + 8H^+ + 4e^- = 0$:

$$E = 1{\cdot}462 - 0{\cdot}1182pH + 0{\cdot}0148 \log \frac{(FeO_4^{--})}{(Fe^{++})}.$$

(6) $FeO_4^{--} - FeO_2H^- - 2H_2O + 5H^+ + 4e^- = 0$:

$$E = 0{\cdot}993 - 0{\cdot}0739pH + 0{\cdot}0148 \log \frac{(FeO_4^{--})}{(FeO_2H^-)}.$$

(7) $FeO_4^{--} - Fe^{+++} - 4H_2O + 8H^+ + 3e^- = 0$:

$$E = 1{\cdot}700 - 0{\cdot}1575pH + 0{\cdot}0197 \log \frac{(FeO_4^{--})}{(Fe^{+++})}.$$

(8) $FeO_4^{--} - FeOH^{++} - 3H_2O + 7H^+ + 3e^- = 0$:

$$E = 1{\cdot}657 - 0{\cdot}1378pH + 0{\cdot}0197 \log \frac{(FeO_4^{--})}{(FeOH^{++})}.$$

2. *Heterogeneous Reactions involving two solid phases*

(9) $Fe(OH)_2 - Fe - 2H_2O + 2H^+ + 2e^- = 0$:
$E = -0{\cdot}045 - 0{\cdot}0591\text{pH}$.

(10) $Fe_3O_4 - 3Fe - 4H_2O + 8H^+ + 8e^- = 0$:
$E = -0{\cdot}085 - 0{\cdot}0591\text{pH}$.

(11) $Fe(OH)_3 - Fe - 3H_2O + 3H^+ + 3e^- = 0$:
(*a*) $E = +0{\cdot}029 - 0{\cdot}0591\text{pH}$.
(*b*) $E = -0{\cdot}044 - 0{\cdot}0591\text{pH}$.

(12) $Fe_3O_4 - 3Fe(OH)_2 + 2H_2O + 2H^+ + 2e^- = 0$:
$E = -0{\cdot}202 - 0{\cdot}0591\text{pH}$.

(13) $Fe(OH)_3 - Fe(OH)_2 - H_2O + H^+ + e^- = 0$:
(*a*) $E = +0{\cdot}179 - 0{\cdot}0591\text{pH}$.
(*b*) $E = -0{\cdot}043 - 0{\cdot}0591\text{pH}$.

(14) $3Fe(OH)_3 - Fe_3O_4 - 5H_2O + H^+ + e^- = 0$:
(*a*) $E = +0{\cdot}941 - 0{\cdot}0591\text{pH}$.
(*b*) $E = +0{\cdot}276 - 0{\cdot}0591\text{pH}$.

3. *Heterogeneous Reactions involving one solid phase*

(*a*) *Without oxidation*

(15) $Fe(OH)_2 - Fe^{++} - 2H_2O + 2H^+ = 0$:
$\log (Fe^{++}) = 13{\cdot}37 - 2\text{pH}$.

(16) $FeO_2H^- - Fe(OH)_2 + H^+ = 0$:
$\log (FeO_2H^-) = -18{\cdot}30 + \text{pH}$.

(17) $Fe(OH)_3 - Fe^{+++} - 3H_2O + 3H^+ = 0$:
(*a*) $\log (Fe^{+++}) = 3{\cdot}78 - 3\text{pH}$.
(*b*) $\log (Fe^{+++}) = 0{\cdot}04 - 3\text{pH}$.

(18) $Fe(OH)_3 - FeOH^{++} - 2H_2O + 2H^+ = 0$:
(*a*) $\log (FeOH^{++}) = 1{\cdot}56 - 2\text{pH}$.
(*b*) $\log (FeOH^{++}) = -2{\cdot}18 - 2\text{pH}$.

(*b*) *With oxidation*

(19) $Fe^{++} - Fe + 2e^- = 0$:
$E = -0{\cdot}441 + 0{\cdot}0295 \log (Fe^{++})$.

(20) $FeO_2H^- - Fe - 2H_2O + 3H^+ + 2e^- = 0$:
$E = 0{\cdot}496 - 0{\cdot}0886\text{pH} + 0{\cdot}0295 \log (FeO_2H^-)$.

(21) $Fe^{+++} - Fe + 3e^- = 0$:
$E = -0{\cdot}045 + 0{\cdot}0198 \log (Fe^{+++})$.

(22) $Fe(OH)_3 - Fe^{++} - 3H_2O + 3H^+ + e^- = 0$:
(*a*) $E = 0{\cdot}969 - 0{\cdot}1773\text{pH} - 0{\cdot}0591 \log (Fe^{++})$.
(*b*) $E = 0{\cdot}748 - 0{\cdot}1773\text{pH} - 0{\cdot}0591 \log (Fe^{++})$.

(23) $Fe(OH)_3 - FeO_2H^- - H_2O + e^- = 0$:
(*a*) $E = -0{\cdot}904 - 0{\cdot}0591 \log (FeO_2H^-)$.
(*b*) $E = -1{\cdot}125 - 0{\cdot}0591 \log (FeO_2H^-)$.

(24) $FeO_4^{--} - Fe(OH)_3 - H_2O + 5H^+ + 3e^- = 0$:
(*a*) $E = 1{\cdot}627 - 0{\cdot}0985\text{pH} + 0{\cdot}0197 \log (FeO_4^{--})$.
(*b*) $E = 1{\cdot}700 - 0{\cdot}0985\text{pH} + 0{\cdot}0197 \log (FeO_4^{--})$.

(25) $Fe_3O_4 - 3Fe^{++} - 4H_2O + 8H^+ + 2e^- = 0$:
$E = 0{\cdot}983 - 0{\cdot}2363\text{pH} - 0{\cdot}0886 \log (Fe^{++})$.

(26) $Fe_3O_4 - 3FeO_2H^- + 2H_2O - H^+ + 2e^- = 0$:
$E = -1{\cdot}826 + 0{\cdot}0295\text{pH} - 0{\cdot}0886 \log (FeO_2H^-)$.

(27) $3Fe^{+++} - Fe_3O_4 + 4H_2O - 8H^+ + e^- = 0$:
$E = 0{\cdot}270 + 0{\cdot}4728\text{pH} + 0{\cdot}1773 \log (Fe^{+++})$.

(28) $3FeOH^{++} - Fe_3O_4 + H_2O - 5H^+ + e^- = 0$:
$E = 0{\cdot}664 + 0{\cdot}2955\text{pH} + 0{\cdot}1773 \log (FeOH^{++})$.

(29) $3FeO_4^{--} - Fe_3O_4 - 8H_2O + 16H^+ + 10e^- = 0$:
$E = 1{\cdot}558 - 0{\cdot}0946\text{pH} + 0{\cdot}0177 \log (FeO_4^{--})$.

The graphical presentation of these equilibrium conditions, in figs. 19, 20*a* and 20*b*, will now be discussed.

Homogeneous equilibria. The thick lines in fig. 19 denote the loci of points at which the activities (or, for an ideal solution, the concentrations) of two different iron-containing solutes are equal to one another; there is a line corresponding to each of the reactions (1) to (8); and the equation of each line is obtained by putting the logarithmic term in the corresponding equilibrium condition equal to zero.

EXAMPLE. The locus of points at which the $FeOH^{++}$ and Fe^{++} activities are equal (reaction (4)) is the line $E = 0{\cdot}877 - 0{\cdot}0591$ pH (V.); the slope is $-59{\cdot}1$ mV. per pH unit.

These eight lines intersect at four points, each of which is common to three lines; at such points, the activities of the three forms of iron coexisting in the solution are equal. The field of the diagram is divided into five domains, each corresponding to the predominance of a particular dissolved species.

The finer lines plotted in fig. 19 also refer to the reactions (1) to (8), and show the conditions under which the logarithms of the activity ratios of the various pairs of iron derivatives have values of 3, 2, 1, —1, —2 and —3—i.e. the activity ratios are respectively 1000, 100, 10, 0·1, 0·01 and 0·001. As in the analogous diagram for copper (fig. 9) each of these lines is brought to an end when it meets another line corresponding to the same relative activity of the predominant solute.

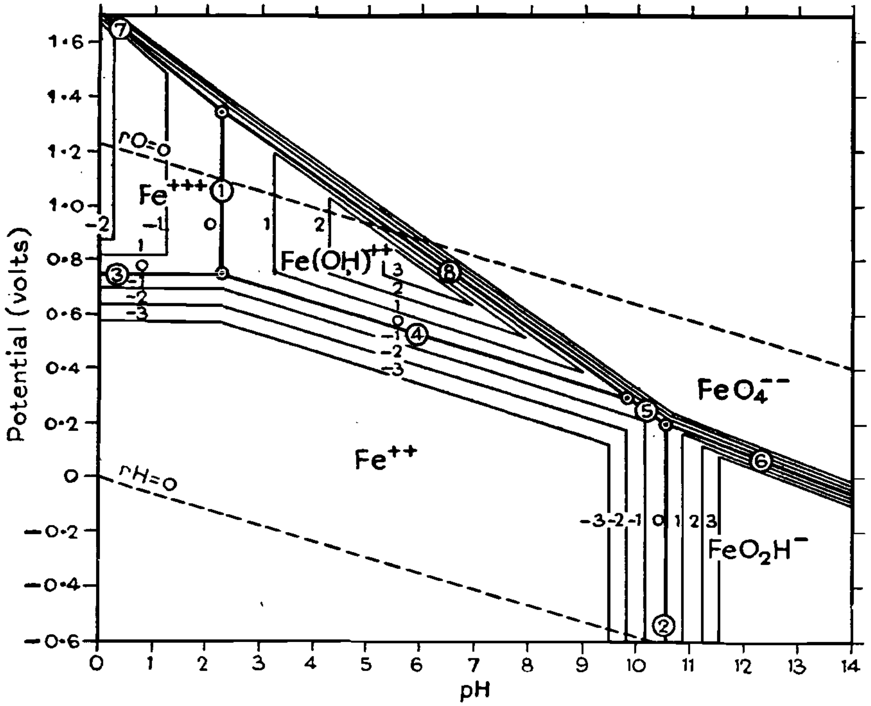


FIG. 19.—System Fe-H_2O. Domains of predominance of solutes.

EXAMPLE. The line (4) of index +1 (for which the $FeOH^{++}$ activity is ten times greater than the Fe^{++} activity) is terminated at the points where it meets line (1) of index +1 $\left(\text{for which } \frac{(FeOH^{++})}{(Fe^{+++})} = 10\right)$ and where it meets line (8) of index −1 $\left(\text{for which } \frac{(FeO_4^{--})}{(FeOH^{++})} = 0{\cdot}1, \text{ or } \frac{(FeOH^{++})}{(FeO_4^{--})} = 10\right)$.

The ratio of the activities of any two of the substances in question at any point of the diagram can be determined without difficulty from these families of lines; the level of the line of the desired family passing through the point can be found (by extrapolation or interpolation, if necessary), and is equal to the logarithm of the required ratio.

EXAMPLE. At $E = 0{\cdot}746$ V., pH $= 3{\cdot}22$, the levels of the lines (4), (1), (8) and (2) are respectively $+1{\cdot}0$, $+1{\cdot}0$, $-8{\cdot}6$, and $-22{\cdot}0$; at this point, therefore

$$\frac{(FeOH^{++})}{(Fe^{++})} = 10, \quad \frac{(FeOH^{++})}{(Fe^{+++})} = 10, \quad \frac{(FeOH^{++})}{(FeO_4^{--})} = 10^{-8\cdot6},$$

and

$$\frac{(Fe^{++})}{(FeO_2H^{-})} = 10^{22\cdot0}.$$

For one part of $FeOH^{++}$, the solution will thus contain 0·1 part Fe^{+++}, and 0·1 part of Fe^{+++}; the concentrations of FeO_4^{--} and of FeO_2H^- are negligible.

Heterogeneous equilibria involving two solid phases. The two thick lines in figs. 20*a* and 20*b* represent the equations (10) and (14*a*), and (10) and (14*b*) respectively. Parallel to these are two broken lines representing equations (9) and (13*a*) or (13*b*). These lines form the boundaries of four domains corresponding to the relative stability of each of the four substances under consideration, i.e. Fe, $Fe(OH)_2$, $Fe(OH)_3$ (or $Fe_2O_3 \,.\, nH_2O$) and Fe_3O_4. In fig, 22*a* the solubility product of Fe_2O_3 has been taken to be $10^{-38\cdot25}$, while fig 22*b* refers to a less soluble Fe_2O_3, with solubility product $10^{-42\cdot00}$.

Heterogeneous equilibria involving only one solid phase. In addition to the lines just mentioned, figs. 20*a* and 20*b* include the lines which separate the domains of predominance of the various solutes (cf. fig. 19). They also show lines which are the loci of points where the *sums* of the activities of all the five iron-containing solutes under consideration have given values (10^0, 10^{-2}, 10^{-4} and 10^{-6} g.-ion per litre). The logarithms of these values are indicated by indices adjoining the appropriate lines.

These various lines limit the "domains of thermodynamic stability" of the different compounds of iron (solid and in solution). The stability domains of iron and its oxides have been outlined in full lines for the case when magnetite, Fe_3O_4, is specifically taken into account; the broken lines show the changes that the figure undergoes when magnetite is not considered. The latter lines evidently refer to thermodynamically unstable equilibria.

2. Discussion of Figs. 20a and 20b

Figs. 20*a* and 20*b* summarize the thermodynamic equilibria of the various iron compounds under consideration. The following facts may be deduced from them.

(a) Stability of Iron Derivatives

According to the diagrams, ferrous hydroxide, $Fe(OH)_2$, is never stable in contact with an aqueous solution at 25°C.* and tends to

* A similar opinion has recently been put forward on other grounds by Fricke and Hüttig.[36]

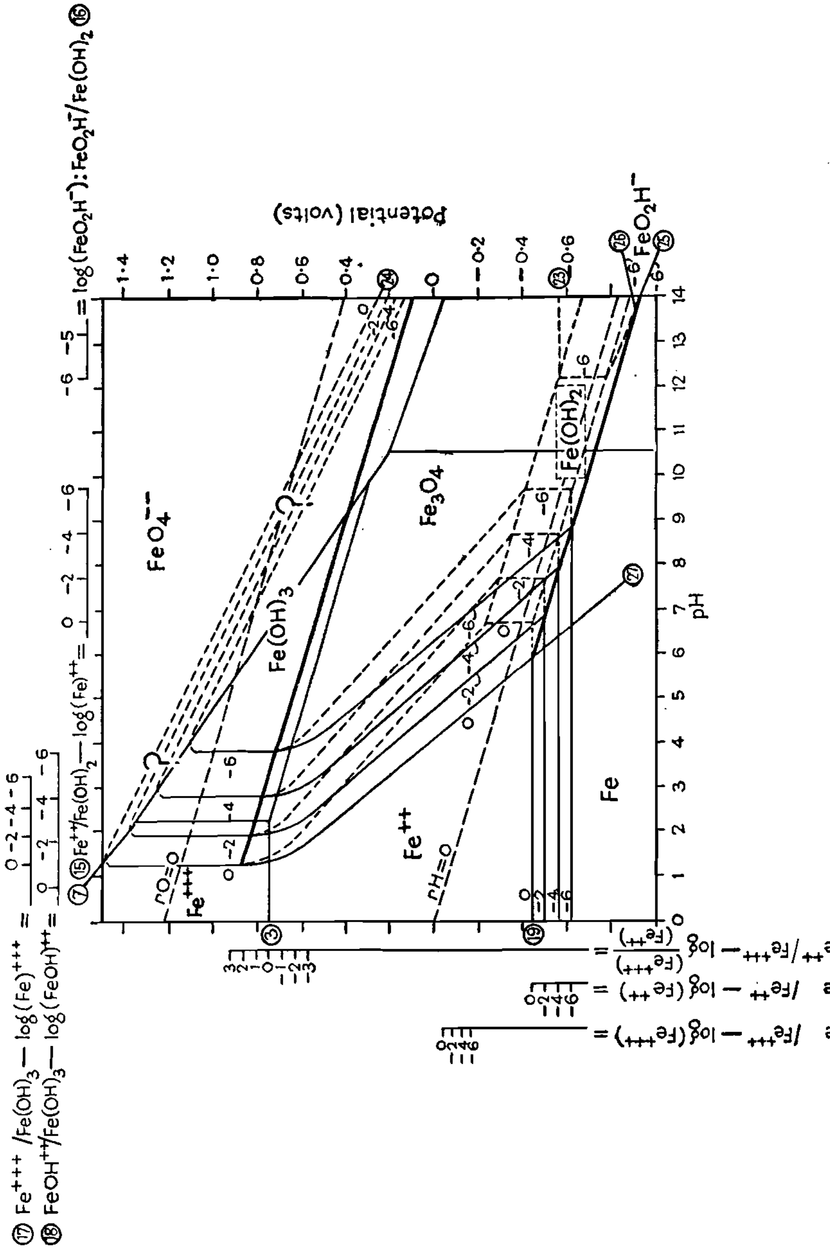


Fig. 20a.—System Fe-H_2O. Combined diagram, assuming solubility product $(Fe^{+++})(OH^-)^3 = 10^{-38 \cdot 25}$.

decompose with the formation of Fe_3O_4 or other ferrites. If the solution contains no oxidizing agent, this decomposition, or, more exactly, oxidation, can occur only if water is reduced to hydrogen, the overall reaction being of the type

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2.$$

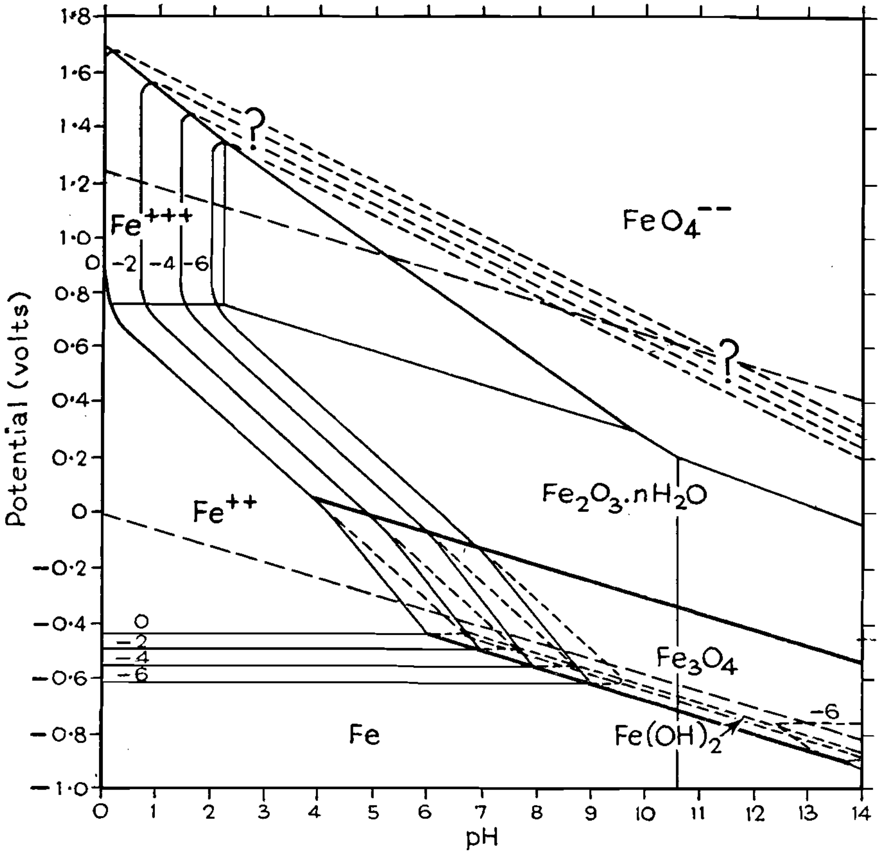


Fig. 20b.—System Fe-H_2O. Combined diagram, assuming solubility product $(Fe^{+++})(OH^-)^3 = 10^{-42 \cdot 00}$.

The hydrogen formed can escape into the surrounding atmosphere, either as bubbles (if rH < 0) or by diffusion through the solution (if rH > 0). This conclusion may be compared with an observation of Thiesse.[116] He determined the pH and redox potential of a suspension of $Fe(OH)_2$, obtained by adding different buffer solutions to a solution of $FeSO_4$, and observed negative rH values, the lowest being rH = − 3 at pH = 7·7 and E_h = − 0·54 V. This rH value corresponds approximately to the Fe/Fe_3O_4 equilibrium (reaction (10)), and, of course, it also implies that gaseous hydrogen may be evolved. It is difficult to say whether this correspondence is due to chance, because the overpotential for evolution of hydrogen on magnetite happens to be the same as the Fe/Fe_3O_4 equilibrium potential (−0·085 V.), or whether metallic iron is in reality formed by the decomposition of $Fe(OH)_2$.

Figs. 20*a* and 20*b* have been simplified too much to permit an accurate evaluation of the conditions of stability of the other oxides of iron, i.e. the various hydrated ferric oxides, $Fe_2O_3 . nH_2O$, magnetite and other ferrites. For the present it is impossible to set up a diagram satisfactory in this respect, mainly because we are ignorant of the properties and conditions of formation of the various types of ferric oxide and ferrites.[*] As already mentioned, only two types of ferric oxide (solubility products $10^{-38·25}$ and $10^{-42·00}$) have been considered in these diagrams, although the literature mentions solubility products ranging from 10^{-36} to $10^{-46·2}$,[†] according to the nature of the oxide. Hydroxides freshly prepared by addition of alkali to ferric chloride have solubility products of the order 10^{-36} to 10^{-38} and are very soluble in 1*N* H_2SO_4; oxides prepared by anodic polarization are distinctly less soluble. Such variations of solubility entail major changes in the equilibrium diagram, and a satisfactory thermodynamic treatment of any process involving any oxide of iron requires a better knowledge of the oxide than generally exists. Nevertheless, we shall see that figs. 20*a* and 20*b* lead to some important conclusions regarding the conditions for corrosion and passivation of iron, and suggest experiments which would add significantly to our understanding of the subject.

(b) "Corrosion Domains" of Iron

The correct establishment of the "corrosion domain" of iron requires accurate knowledge of the thermodynamic properties of the different substances that may cover the surface of the metal. In actual fact, this knowledge is not available for any of the three oxides ($Fe(OH)_2$, $Fe_2O_3 . nH_2O$ and Fe_3O_4) here considered.

It is generally admitted that a protective film of Fe_3O_4 is formed by anodic passivation in concentrated NaOH solutions (Grube and Gmelin[44]), although precise information is lacking as to the conditions of stability of this substance. Evans,[29] however, has shown that the superficial oxide formed on iron by anodic passivation in dilute sulphuric acid consists of Fe_2O_3, and that it does not dissolve in 0·1*N* H_2SO_4 (pH 1·3), when it is separated from its metallic basis. The implication is that the solubility product of the oxide is not greater than 10^{-42}.

---

[*] See, for example, the work of Chaudron, Hüttig, Fricke, Dreschler and Krause;[65] a summary is given by Masing[1] (pp. 186 ff.).

[†] E. Müller,[85] see also Gmelin,[41] p. 133.

In order to estimate the extent of the corrosion domain, we assume that passivation of iron occurs through the formation of an adherent film of $Fe(OH)_2$, or of Fe_2O_3 with solubility product 10^{-42}, thus neglecting cases in which passivation results from the formation of Fe_3O_4. Fig. 21 has been drawn on this assumption, the boundaries of the corrosion domain being lines for which the total concentration of dissolved iron (as Fe^{++}, Fe^{+++}, FeO_4^{--} and FeO_2H^-) is equal to 10^{-6} g.-atom per litre. These lines are derived from fig. 20*b*. In accordance with the definitions on p. 51, iron will be termed *immune* in the region where the stable solid phase is the metal, and *passivated* when the stable solid is $Fe(OH)_2$ or Fe_2O_3.

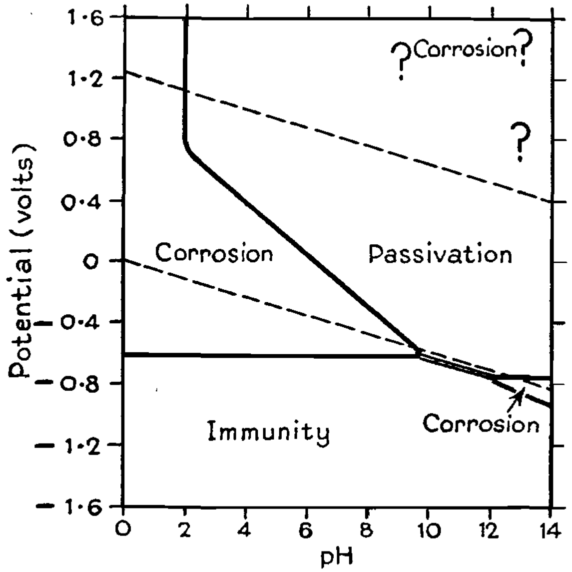


FIG. 21.—Domains of corrosion, immunity and passivation for iron.

Apart from the highly oxidizing region, which we have to neglect owing to lack of data, the corrosion domain shown in fig. 19 consists essentially of two triangular areas. At pH's less than approximately 9·6, the iron in solution exists principally as Fe^{++} ions. The lower limit of the corrosion domain is shown by a horizontal line at a potential close to −0·62 V. and refers to a specimen with a true metallic surface; the upper limit is a line with a slope of −177·5 mV. per pH unit, corresponding to a specimen covered with Fe_2O_3, more or less hydrated. At pH's greater than approximately 12·2, the iron in solution exists essentially as "bihypoferrite" ions, FeO_2H^-. The lower limit of this part of the corrosion domain is an oblique line with a slope of

$-88{\cdot}6$ mV. per pH unit; the upper limit is a horizontal line corresponding to metal covered by Fe_2O_3, as mentioned above. It should be noted that, in all probability, a film of Fe_3O_4 rather than Fe_2O_3 is sometimes responsible for passivation in these highly alkaline media.

The remarks made on pp. 78–80 with reference to copper can be transposed to the case of iron; in particular, passivation only implies absence of corrosion if the oxide covering the metal forms an adherent and non-porous layer. Furthermore, the domains of corrosion, immunity and passivation shown in fig. 21 are valid only in so far as iron is not present in solution in forms other than those mentioned (Fe^{++}, Fe^{+++}, FeO_4^{--} and FeO_2H^-); if the solution contains substances such as chlorides, cyanides or tartrates, which are capable of forming soluble complex ions with iron, the extent of the corrosion domains is increased, and possibly very considerably increased. Conversely, the area of these domains may be reduced if the solution contains substances which can form insoluble and adherent precipitates on the metal.

The corrosion and passivation of iron in various media, in relation to the pH and potential, has been investigated experimentally by the writer; the iron specimens were either insulated or used as anodes.* In agreement with fig. 21, it was found that corrosion always occurred when the potential lay in one or other of the corrosion domains shown, and that the iron was passivated when the potential lay in the passivation domain. The study of the anodic passivation of iron in media of differing pH's (solutions of sulphuric acid and bisulphate, acetic acid and acetate, bicarbonate and carbonate and sodium hydroxide) has also led the writer to the view that passivation is very probably due to a film of the *same nature* in *all* the solutions used, when the pH is less than 12. It thus seems that W. J. Müller[86,87] is wrong in attributing the anodic passivation of iron in sulphuric acid to a film of ferrous sulphate; it should be attributed rather to the formation of an oxide, probably Fe_2O_3. Evans, Chaudron and their collaborators have shown that such oxides are present in passivating films, and we assumed their formation in deriving the domain of passivation shown in fig. 21.

(c) Protection of Iron against Corrosion

According to fig. 21, corrosion of iron in ordinary waters, with pH's between 5 and 9, depends on the existence of a "dangerous triangle" in the potential-pH diagram. Iron can thus be protected against corrosion by maintaining the pH and potential at values such that the representative point lies outside this triangle, or by modifying the corrosion domain so that the triangle is partly or completely suppressed.

On these grounds one may divide the methods of protecting iron against corrosion into four groups: (i) increasing pH or alkalinity; (ii) lowering the potential to more negative values; (iii) raising the potential sufficiently in the positive direction; (iv) producing some additional solid phase, which forms a protective film on the metal and so enlarges the passivation domain.

Protection of iron by these methods can actually be achieved under the following conditions:

(i) The pH is maintained above approximately 9·6. Iron which has not previously been superficially oxidized must not, however, be put into contact with a solution which is both strongly alkaline and non-oxidizing.

(ii) The potential is maintained at a value lower than approximately $-0{\cdot}6$ V.; if the solution contains substances which form complexes with Fe^{++} and FeO_2H^- ions, such as cyanides, ammonium salts or tartrates, the potential will have to be made still lower to ensure protection of the metal. This condition is realized in practice in the protection of underground pipelines by "cathodic protection" and "electrical drainage", and by putting metals such as aluminium, magnesium or zinc in contact with the iron. Although the iron presents a true metallic surface, it does not corrode; on the other hand, the water is decomposed, with liberation of hydrogen and production of alkali. It is worth noting, as Evans[30] has pointed out, that the zinc, aluminium, etc. must be corroded if they are to protect the iron in contact with them; unless this condition is fulfilled, the potential of the iron cannot be lowered to the values required for protection. In cathodic protection, the current density which must be maintained between the pipeline and the ground will have to be increased if the pH of the soil is reduced; it will also have to be increased if the soil contains complex-forming substances.

(iii) The potential is maintained at a value sufficiently high for the representative point to lie in the passivation domain, where the metal becomes covered with a protective film of Fe_2O_3 (or Fe_3O_4). This condition is realized in passivation by oxidizing agents such as air or nitric acid, and in anodic passivation. Fig. 21 shows, however, that an oxidizing agent or anodic polarization cannot cause passivation unless the resulting rise of potential is sufficiently large; if it is not so, the representative point may remain in the corrosion domain and fail to reach the passivation domain. In these circumstances there is an actual increase in the corrosion velocity instead of passivation; the remedy is worse than the disease.

This is probably the explanation of certain observations made by Groesbeck and Waldron[42] (see Evans,[32] p. 543). These authors found that the addition of increasing quantities of oxygen to neutral or

---

* A short summary of this work has recently been published.[133, 135]

alkaline waters caused activation or passivation of iron according as the dissolved oxygen content was below or above a certain critical value, which depended on the pH. Similar considerations can also be applied to the differential aeration of iron; the experiments of Evans,[28, 32] on this subject are well known, and it has also been studied by Herzog and Chaudron,[48, 49] by Chaudron[11] and, more recently by Reiller.[102, 103] If the representative point of the aerated electrode falls in the passivation domain, it will corrode less rapidly than the unaerated electrode; on the other hand, the aerated electrode will corrode more rapidly than the unaerated if its representative point falls in the corrosion domain. Reiller has shown that differential aeration cells cease to function when the pH reaches 9·6, in agreement with fig. 21; this diagram also suggests that they should start to act once more if the pH is raised above 12·2. Experimental work in this range would be interesting.

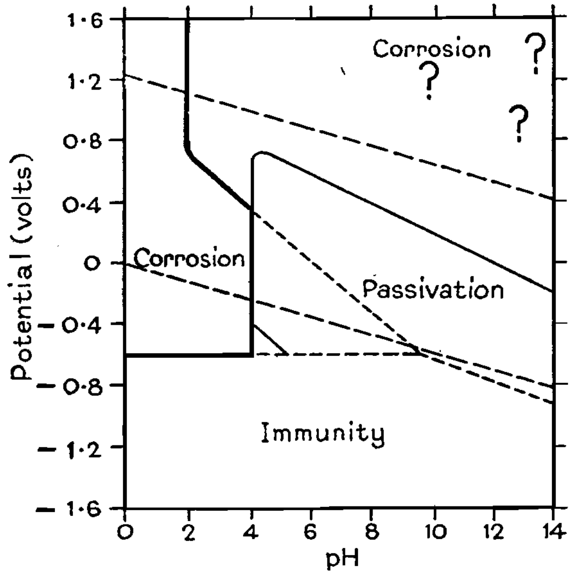


FIG. 22.—Domains of corrosion, immunity and passivation for iron in presence of chromate (solution containing 155 g. K_2CrO_4 and 3·5 g. Cl^- per l.).

(iv) An adherent surface film is formed, containing some stable foreign substance; passivation by chromates comes into this category. Comparison of the equilibrium diagrams of the systems $Fe\text{-}H_2O$ (figs. 20*a*, 20*b* and 21) and $Cr\text{-}H_2O$ (fig. 24) shows that chromates and bichromates may be reduced to some hydrated oxide of trivalent chromium (Cr_2O_3) at pH's and potentials corresponding to the "dangerous triangle" of iron. As far as thermodynamics is concerned, the reduction may be brought about either by ferrous ions or by metallic iron; in both cases the final oxidation product of the iron can be hydrated Fe_2O_3, Fe_3O_4 or other ferrites.

A chromate solution of sufficiently high concentration in contact with iron can thus be reduced in accordance with either of two reactions:

By ferrous ions

$$6Fe^{++} + 2CrO_4^{--} + 4H_2O \rightarrow 3Fe_2O_3 + Cr_2O_3 + 8H^+. \qquad (a)$$

By metallic iron

$$2Fe + 2CrO_4^{--} + 4H^+ \rightarrow Fe_2O_3 + Cr_2O_3 + 2H_2O. \qquad (b)$$

Hoar and Evans[55] have shown experimentally that the oxidation of a ferrous solution by chromates does in fact give rise to a mixture of ferric and chromic hydroxides, as in reaction (*a*); they have also shown that the corrosion product of iron in presence of chromates is a heterogeneous mixture of these two hydroxides, and that the protective film on a specimen passivated by chromates contains trivalent chromium. They suppose that the chromate "repairs" the original oxide film on the metal and explain its passivating action in this way.

It thus appears that reactions (*a*) and/or (*b*) do actually take place, and that any crack in the natural oxide film that exposes the metallic surface with its low potential, can be blocked by a mixture of Fe_2O_3 and Cr_2O_3. The relative amounts of the two oxides formed in the cracks will vary between 1/3 and 1 according as the reduction is due to ferrous ions (reaction (*a*)) or to the iron itself (reaction (*b*)).

The above discussion leads to the conclusion that the very specific protective action of chromates arises from a characteristic property of the $Cr\text{-}H_2O$ system—the existence of a soluble compound (chromate or bichromate) under oxidizing conditions (e.g. at $rO = 0$) and the existence of a sparingly soluble gelatinous compound ($Cr_2O_3 \,.\, nH_2O$) under reducing conditions (e.g. at $rH = 0$), the former being converted into the latter by reduction. It follows that the conditions under which chromates bring about passivation must be closely connected with the conditions under which Cr_2O_3 is stable, i.e. passivation will occur only if the chromium content of the solution (as chromate) is higher than that corresponding to saturation of the solution with Cr_2O_3 at the same pH and potential. Passivation will be hindered by ions which form soluble complexes with Cr^{+++} (e.g. Cl^-, which forms $CrCl^{++}$, $CrCl_2^+$ and $CrCl_3$aq.), and thereby increase the solubility of Cr_2O_3.

The experiments of Bjerrum[4] on solutions of trivalent chromium, containing 0·8 g.-ion Cr per litre and 3·2 g. Cl^- per litre, show that these solutions are saturated with Cr_2O_3 at pH's of approximately 4·2 and 14·9. Fig. 22 has been obtained by combining the equilibrium diagram of the $Cr\text{-}H_2O$ system (fig. 24), which is based on Bjerrum's data, with fig. 21, and shows the domains of corrosion, immunity and passivation of iron in a solution containing 3·2 g. of Cl^- and 0·8 g.-ion of Cr per litre as chromate (i.e. 155 g. K_2CrO_4 per litre). It will be seen that the "dangerous triangle" has disappeared and that this chromate solution produces passivation if the pH is above 4·2, but not if it is below 4·2. This conclusion has been confirmed experimentally by the author.*

C. THE SYSTEM Cr-H_2O

It is not possible to formulate the equilibrium conditions in the Cr-H_2O system with any degree of accuracy, owing to the complexity of the reactions involved and to the lack of relevant data. The discussion given below rests on a number of simplifying hypotheses and is only a rough approximation. The chemical potentials are not known with accuracy for any of the ten chromium compounds considered; we have therefore had to evaluate each of them by making assumptions which are no doubt inaccurate in several cases. In calculating chemical potentials from experimental values of dissociation constants, solubility products and redox potentials, for example, it has been assumed that the chromium compounds in question have certain simple formulae (indicated below) and are not associated with extraneous substances; e.g. it is assumed that chromous and chromic solutions contain only the ionic species Cr^{++}, Cr^{+++}, $CrOH^{++}$ and $Cr(OH)_2^+$, and no complex ions, such as chloro-chromic ions, which certainly exist. In the case of bichromate solutions, we consider the ion $HCrO_4^-$, but not the polymerized ion $Cr_2O_7^{--}$. The only solid phases considered are metallic chromium and the two hydroxides $Cr(OH)_2$ and $Cr(OH)_3$ (both freshly precipitated, or "young").

The calculations of the standard chemical potentials are based on the following data:

Cr^{++}. Solution potential

$$E^0_{Cr/Cr^{++}} = -\ 0{\cdot}557 \text{ V. (Grübe and Breitinger}^{43}\text{).}$$

Cr^{+++}. Solution potential

$$E^0_{Cr/Cr^{++}} = -\ 0{\cdot}509 \text{ V. (Grübe and Breitinger}^{43}\text{),}$$

which leads to the standard chemical potential

$$\mu^0_{Cr^{+++}} = -\ 35{,}220 \text{ cal.}$$

$Cr(OH)^{++}$, $Cr(OH)_2^+$. Dissociation constants

$$(CrOH^{++}).(H^+)/(Cr^{+++}).(H_2O) = 0{\cdot}62 \times 10^{-4},$$

$$\text{and } (Cr(OH)_2^+).(H^+)/(CrOH^{++}).(H_2O) = 0{\cdot}0060 \times 10^{-4}.$$

These are the values found by Bjerrum,[4] expressed in g.-ions per litre; they refer to chloride solutions, and the ions represented by the formulae $Cr(OH)^{++}$ and $Cr(OH)_2^+$ (following Bjerrum) are in reality chloride complexes. These values are used in conjunction with the standard chemical potential.

$$\mu^0_{Cr^{+++}} = -\ 35{,}220 \text{ cal.}$$

$HCrO_4^-$. The redox potential

$$E^0_{HCrO_4^-/Cr^{+++}} = +\ 1{\cdot}300 \text{ V.,}$$

following Latimer and Hildebrand,[56] who quote an approximate value of $+\,1{\cdot}3$ V., and the standard chemical potential

$$\mu^0_{Cr^{+++}} = -\ 35{,}220 \text{ cal.}$$

H_2CrO_4aq. Dissociation constant

$$(HCrO_4^-).(H^+)/(H_2CrO_4) = 0{\cdot}18,$$

(Landolt-Börnstein, III Erg. 2103) and standard chemical potential $\mu^0_{HCrO_4^-} = -\ 171{,}560.$

CrO_4^{--}. Dissociation constant

$$(CrO_4^{--}).(H^+)/(HCrO_4^-) = 10^{-6{\cdot}50},$$

(Landolt-Börnstein, III Erg. 2103) and standard chemical potential $\mu^0_{HCrO_4^-} = -\ 171{,}560.$

$Cr(OH)_2$. Solubility product

$$(Cr^{++}).(OH)^2 = 10^{-19{\cdot}70},$$

as determined by Bennett[3] by precipitation of $Cr(OH)_2$ from sulphuric acid solution. Standard chemical potential

$$\mu^0_{Cr^{++}} = -\ 25{,}670 \text{ cal.}$$

$Cr(OH)_3$. Solubility product (see reaction (21) below)

$$(CrOH^{++})/(H^+)^2 = 10^{8{\cdot}01},$$

as determined by Bjerrum[4] by precipitation of $Cr(OH)_3$ on addition of alkali to an acid chloride solution at 17°C. Standard chemical potential

$$\mu^0_{CrOH^{++}} = -\ 86{,}040 \text{ cal.}$$

CrO_2^-. Solubility product

$$(CrO_2^-).(H^+) = 10^{-15{\cdot}0}.$$

This value has been determined by the author (unpublished work) by precipitation of $Cr(OH)_3$ from an alkaline chloride solution by addition of acid.

---

* A summary has recently been published.[133, 135]

1. Derivation of Figs. 23 and 24

The values of the standard chemical potentials used in subsequent calculations are summarized in the following table:

Solvents and solutes

$\mu^0_{H_2O} = -56{,}560$ cal.[75]
$\mu^0_{H^+} = 0$ cal.
$\mu^0_{OH^-} = -37{,}455$ cal.[121]
$\mu^0_{Cr^{++}} = -25{,}670$ cal.
$\mu^0_{Cr^{+++}} = -35{,}220$ cal.
$\mu^0_{CrOH^{++}} = -86{,}040$ cal.
$\mu^0_{Cr(OH)_2^+} = -134{,}120$ cal.
$\mu^0_{H_2CrO_4aq.} = -172{,}569$ cal.
$\mu^0_{HCrO_4^-} = -171{,}560$ cal.
$\mu^0_{CrO_4^{--}} = -162{,}700$ cal.
$\mu^0_{CrO_2^-} = -111{,}260$ cal.

Solids

$\mu^0_{Cr} = 0$ cal.
$\mu^0_{Cr(OH)_2} = -127{,}440$ cal.
$\mu^0_{Cr(OH)_3} = -188{,}260$ cal.

The equilibrium conditions listed below are readily obtained from the chemical potentials by the use of the equations given on p. 54; the potentials are in volts with respect to the standard hydrogen electrode.

1. *Homogeneous Reactions*

(*a*) *Without oxidation*

(1) $CrO_4^{--} - HCrO_4^- + H^+ = 0$:

$$\log \frac{(CrO_4^{--})}{(HCrO_4^-)} = -6{\cdot}50 + \text{pH}.$$

(2) $HCrO_4^- - H_2CrO_4aq. + H^+ = 0$:

$$\log \frac{(HCrO_4^-)}{(H_2CrO_4aq.)} = -0{\cdot}74 + \text{pH}.$$

(3) $CrO_2^- - Cr^{+++} - 2H_2O + 4H^+ = 0$:

$$\log \frac{(CrO_2^-)}{(Cr^{+++})} = -27{\cdot}21 + 4\text{pH}.$$

(4) $CrO_2^- - Cr(OH)_2^+ + 2H^+ = 0$:

$$\log \frac{(CrO_2^-)}{(Cr(OH)_2^+)} = -16{\cdot}77 + 2\text{pH}.$$

(5) $Cr(OH)_2^+ - CrOH^{++} - H_2O + H^+ = 0$:

$$\log \frac{(Cr(OH)_2^+)}{(CrOH^{++})} = -6{\cdot}22 + \text{pH}.$$

(6) $CrOH^{++} - Cr^{+++} - H_2O + H^+ = 0$:

$$\log \frac{(CrOH^{++})}{(Cr^{+++})} = -4{\cdot}21 + \text{pH}.$$

(*b*) *With oxidation*

(7) $Cr^{+++} - Cr^{++} + e^- = 0$:

$$E = -0{\cdot}414 + 0{\cdot}0591 \log \frac{(Cr^{+++})}{(Cr^{++})}.$$

(8) $CrOH^{++} - Cr^{++} - H_2O + H^+ + e^- = 0$:

$$E = -0{\cdot}165 - 0{\cdot}0591\text{pH} + 0{\cdot}0591 \log \frac{(CrOH^{++})}{(Cr^{++})}.$$

(9) $Cr(OH)_2^+ - Cr^{++} - 2H_2O + H^+ + e^- = 0$:

$$E = 0{\cdot}203 - 0{\cdot}1182\text{pH} + 0{\cdot}0591 \log \frac{(Cr(OH)_2^+)}{(Cr^{++})}.$$

(10) $CrO_2^- - Cr^{++} - 2H_2O + 4H^+ + e^- = 0$:

$$E = 1{\cdot}194 - 0{\cdot}2364\text{pH} + 0{\cdot}0591 \log \frac{(CrO_2^-)}{(Cr^{++})}.$$

(11) $H_2CrO_4aq. - Cr^{+++} - 4H_2O + 6H^+ + 3e^- = 0$:

$$E = 1{\cdot}284 - 0{\cdot}1182\text{pH} + 0{\cdot}0197 \log \frac{(H_2CrO_4)}{(Cr^{+++})}.$$

(12) $HCrO_4^- - Cr^{+++} - 4H_2O + 7H^+ + 3e^- = 0$:

$$E = 1{\cdot}300 - 0{\cdot}1378\text{pH} + 0{\cdot}0197 \log \frac{(HCrO_4^-)}{(Cr^{+++})}.$$

(13) $HCrO_4^- - CrOH^{++} - 3H_2O + 6H^+ + 3e^- = 0$:

$$E = 1{\cdot}216 - 0{\cdot}1182\text{pH} + 0{\cdot}0197 \log \frac{(HCrO_4^-)}{(CrOH^{++})}.$$

(14) $HCrO_4^- - Cr(OH)_2^+ - 2H_2O + 5H^+ + 3e^- = 0$:

$$E = 1{\cdot}094 - 0{\cdot}0985\text{pH} + 0{\cdot}0197 \log \frac{(HCrO_4^-)}{(Cr(OH)_2^+)}.$$

(15) $CrO_4^{--} - Cr(OH)_2^+ - 2H_2O + 6H^+ + 3e^- = 0$:

$$E = 1{\cdot}222 - 0{\cdot}1182\text{pH} + 0{\cdot}0197 \log \frac{(CrO_4^{--})}{(Cr(OH)_2^+)}.$$

(16) $CrO_4^{--} - CrO_2^- - 2H_2O + 4H^+ + 3e^- = 0$:

$$E = 0{\cdot}892 - 0{\cdot}0788\text{pH} + 0{\cdot}0197 \log \frac{(CrO_4^{--})}{(CrO_2^-)}.$$

2. *Heterogeneous Reactions involving two solid phases*

(17) $Cr(OH)_2 - Cr - 2H_2O + 2H^+ + 2e^- = 0$:
$E = -0{\cdot}310 - 0{\cdot}0591\text{pH}.$

(18) $Cr(OH)_3 - Cr(OH)_2 - H_2O + H^+ + e^- = 0$:
$E = -0{\cdot}185 - 0{\cdot}0591\text{pH}.$

3. *Heterogeneous reactions involving one solid phase*

(*a*) *Without oxidation*

(19) $Cr(OH)_2 - Cr^{++} - 2H_2O + 2H^+ = 0$:
$\log (Cr^{++}) = 8{\cdot}32 - 2pH$.

(20) $Cr(OH)_3 - Cr^{+++} - 3H_2O + 3H^+ = 0$:
$\log (Cr^{+++}) = 12{\cdot}21 - 3pH$.

(21) $Cr(OH)_3 - CrOH^{++} - 2H_2O + 2H^+ = 0$:
$\log (CrOH^{++}) = 8{\cdot}01 - 2pH$.

(22) $Cr(OH)_3 - Cr(OH)_2^+ - H_2O + H^+ = 0$:
$\log (Cr(OH)_2^+) = 1{\cdot}77 - pH$.

(23) $CrO_2^- - Cr(OH)_3 + H_2O + H^+ = 0$:
$\log (CrO_2^-) = -15{\cdot}00 + pH$.

(*b*) *With oxidation*

(24) $Cr^{++} - Cr + 2e^- = 0$:
$E = -0{\cdot}557 + 0{\cdot}0295 \log (Cr^{++})$.

(25) $CrO_2^- - Cr - 2H_2O + 4H^+ + 3e^- = 0$:
$E = 0{\cdot}027 - 0{\cdot}0788pH + 0{\cdot}0197 \log (CrO_2^-)$.

(26) $Cr^{+++} - Cr + 3e^- = 0$:
$E = -0{\cdot}509 + 0{\cdot}0197 \log (Cr^{+++})$.

(27) $Cr(OH)_2^+ - Cr(OH)_2 + e^- = 0$:
$E = 0{\cdot}290 + 0{\cdot}0591 \log (Cr(OH)_2^+)$.

(28) $CrO_2^- - Cr(OH)_2 + 2H^+ + e^- = 0$:
$E = 0{\cdot}702 - 0{\cdot}1182pH + 0{\cdot}0591 \log (CrO_2^-)$.

(29) $Cr(OH)_3 - Cr^{++} - 3H_2O + 3H^+ + e^- = 0$:
$E = 0{\cdot}308 - 0{\cdot}1772pH - 0{\cdot}0591 \log (Cr^{++})$.

(30) $HCrO_4^- - Cr(OH)_3 - H_2O + 4H^+ + 3e^- = 0$:
$E = 1{\cdot}058 - 0{\cdot}0788pH + 0{\cdot}0197 \log (HCrO_4^-)$.

(31) $CrO_4^{--} - Cr(OH)_3 - H_2O + 5H^+ + 3e^- = 0$:
$E = 1{\cdot}187 - 0{\cdot}0985pH + 0{\cdot}0197 \log (CrO_4^{--})$.

These conditions are represented graphically in figs. 23 and 24 by a procedure similar to that previously used for copper and iron; a description of the diagrams follows.

Homogeneous equilibria. The thick lines in fig. 23 are the loci of points at which the activities of two chromium-containing solutes are equal; there is a line corresponding to each of the equations (1) to (16). The diagram is thus divided into eight domains, each of which corresponds to predominance of one of the eight compounds of chromium under discussion. For most of these reactions, fine lines have also been plotted in fig. 23, showing the conditions under which the ratio of the activities of two chromium derivatives has the values 10^3, 10^2, 10, 10^{-1}, 10^{-2} and 10^{-3}.

Heterogeneous equilibria involving two solids. Relations (17) and (18) have been plotted as thick lines in fig. 24; these lines divide the diagram into three domains corresponding to the relative stability of each of the three solids considered, i.e. Cr, $Cr(OH)_2$ and $Cr(OH)_3$, the two hydroxides being in the freshly precipitated condition.

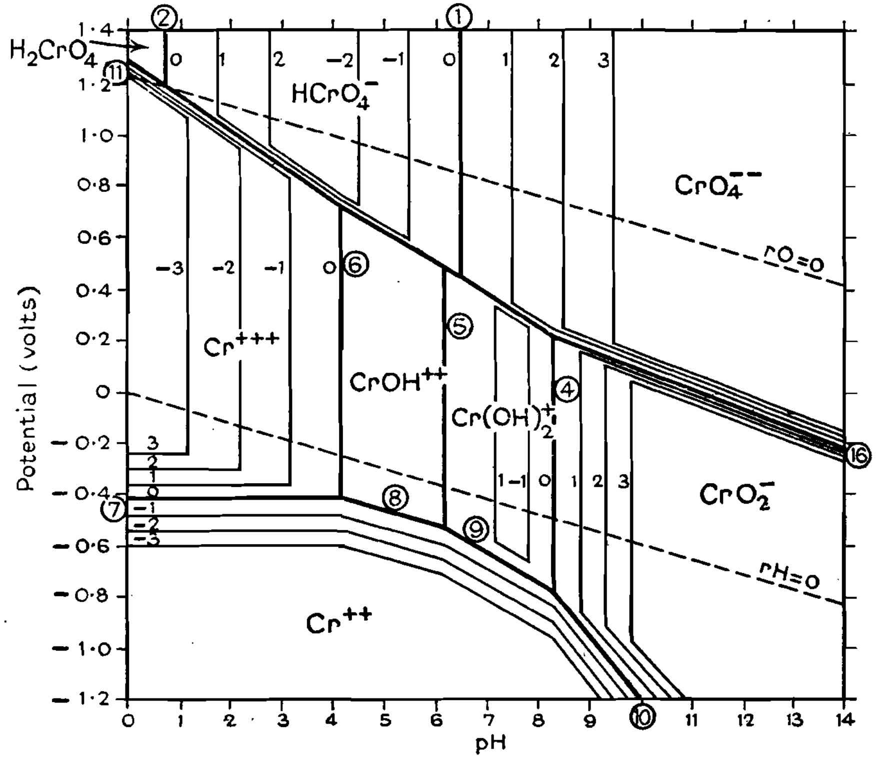


FIG. 23.—System $Cr\text{-}H_2O$. Domains of predominance of solutes (schematic).

Heterogeneous equilibria involving only one solid. The combined diagram, fig. 24, shows:

(*a*) the lines (1) to (16) separating the domains of predominance of the solutes, and the lines (17) and (18) separating the domains of relative stability of the solids;

(*b*) the loci of points at which the *sums* of the activities of all the eight solute species containing chromium have certain fixed values, namely, 10^0, 10^{-2}, 10^{-4} and 10^{-6} g.-ions per litre.

From the section of fig. 2 relating to trivalent metals one may readily calculate the pH's at which the total concentration of trivalent chromium (Cr^{+++}, $CrOH^{++}$, $Cr(OH)_2^+$ and CrO_2^-) in a solution saturated with $Cr(OH)_3$, has the above values. Experiments carried out by the writer have shown that the solubilities calculated in this way are substantially accurate for pH's below c. 5·5 or above c. 11·5, i.e. when the chromium content exceeds 10^{-3} or 10^{-2} g.-atoms Cr per litre. At pH's between 5·5 and 11·5 the experimentally found solubilities are greater than those shown in fig. 2; the cause of this discrepancy has not been investigated.

2. Discussion of Fig. 24

We must emphasize that the data on which fig. 24 is based are too uncertain and too much simplified for this diagram to be more than schematic. It would be difficult to justify its application to specific problems until its accuracy has been improved by inclusion of the appropriate experimental data. For example, we have just mentioned that the solubility data for $Cr(OH)_3$ in trivalent chromium solutions refer to certain chloride solutions; these data may be used in the discussion of phenomena occurring in such solutions (e.g. the passivating action of chromates on iron in chloride solutions mentioned on p. 95), but they must be verified before they are applied to other systems.

Nevertheless, fig. 24 illustrates several well-known aspects of the chemistry of chromium. In acid solutions the oxidation of chromium metal gives rise to the blue chromous ion Cr^{++}, the chromic ion Cr^{+++} (mainly blue-green), and the orange chromic acid H_2CrO_4 and bichromate $HCrO_4^-$ (or $Cr_2O_7^{--}$); addition of alkali to bichromate leads to the yellow chromate ion CrO_4^{--}, which on reduction forms the green chromite ion CrO_2^-, and on further reduction, $Cr(OH)_2$ or metallic chromium, according to the pH and potential. $Cr(OH)_3$, which occupies the centre of the diagram, can be obtained by addition of alkali to Cr^{+++} solutions, by acidification of CrO_2^- solutions, or by reduction of solutions containing $HCrO_4^-$ or CrO_4^{--}.

D. *THE SYSTEM N-H_2O*

The conditions of thermodynamic equilibrium between nitrogen and certain of its compounds, in presence of an aqueous solution at 25°C., are shown approximately in figs. 25, 26 and 27.

1. Derivation of Figs. 25, 26 and 27

The following values are adopted for the standard chemical potentials:

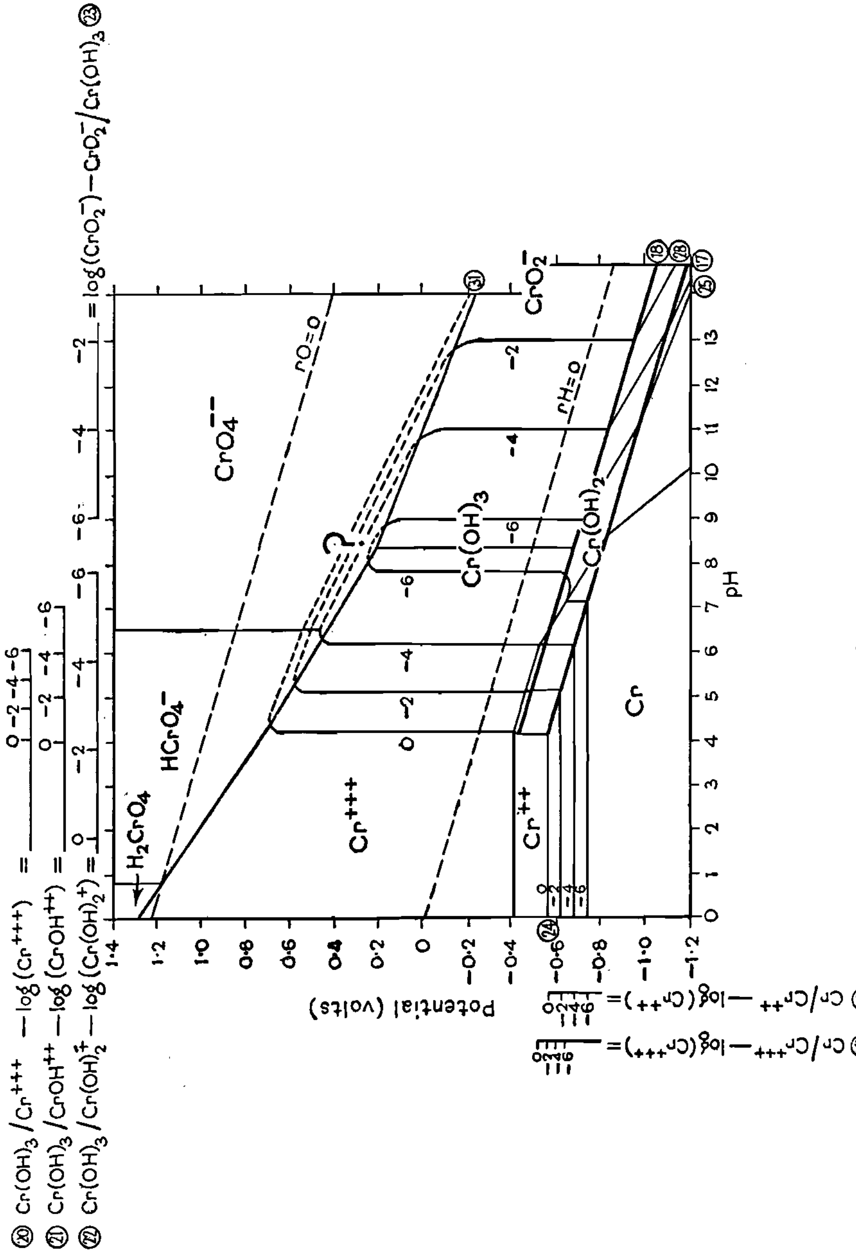


FIG. 24.—System Cr-H_2O. Combined diagram (schematic).

Solvent and solutes	Gases
$\mu^0_{H_2O} = -56{,}560$ cal.[75]	
$\mu^0_{H^+} = 0$ cal.	
$\mu^0_{OH^-} = -37{,}455$ cal.[121]	$\mu^0_{N_2} = 0$ cal.
$\mu^0_{NO_3^-} = -26{,}500$ cal.[75]	$\mu^0_{N_2O} = +24{,}770$ cal.[63]
$\mu^0_{HNO_2aq.} = -13{,}070$ cal.[75]	$\mu^0_{NO} = +20{,}850$ cal.[75]
$\mu^0_{NO_2^-} = -8{,}500$ cal.[75]	$\mu^0_{NO_2} = +11{,}920$ cal.[75]
$\mu^0_{NH_4^+} = -18{,}930$ cal.[75]	$\mu^0_{N_2O_4} = +22{,}640$ cal.[75]
$\mu^0_{NH_4OHaq.} = -62{,}860$ cal.[75]	$\mu^0_{NH_3} = -3{,}910$ cal.[75]

The equilibrium conditions for the reactions under consideration may now be formulated, using the equations summarized on p. 54. They are tabulated below, the potentials being, as usual, referred to the standard hydrogen electrode.

1. *Homogeneous Reactions*

(*a*) *Without oxidation*

(1) $NO_2^- - HNO_2aq. + H^+ = 0$:

$$\log \frac{(NO_2^-)}{(HNO_2)} = -3{\cdot}35 + pH.$$

(2) $NH_4OHaq. - NH_4^+ - H_2O + H^+ = 0$:

$$\log \frac{(NH_4OH)}{(NH_4^+)} = -9{\cdot}25 + pH.$$

(*b*) *With oxidation*

(3) $NO_3^- - HNO_2aq. - H_2O + 3H^+ + 2e^- = 0$:

$$E = 0{\cdot}935 - 0{\cdot}0886pH + 0{\cdot}0295 \log \frac{(NO_3^-)}{(HNO_2)}.$$

(4) $NO_3^- - NO_2^- - H_2O + 2H^+ + 2e^- = 0$:

$$E = 0{\cdot}836 - 0{\cdot}0591pH + 0{\cdot}0295 \log \frac{(NO_3^-)}{(NO_2^-)}.$$

(5) $HNO_2aq. - NH_4^+ - 2H_2O + 7H^+ + 6e^- = 0$:

$$E = 0{\cdot}860 - 0{\cdot}0689pH + 0{\cdot}0098 \log \frac{(HNO_2)}{(NH_4^+)}.$$

(6) $NO_2^- - NH_4^+ - 2H_2O + 8H^+ + 6e^- = 0$:

$$E = 0{\cdot}893 - 0{\cdot}0788pH + 0{\cdot}0098 \log \frac{(NO_2^-)}{(NH_4^+)}.$$

(7) $NO_2^- - NH_4OHaq. - H_2O + 7H^+ + 6e^- = 0$:

$$E = 0{\cdot}802 - 0{\cdot}0689pH + 0{\cdot}0098 \log \frac{(NO_2^-)}{(NH_4OH)}.$$

2. *Heterogeneous Reactions*

(*a*) *Without oxidation*

(8) $NH_3 - NH_4OHaq. + H_2O = 0$:

$$\log \frac{p_{NH_3}}{(NH_4OH)} = -1{\cdot}752.$$

(9) $NH_3 - NH_4^+ + H^+ = 0$:

$$\log \frac{p_{NH_3}}{(NH_4^+)} = -11{\cdot}00 + pH.$$

(*b*) *With oxidation*

We tabulate in succession reactions involving the solutes NO_3^-, HNO_2aq. and NO_2^-, NH_4^+ and NH_4OHaq., in order of decreasing levels of oxidation; for each of these solutes, the reactions are classified in order of decreasing level of oxidation of the participating gas, i.e. in the order NO_2 and N_2O_4, NO, N_2O, N_2, NH_3. It will be recalled that, by the convention adopted, the coefficient *n* of electrons, e^-, is given a positive sign, and that the first term in the reaction equation represents the more *oxidized* compound of nitrogen, while the second is the *reduced* compound. Reactions between derivatives of ammonia (NH_3, NH_4^+ and NH_4OH), on the one hand, and NO_3^-, NO_2 and N_2O_4 on the other are omitted.

(10) $NO_3^- - NO_2 - H_2O + 2H^+ + e^- = 0$:

$$E = 0{\cdot}787 - 0{\cdot}1182pH + 0{\cdot}0591 \log \frac{(NO_3^-)}{p_{NO_2}}.$$

(11) $2NO_3^- - N_2O_4 - 2H_2O + 4H^+ + 2e^- = 0$:

$$E = 0{\cdot}813 - 0{\cdot}1182pH + 0{\cdot}0295 \log \frac{(NO_3^-)^2}{p_{N_2O_4}}.$$

(12) $NO_3^- - NO - 2H_2O + 4H^+ + 3e^- = 0$:

$$E = 0{\cdot}951 - 0{\cdot}0788pH + 0{\cdot}0197 \log \frac{(NO_3^-)}{p_{NO}}.$$

(13) $2NO_3^- - N_2O - 5H_2O + 10H^+ + 8e^- = 0$:

$$E = 1{\cdot}112 - 0{\cdot}0739pH + 0{\cdot}0074 \log \frac{(NO_3^-)^2}{p_{N_2O}}.$$

(14) $2NO_3^- - N_2 - 6H_2O + 12H^+ + 10e^- = 0$:

$$E = 1{\cdot}242 - 0{\cdot}0709pH + 0{\cdot}0059 \log \frac{(NO_3^-)^2}{p_{N_2}}.$$

(15) $NO_2 - HNO_2aq. + H^+ + e^- = 0$:

$$E = 1{\cdot}084 - 0{\cdot}0591pH + 0{\cdot}0591 \log \frac{p_{NO_2}}{(HNO_2)}.$$

(16) $NO_2 - NO_2^- + e^- = 0$:

$$E = 0{\cdot}886 + 0{\cdot}0591 \log \frac{p_{NO_2}}{(NO_2^-)}.$$

(17) $N_2O_4 - 2HNO_2aq. + 2H^+ + 2e^- = 0$:

$$E = 1{\cdot}057 - 0{\cdot}0591pH + 0{\cdot}0295 \log \frac{p_{N_2O_4}}{(HNO_2)^2}.$$

(18) $N_2O_4 - 2NO_2^- + 2e^- = 0$:

$$E = 0{\cdot}859 + 0{\cdot}0295 \log \frac{p_{N_2O_4}}{(NO_2^-)^2}.$$

(19) $HNO_2aq. - NO - H_2O + H^+ + e^- = 0$:

$$E = 0{\cdot}982 - 0{\cdot}0591pH + 0{\cdot}0591 \log \frac{(HNO_2)}{p_{NO}}.$$

(20) $NO_2^- - NO - H_2O + 2H^+ + e^- = 0$:

$$E = 1{\cdot}180 - 0{\cdot}1182pH + 0{\cdot}0591 \log \frac{(NO_2^-)}{p_{NO}}.$$

(21) $2HNO_2aq. - N_2O - 3H_2O + 4H^+ + 4e^- = 0$:

$$E = 1{\cdot}288 - 0{\cdot}0591pH + 0{\cdot}0148 \log \frac{(HNO_2)^2}{p_{N_2O}}.$$

(22) $2NO_2^- - N_2O - 3H_2O + 6H^+ + 4e^- = 0$:

$$E = 1{\cdot}387 - 0{\cdot}0887pH + 0{\cdot}0148 \log \frac{(NO_2^-)^2}{p_{N_2O}}.$$

(23) $2HNO_2aq. - N_2 - 4H_2O + 6H^+ + 6e^- = 0$:

$$E = 1{\cdot}446 - 0{\cdot}0591pH + 0{\cdot}0098 \log \frac{(HNO_2)^2}{p_{N_2}}.$$

(24) $2NO_2^- - N_2 - 4H_2O + 8H^+ + 6e^- = 0$:

$$E = 1{\cdot}513 - 0{\cdot}0788pH + 0{\cdot}0098 \log \frac{(NO_2^-)^2}{p_{N_2}}.$$

(25) $HNO_2aq. - NH_3 - 2H_2O + 6H^+ + 6e^- = 0$:

$$E = 0{\cdot}751 - 0{\cdot}0591pH + 0{\cdot}0098 \log \frac{(HNO_2)}{p_{NH_3}}.$$

(26) $NO_2^- - NH_3 - 2H_2O + 7H^+ + 6e^- = 0$:

$$E = 0{\cdot}784 - 0{\cdot}0689pH + 0{\cdot}0098 \log \frac{(NO_2^-)}{p_{NH_3}}.$$

(27) $NO - NH_4^+ - H_2O + 6H^+ + 5e^- = 0$:

$$E = 0{\cdot}835 - 0{\cdot}0709pH + 0{\cdot}0118 \log \frac{p_{NO}}{(NH_4^+)}.$$

(28) $NO - NH_4OHaq. + 5H^+ + 5e^- = 0$:

$$E = 0{\cdot}724 - 0{\cdot}0591pH + 0{\cdot}0118 \log \frac{p_{NO}}{(NH_4OH)}.$$

(29) $N_2O - 2NH_4^+ - H_2O + 10H^+ + 8e^- = 0$:

$$E = 0{\cdot}646 - 0{\cdot}0739pH + 0{\cdot}0074 \log \frac{p_{N_2O}}{(NH_4^+)^2}.$$

(30) $N_2O - 2NH_4OHaq. + H_2O + 8H^+ + 8e^- = 0$:

$$E = 0{\cdot}509 - 0{\cdot}0591pH + 0{\cdot}0074 \log \frac{p_{N_2O}}{(NH_4OH)^2}.$$

(31) $N_2 - 2NH_4^+ + 8H^+ + 6e^- = 0$:

$$E = 0{\cdot}273 - 0{\cdot}0788pH + 0{\cdot}0098 \log \frac{p_{N_2}}{(NH_4^+)^2}.$$

(32) $N_2 - 2NH_4OHaq. + 2H_2O + 6H^+ + 6e^- = 0$:

$$E = 0{\cdot}091 - 0{\cdot}0591pH + 0{\cdot}0098 \log \frac{p_{N_2}}{(NH_4OH)^2}.$$

These conditions have been used in drawing figs. 25, 26 and 27. The combined diagram, fig. 25, shows the more important characteristics of equilibria in the N-H$_2$O system; figs. 26 and 27 show parts of fig. 25 on a larger scale and in more detail. The derivation of fig. 25 is as follows:

Homogeneous equilibria. For each of the reactions (1) to (7) lines have been drawn for which the activities of the two nitrogen-containing solutes in question are equal. These lines divide the diagram into five domains, each corresponding to the predominance of one of the five solutes.*

Heterogeneous equilibria between solution and gas. Broken lines have been drawn in each domain of predominance; each line shows the conditions under which the equilibrium pressures of the gas in question amounts to 1 atm. when the solution contains 1 g.-ion per litre of the predominant solute. The lines shown refer to reactions (12), (13), (14), (20), (27) and (29) to (32).

These lines form the boundaries of a series of domains, in each of which the equilibrium pressure of a particular gas exceeds 1 atm. when the solution contains 1 g.-atom per litre of nitrogen in the particular solute species under consideration. The upper boundary of the domain shows the potentials below which NO_3^-, $HNO_2aq.$ or NO_2^- can be

* Cf. the representation of the Cu-H$_2$O system (p. 56 and fig. 9).

reduced (with liberation of N_2, N_2O or NO at atmospheric pressure); the lower limit shows potentials above which NH_4^+ or NH_4OHaq. can be oxidized (with liberation of the same gases).

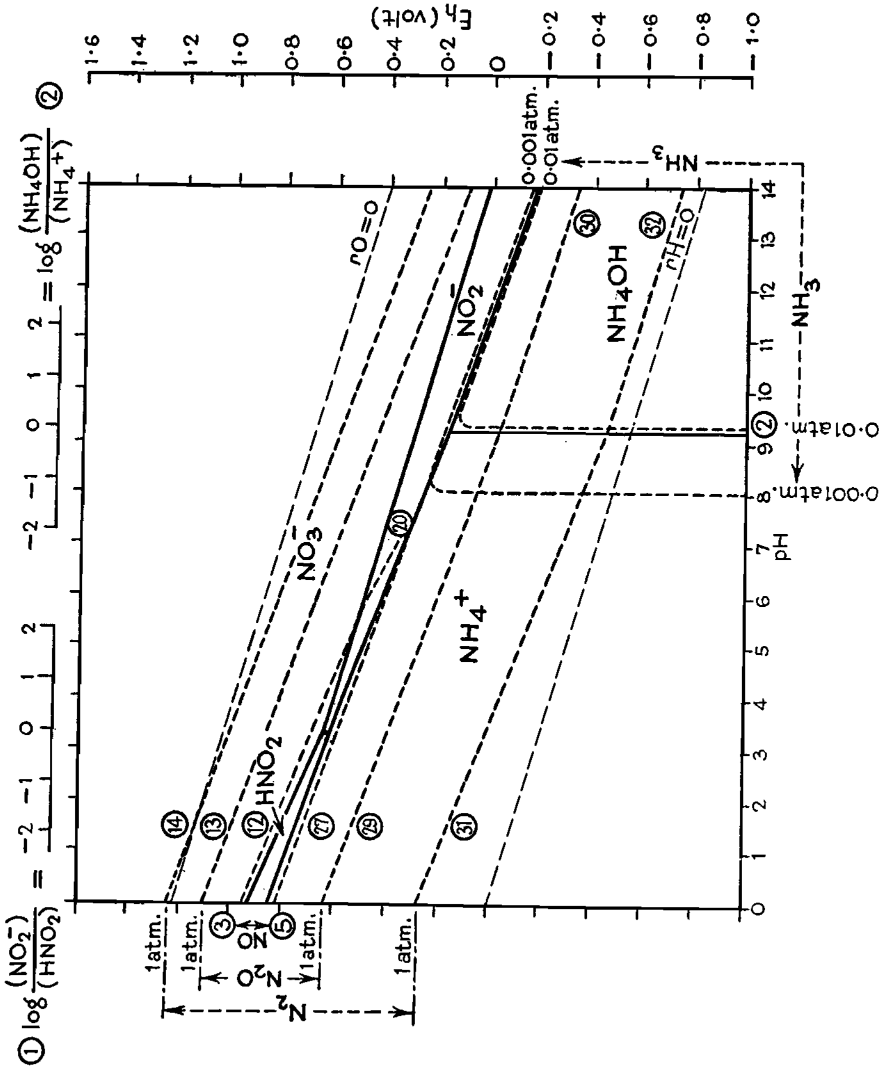


FIG. 25.—System N-H_2O. Combined diagram.

Fig. 26. Five lines have been drawn for each of the reactions (1), (3), (4), (5) and (6), which have already been discussed in connexion with fig. 25; at points on these lines the ratios of the activities of the two solutes in question have certain fixed values, namely 10^2, 10^1, 10^0, 10^{-1} and 10^{-2}.

EXAMPLE. Along the line (3) of index −1, the activity ratio $\frac{(NO_3^-)}{(HNO_2)}=0{\cdot}10$, or $\frac{(HNO_2)}{(NO_3^-)} = 10$; this line is terminated when it meets line (5) of index +1 (at $E = 0{\cdot}744$ V., pH = 1·80) along which the activity ratio $\frac{(HNO_2)}{(NH_4^+)}=10$.

The influence of pH on the redox potential of 0·0577N solutions of nitric acid, nitrous acid and ammonium sulphate in various buffers has been studied by Thiesse,[116] who found the following values:

Nitric acid:

pH	−0·90	−0·29	+0·55	+2·72	+7·38
E	1·050	0·975	0·920	0·715	0·485

Nitrous acid:

pH	−0·9	−0·3	+0·65	+1·32	+3·45	+5·55	+7·20	+7·33	+9·80	11·14
E	0·935	0·917	0·850	0·829	0·715	0·625	0·470	0·403	0·280	0·190

Ammonium sulphate:

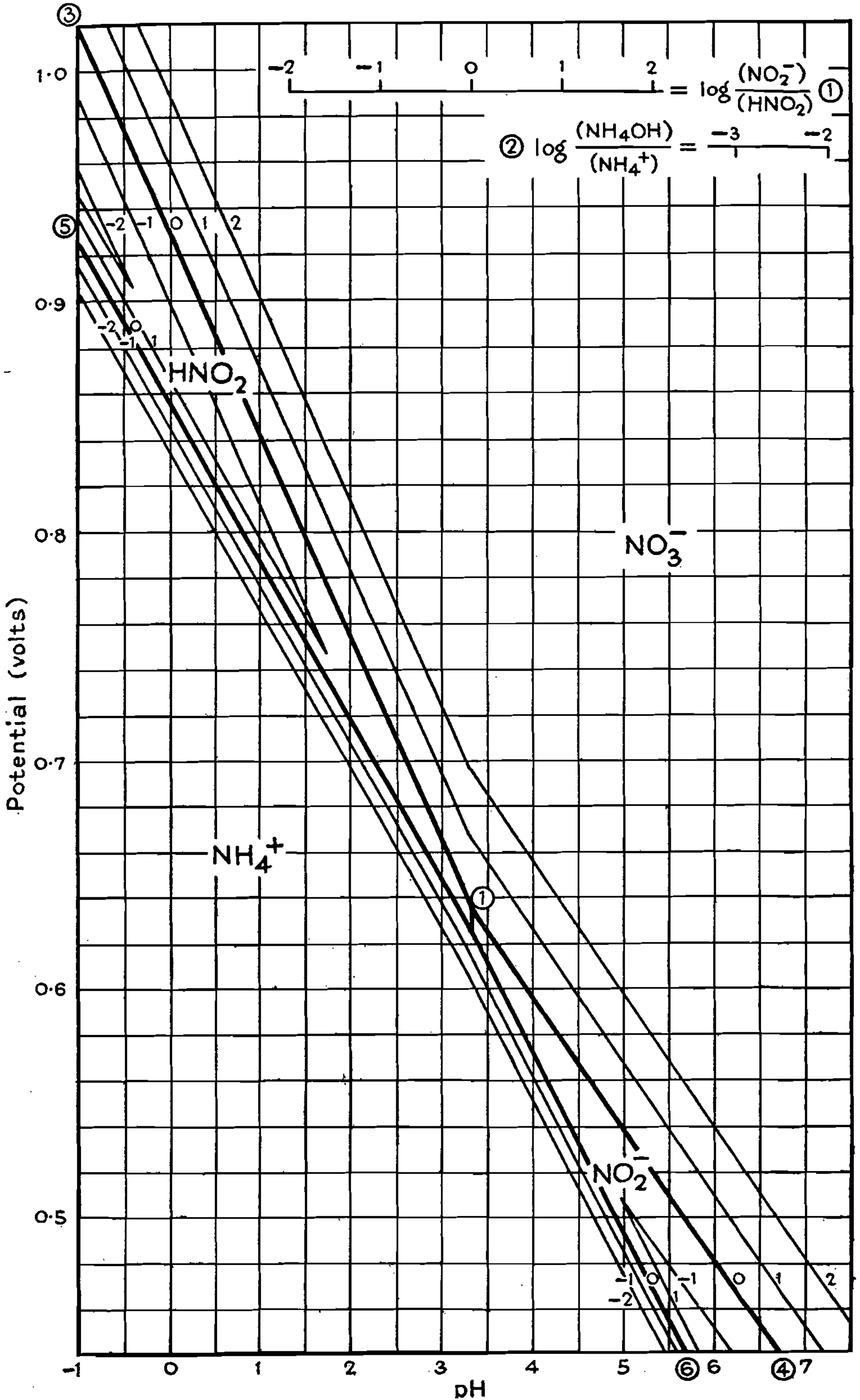
pH	2·85	3·87	4·95	7·25	9·91
E	0·660	0·580	0·530	0·440	0·262

On plotting these values in figs. 25 and 26 it is found that the five points for nitric acid all fall within the domain of predominance of the NO_3^- ion, as would be expected. Although the fifth value (for pH=7·38) is well away from the domain of predominance of NO_2^- and thus corresponds to equilibrium in a nitric acid solution containing only a small proportion of nitrite (the calculated value of the ratio $(NO_3^-)/(NO_2^-)$ is 194 at the point in question), the first four points lie close to the domain of predominance of HNO_2, i.e. in a region representing equilibria of nitric/nitrous solutions containing an appreciable proportion of nitrous acid. The calculated values of the $(NO_3^-)/(HNO_2)$ ratio are 15·4, 3·0, 15·4 and 1·6 respectively. Thiesse was careful to use the purest possible nitric acid, and to remove nitrous gases by passing nitrogen through the solution for a prolonged period, and it is thus improbable that the nitric acid actually contained such a high proportion of nitrous acid. It is conceivable that the sulphuric acid, acetic acid and sodium acetate contained in the buffer mixtures used by Thiesse interact with nitric acid, particularly in contact with the platinum electrode employed in the potential measurements.

Similar experiments were made by Thiesse in solutions of sulphuric and acetic acid buffers containing nitrous acid and nitrites, prepared from recrystallized $NaNO_2$. For pH's less than 1, the observed values fall in the domain of predominance of HNO_2, as would be expected; for pH's between 1 and 1·75, on the other hand, they lie in the domain of predominance of NO_3^- and are even higher than the values for nitric acid solutions. Thiesse draws attention to this anomaly. For pH's higher than 7·25, the values lie substantially on the line separating the domains of predominance of NO_2^- and NO_3^-; an investigation of the cause of these anomalies would be interesting.

In ammonium sulphate solutions, the potentials at pH's less than 4 lie in the domain of predominance of NH_4^+, but close to the domain of HNO_2 or NO_2^-; above pH 4, the values lie, like those for nitrite, very close to the line separating the domains of predominance of NO_2^- and NO_3^-. These facts show that the potential in such solutions of ammonium sulphate is not due to NH_4^+/NO_2^- equilibrium and that the change from NH_4^+ to NO_2^- and vice versa is not reversible. The potential must be controlled by some other process, as yet unknown.

Fig. 27. This diagram has been drawn to illustrate the stability of nitric and nitrous solutions in presence of NO, NO_2 and N_2O_4, and shows the domains of predominance of the various solutes, which have already been plotted in fig. 26. In addition, five lines have been drawn with reference to the reactions between NO_3^-, HNO_2 and NO_2^- on the one hand, and NO, NO_2 and N_2O_4 on the other. Along each of these lines the logarithm of the function of solute activity and gas pressure, which appears as the last term in the corresponding equilibrium condition (equations (10) to (13) and (15) to (20)), has a fixed value. The values corresponding to the five lines in each set are 2, 1, 0, —1 and —2. For equilibria involving HNO_2 and NO_2^- and a given gas, the two lines relating to the two solute species have both been terminated at their meeting point (i.e. at pH = 3·35, which corresponds to equal HNO_2 and NO_2^- activities). Curves have also been drawn for constant values of the ratio $(HNO_2) + (NO_2^-)/p_{NO}$, and of analogous ratios involving p_{NO_2} and $p_{N_2O_4}$; they thus relate to the total activity of nitrous acid and nitrite, instead of the activity of the separate species. The equations of these curves can be derived by a method given below. They are inscribed within two straight lines of the same index which refer to HNO_2 and NO_2^- separately; and they can be plotted by application of the following rule, which is analogous to that given in Appendix B, section (1), in connexion with the solubilities of solids: at the pH corresponding to the intersection of the two straight lines enclosing the curve, the potential of the curve differs by 0·0178 V. from the potential of intersection; at pH's 0·5 and 1·0 unit higher or lower than the intersection, the potentials of the curve differ by 0·0070 and 0·0024 V. respectively from the line relating to the predominate solute. The sign of these differences is such that the curve lies within the angle formed by the two straight lines, i.e. they are positive or negative according as the solute (HNO_2 or NO_2^-) is a stronger reducing agent or a stronger oxidizing agent than the gas concerned.



As an example, we give some values for potentials corresponding to the equilibria HNO_2/NO, NO_2^-/NO, and $(HNO_2 + NO_2^-)/NO$:

pH		2·35	2·85	3·35	3·85	4·35
For log $\frac{(HNO_2)}{p_{NO}} = 0$:	$E =$	0·843	0·814	0·784	—	— V.
For log $\frac{(NO_2^-)}{p_{NO}} = 0$:	$E =$	—	—	0·784	0·725	0·666 V.
Deviation as given above:		$-$0·002	$-$0·007	$-$0·018	$-$0·007	$-$0·002 V.
For log $\frac{(HNO_2)+(NO_2^-)}{p_{NO}} = 0$:	$E =$	0·841	0·807	0·766	0·718	0·664 V.

Curves with index zero have been drawn as thick lines in fig. 27.

2. Discussion of Figs. 25, 26 and 27

A number of conclusions regarding the chemistry of nitrogen and its compounds may be drawn from figs. 25, 26 and 27. In subsequent paragraphs the following are discussed: the stability of nitrous acid and nitrites; the reduction of nitric acid by NO; the stability of gaseous ammonia; the chemical and electrochemical decomposition of nitric acid and nitrates; the electrochemical fixation of nitrogen.

(a) Stability of Nitrous Acid and Nitrites*

Figs. 26 and 27 show that nitrous acid is essentially unstable. As far as equilibria with other solutes are concerned, it is clear that nitrous acid is thermodynamically stable only in presence of appreciable proportions of NO_3^-, NH_4^+ and in some cases NO_2^-, even at points lying within the truncated triangle defined by the lines (3) and (5) and the abscissa pH = 3·35, where HNO_2 is the predominate solute (fig. 26). For example, at a potential of 0·774 V. and pH 1·80 (cf. p. 109), the concentrations of NO_3^-, NH_4^+ and NO_2^- should be such that

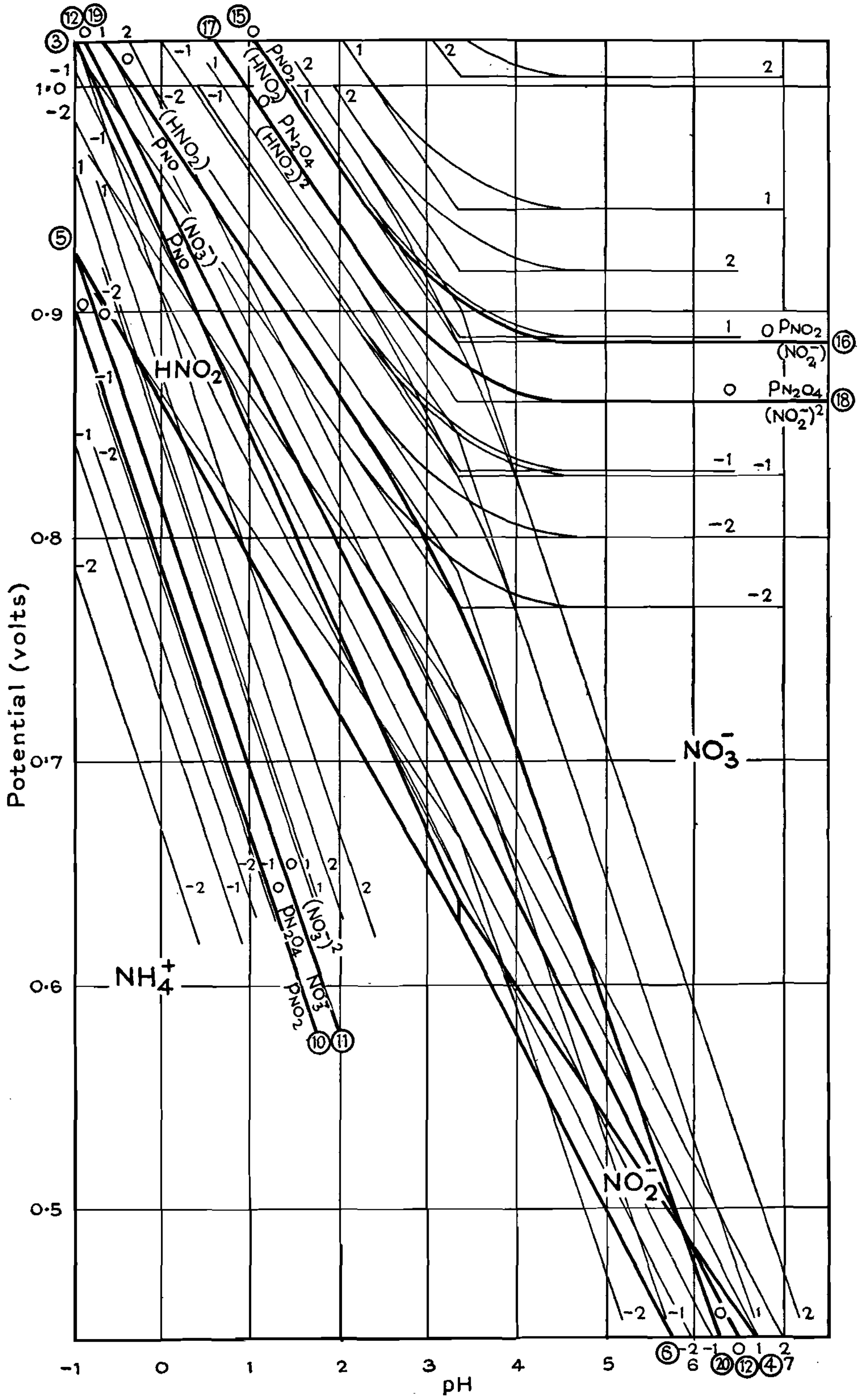
$$\frac{(NO_3^-)}{(HNO_2)} = 0{\cdot}10, \quad \frac{(NH_4^+)}{(HNO_2)} = 0{\cdot}10 \quad \text{and} \quad \frac{(NO_2^-)}{(HNO_2)} = 0{\cdot}028.$$

We thus have a solution containing ammonium nitrate and a little nitrite, as well as nitrous acid, the proportions being 10·28 parts of nitrogen as nitrous acid and nitrite to 1 part nitrate nitrogen and 1 part ammoniacal nitrogen.

When we consider equilibria involving nitrous acid and gaseous compounds of nitrogen (fig. 25), we find that the domain of predominance of HNO_2 lies below the upper stability limits of N_2 and N_2O,

---

* See Gmelin,[40] p. 898.



and close to that of NO. It may easily be shown that this region corresponds to very high pressures of N_2 and N_2O (in the range 10^{24} to 10^{52} atm. or higher, for solutions normal with respect to HNO_2), and to lower but still quite appreciable NO pressures.

Thermodynamically, therefore, HNO_2 tends to decompose by oxidation according to

$$(3) \qquad HNO_2 + H_2O = NO_3^- + 3H^+ + 2e^-,$$

and by reduction

$$\begin{array}{ll} (23) & 2HNO_2 + 6H^+ + 6e^- = N_2 + 4H_2O, \\ (21) & 2HNO_2 + 4H^+ + 4e^- = N_2O + 3H_2O, \\ (19) & HNO_2 + H^+ + e^- = NO + H_2O, \\ (5) & HNO_2 + 7H^+ + 6e^- = NH_4^+ + 2H_2O. \end{array}$$

The overall reactions possible in absence of other oxidizing or reducing agents are limited to certain combinations of the above:

$$\begin{array}{rl} 3(3) + (23): & 5HNO_2 = 3NO_3^- + N_2 + 3H^+ + H_2O, \\ 2(3) + (21): & 4HNO_2 = 2NO_3^- + N_2O + 2H^+ + H_2O, \\ (3) + 2(19): & 3HNO_2 = NO_3^- + 2NO + H^+ + H_2O, \\ 3(3) + (5): & 4HNO_2 + H_2O = 3NO_3^- + NH_4^+ + 2H^+. \end{array}$$

The fourth of these reactions will not be considered further. Of the other three, only the third actually occurs under ordinary conditions, and experiment shows that it is reversible. We shall now discuss some features of this reaction, which plays an important part in the manufacture of nitric acid by absorption of nitrous gases in water in presence of air.

Consider solutions which are 0·1 M. in $HNO_2 + NO_2^-$ and in equilibrium with NO at 1 atm. pressure. The properties of such solutions are shown in fig. 27 by the curve ((19)(20)) joining the two straight lines (19) and (20) with indices −1, which corresponds to

$$\chi_s \equiv \log \frac{(HNO_2) + (NO_2^-)}{p_{NO}} = \log \frac{0{\cdot}1}{1} = -1.$$

For any point on this curve, the corresponding concentration of nitric acid (or rather nitrate ion) can be deduced from the level of the line of family (12) which passes through the point in question. The scale of levels is graduated in $\log \frac{(NO_3^-)}{p_{NO}}$.

It is apparent from fig. 27 that the lines (12) are chords of the curve ((19) (20))* of index −1, except when the level of the lines exceeds a certain limiting value, corresponding to a line which is a tangent to the curve. The limiting level is slightly greater than 1 and the point of contact is at pH 3·05.

From this result one may calculate the maximum degree of conversion of $HNO_2 + NO_2^-$ into nitrate in presence of NO, assuming that the system is in equilibrium under all the relevant conditions and that no other reactions occur. If the pressure of NO is 1 atm. and the final solution contains 0·1 g. mol. of unchanged $HNO_2 + NO_2^-$ per litre, the maximum concentration of nitrate will be about a hundred times that of the unchanged $HNO_2 + NO_2^-$, and will be attained at pH = 3·05.

The pH's and potentials corresponding to various degrees of conversion are given by the intersections of the appropriate curve of the ((19) (20)) family with the lines of various indices belonging to family (12). Some values are given in the following table, which refers to the solution considered above. The index of the ((19) (20)) curve is thus −1. Approximate numerical values can be determined graphically from fig. 27, but an exact calculation may easily be made by equations (12) and ((19) (20)) (see Appendix B, section (2)).

Potential (V.)	0·897	0·790	0·719	0·662	0·617	0·553	0·494	0·426
pH	0·43	1·45	2·69	3·42	4·24	4·80	5·30	5·81
Index $\chi_s = \log \frac{(HNO_2)+(NO_2^-)}{p_{NO}}$	−1	−1	−1	−1	−1	−1	−1	−1
Index $\chi_{12} = \log \frac{(NO_3^-)}{p_{NO}}$	−1	0	+1	+1	0	−1	−2	−3
$(HNO_2) + (NO_2^-)$	0·1	0·1	0·1	0·1	0·1	0·1	0·1	0·1
(NO_3^-)	0·1	1	10	10	1	0·1	0·01	0·001
$\frac{(NO_3^-)}{(HNO_2) + (NO_2^-)}$	1	10	100	100	10	1	0·1	0·01

This table also shows that the decomposition of $HNO_2 + NO_2^-$ into NO and NO_3^- becomes appreciable only in acid media—unless, of course, the NO pressure is reduced below 1 atm., e.g. by agitation with air or an inert gas. In agreement with this conclusion, the nitrites of

---

* See Appendix B, section (2). The equation of the curve ((19) (20)) is

$$E_s = 1{\cdot}180 - 0{\cdot}1182\text{pH} + 0{\cdot}0591\,[\chi_s - \log(1 + 10^{3{\cdot}35-\text{pH}})],$$

and its tangents are defined by

$$\frac{dE_s}{d\text{pH}} = -\,0{\cdot}1182 + 0{\cdot}0591\,\frac{10^{3{\cdot}35-\text{pH}}}{1 + 10^{3{\cdot}35-\text{pH}}}.$$

The slope of the straight lines (12) is −0·0788 V. per pH unit and the tangent of the curve is thus a member of this family when

$$\frac{dE_s}{d\text{pH}} = -\,0{\cdot}0788.$$

Equating these two expressions for $\frac{dE_s}{d\text{pH}}$, we find pH = 3·05 for the point on the curve at which the tangent is one of the parallel lines of family (12).

weak bases, which are hydrolysed in solution, are known* to decompose readily, whereas those of the alkali and alkaline earth metals are stable.

The effect of agitation with a non-reactive gas can also be estimated from fig. 27. We assume that the partial pressure of NO is reduced in this way from 1 to 0·1 atm., and that the solution is 0·1 M. in $HNO_2 + NO_2^-$, as before. The operating conditions are now represented by the curve ((19) (20)) of index 0, instead of index −1, and the resulting rise in potential corresponds to a considerable increase of the NO_3^- concentration. In the case discussed previously (i.e. for $p_{NO} = 1$ atm.) the maximum ratio of (HNO_3) to $(HNO_2) + (NO_2^-)$ is 115, but it becomes 11,500 when the pressure of NO is reduced to 0·1 atm.

The maximum degree of conversion under various circumstances may be calculated as follows.

It has already been shown that the pH at which conversion is maximum is always 3·05, whatever the value of χ_s. Substituting this pH in the first of equations ((19) (20)) of p. 128, we find

$$E'_s = 0{\cdot}791 + 0{\cdot}0591\chi_s,$$

where E'_s is the potential corresponding to maximum conversion of $HNO_2 + NO_2^-$ into NO_3^- for any given value of χ_s, where

$$\chi_s = \log \frac{(HNO_2) + (NO_2^-)}{p_{NO}}.$$

Furthermore, by putting pH = 3·05 in equation (12), we find

$$E_{12} = 0{\cdot}711 + 0{\cdot}0197\chi_{12},$$

where $\chi_{12} = \log \dfrac{(NO_3^-)}{p_{NO}}$.

Equating E'_s and E'_{12} we obtain

$$\chi_{12} = 4{\cdot}06 + 3\chi_s.$$

The following values of χ_{12} and of the maximum degree of conversion, ρ_{max}, are derived from this relation:

$\chi_s = \log \dfrac{(HNO_2)+(NO_2^-)}{p_{NO}}$	=	−2	−1	0	+1
$\chi_{12} = \log \dfrac{(NO_3^-)}{p_{NO}}$	=	−1·94	+1·06	+4·06	+7·06
$\log \dfrac{(NO_3^-)}{(HNO_2)+(NO_2^-)}$	=	0·06	2·06	4·06	6·06
$\rho_{max} = \dfrac{(NO_3^-)}{(HNO_2)+(NO_2^-)}$	=	1·15	115	11,500	1·15 × 10^6

(b) Reduction of Nitric Acid by NO

NO can react with nitric acid, to form gaseous NO_2, by the reaction

$$NO + HNO_3 = 3NO_2 + H_2O.$$

---

* See Pick.[93]

Consider a solution in which the nitrate ion concentration is held constant at 1 g.-ion NO_3^- per litre, while it is agitated with NO at 1 atm. pressure. The equilibria attained in this way are represented in fig. 27 by points lying on the line (12), with the index,

$$\chi_{12} = \log \frac{(NO_3^-)}{p_{NO}} = 0.$$

The logarithms of the corresponding pressures of NO_2 and N_2O_4 (formed by dimerization of NO_2) are given by the indices of lines (10) and (11), after changing the signs.* In fact, since log (NO_3^-) is zero

$$\text{index of lines (10)} = \log \frac{(NO_3^-)}{p_{NO_2}} = -\log p_{NO_2},$$

$$\text{index of lines (11)} = \log \frac{(NO_3^-)^2}{p_{N_2O_4}} = -\log p_{N_2O_4}.$$

In addition, fig. 26 shows that appreciable quantities of HNO_2 may be formed at the potentials and pH's which will be attained; the concentration of HNO_2 is given by the index of lines (3), with change of sign.

Some potentials and pH's corresponding to the points of intersection of line (12) index 0 with various lines of family (10) are tabulated below; these values are only indicative, since the diagram is not valid for concentrated solutions such as those required to obtain the first two pH's.

Index of line (12), $\log \dfrac{(NO_3^-)}{p_{NO}}$	=	0	0	0
Index of lines (10), $\log \dfrac{(NO_3^-)}{p_{NO_2}}$	=	2	3	4
Potential (V.)		1·043	0·925	0·807
pH		−1·17	+0·33	+1·83
log (NO_3^-)		0·000	0·000	0·000
log (HNO_2)		−0·136	−0·644	−1·152
log p_{NO}		0·000	0·000	0·000
log p_{NO_2}		−2·000	−3·000	−4·000
log $p_{N_2O_4}$		−3·119	−5·119	−7·119
or				
(NO_3^-) (g.-ion per litre)		1·000	1·000	1·000
(HNO_2) (g.-ion per litre)		0·732	0·227	0·070
p_{NO} (atm.)		1·000	1·000	1·000
p_{NO_2} (atm.)		0·010	0·001	0·0001
$p_{N_2O_4}$ (atm.)		$7{\cdot}6 \times 10^{-4}$	$7{\cdot}6 \times 10^{-6}$	$7{\cdot}6 \times 10^{-8}$

---

* The N_2O_4 pressure can also be calculated from the NO_2 pressure by the relation $\log p_{N_2O_4} = 0{\cdot}881 + 2 \log p_{NO_2}$, derived from (10).

It will be seen that the reducing action of NO becomes weaker as the solutions become less acid.

(c) Stability of Gaseous Ammonia

The equilibrium between gaseous ammonia and an aqueous solution is governed by equations (8) and (9), which have already been used in drawing fig. 3. The highest equilibrium pressure possible over a solution containing a given concentration of ammoniacal nitrogen will be realized when all the nitrogen is present as NH_4OHaq. (i.e. no NH_4^+) and is given by

$$\log p_{NH_3} = -1{\cdot}752 + \log (NH_4OH).$$

It follows that a solution containing 1 g.-atom of nitrogen per litre can never exhibit an NH_3 pressure greater than $10^{-1{\cdot}752}$ atm. at 25°C. Fig. 25, which refers to solutions containing 1 g.-atom of total nitrogen per litre, shows domains in which the equilibrium pressures of N_2, N_2O and NO exceed 1 atm., but there can be no such domain for NH_3. The maximum pressure of NH_3 will be realized at points lying well within the domain of predominance of NH_4OH; pressures of 10^{-2} and 10^{-3} atm. correspond to NH_4OH concentrations of 0·565 and 0·0565 g.-molecules per litre, respectively. The following table shows some values of (NH_4^+) and (NO_2^-) compatible with these values of (NH_4OH), and the logarithms of the corresponding concentration or activity ratios:

	$p_{NH_3} = 10^{-2}$ atm.			$p_{NH_3} \doteq 10^{-3}$ atm.		
(NH_4OH) . .	0·565	0·565	0·565	0·0565	0·0565	0·0565
(NH_4^+) . .	0·435	—	0·2175	0·9435	—	0·47175
(NO_2^-) . .	—	·435	0·2175	—	0·9435	0·47175
(Total N) . .	1·000	1·000	1·000	1·0000	1·0000	1·0000
Whence we obtain:						
$\log \frac{(NH_4^+)}{(NH_4OH)}$	−0·114	—	−0·415	1·222	—	0·921
$\log \frac{(NO_2^-)}{(NH_4OH)}$	—	−0·114	−0·415	—	1·222	0·921

The first column in each group refers to the domain of predominance of NH_4OH and NH_4^+, the second to the domain of NO_2^- and the third to points on the line separating these domains. Introducing the values of the logarithms into equations (2) and (7), we find the loci on the pH-potential diagram corresponding to these pressures of NH_3:

Domain of:	$p_{NH_3} = 10^{-2}$ atm.	$p_{NH_3} = 10^{-3}$ atm.
NH_4OH and NH_4^+	the lines pH = 9·36	pH = 8·03
NO_2^-	the lines $E = 0{\cdot}801 - 0{\cdot}0689$pH	$E = 0{\cdot}814 - 0{\cdot}0689$pH
On the line separating these domains	the points $\begin{cases} \text{pH} = 9{\cdot}66 \\ E = 0{\cdot}133 \end{cases}$	$\begin{cases} \text{pH} = 8{\cdot}33 \\ E = 0{\cdot}237 \end{cases}$

With the aid of these values one may draw the curves for which the NH_3 pressure is 10^{-2} and 10^{-3} atm. (fig. 25). The curves in question rise vertically from the pH axis until they reach the neighbourhood of the domain of predominance of NO_2^-, when they bend, and their subsequent course is almost coincident with the line separating the domains of NO_2^- and NH_4OH.

(d) Chemical and Electrochemical Decomposition of Nitric Acid and Nitrates

The problem of the chemical and electrochemical reduction of nitric acid and nitrates is complex; references to the abundant literature on the subject are given by Gmelin[40] (pp. 989 and 997).

It has been shown, particularly by Tafel,[113] that cathodic reduction of aqueous solutions of nitric acid can give rise to a number of different products, according to the nature of the cathode and the concentration of acid (e.g. hydrogen, oxides of nitrogen, nitrous acid and nitrites, hydroxylamine, ammonium salts). For example, Tafel observed that a spongy copper cathode in an aqueous solution of HNO_3 and H_2SO_4 gave a yield of 1% hydroxylamine and 99% ammonia, whereas the respective yields were 100% and 0% when a mercury cathode was used in the same electrolyte. These various reduction products can also be obtained by chemical reaction with hydrogen or metals, suitable catalysts being required in some cases.

It would be interesting to have further information about the potential of the cathode or metal* used as reducing agent, as well as the pH. A comparison of the reduction products actually obtained with those whose formation is thermodynamically possible at the potential and pH employed, might also give valuable results.

---

* The potentials of iron specimens undergoing "periodic dissolution" in nitric acid of certain concentrations have been measured by Karschulin.[61] It appears that this phenomenon is connected with a periodic variation of the potential of the iron. During the dissolution phase in 36·3% HNO_3, the potential is in the neighbourhood of +0·180 V. (on the hydrogen scale), and the occurrence of the short phase, during which violent liberation of gas and subsequently passivation take place, is connected with a sudden jump of potential to appreciably higher values. It would be instructive to measure these potentials under conditions which would allow comparison with the corrosion and passivation potentials of iron (fig. 19) and with the conditions of stability of the oxides of nitrogen (fig. 25).

(e) Electrochemical Fixation of Nitrogen

Fig. 25 shows that nitrogen and its oxides N_2O and NO are all thermodynamically unstable at pH's and potentials outside the lines $rH = 0$ and $rO = 0$, except for a small region at the acid end of the line $rO = 0$ in the case of nitrogen.

It is thus thermodynamically possible for nitrogen to be reduced at a cathode at which hydrogen is being liberated electrolytically, the reaction being

$$N_2 + 3H_2 + 2H_2O = 2NH_4OH\text{aq.},$$

or

$$N_2 - 2NH_4OH\text{aq.} + 3H_2 + 2H_2O = 0.$$

In principle, it should be possible to observe this "electrochemical fixation" of nitrogen when the gas is bubbled around a cathode, but it would no doubt be necessary to find a suitable catalyst.

In the same way, it is thermodynamically possible to oxidize nitrogen (or a gas such as air which contains it), N_2O or NO by bubbling the gas through the solution around an anode at which oxygen is being evolved; the nitrogen should be oxidized to nitrate

$$N_2 + 2{\cdot}5O_2 + H_2O = 2NO_3^- + 2H^+,$$

or

$$N_2 + 2{\cdot}5O_2 - 2NO_3^- + H_2O - 2H^+ = 0.$$

A double fixation of nitrogen, forming ammonia and nitric acid simultaneously, is thus in principle possible by carrying out these two reactions in a diaphragm cell.

APPENDIX A

STANDARD CHEMICAL POTENTIALS OF INORGANIC SUBSTANCES AT 25·0° C.

The majority of the values listed have been taken from tables given by Ulich in Landolt-Börnstein's *Tabellen** and by Wohl in the *Chemiker Taschenbuch*,‡ where they appear under the name "Standardbildungsarbeiten". The values have not in general been critically examined; those marked † have been evaluated by the writer. The unit is the calorie.

Latimer's important book[71] did not come to our knowledge until after the completion of this monograph. In consequence, none of Latimer's values have been used in the present tables, although in some cases they differ appreciably from the values given. Latimer gives a critical discussion of thermodynamic data for a large number of substances, and we strongly recommend any reader interested in chemical and electro-chemical equilibria to use his book.

The state of substances appearing in the tables which follow is indicated thus (Ulich's symbols*):

solids	[M]
liquids	M
gases	(M)
substances in aqueous solution	Maq.

The unit is the calorie.

STANDARD CHEMICAL POTENTIALS AT 25·0° C.

Aluminium	
[Al]	0
Al^{+++}aq.	−116,900
AlO_2^-aq.	−201,130†
$[Al_2O_3]$	−371,100
$(AlCl_3)$	−144,600
[AlN]	− 71,411
$[Al_4C_3]$	− 53,240
Antimony	
[Sb]	0
$[Sb_2O_3]$ cub.	−149,690
$[Sb_2O_3]$ rhomb.	−147,890
Arsenic	
[As]	0
$[As_2O_3]$	−137,300
$[As_2O_5]$	−185,400
AsF_3	−189,000
(AsF_3)	−188,000
$AsCl_3$	− 64,550
$(AsCl_3)$	− 62,075
Barium	
[Ba]	0
Ba^{++}aq.	−136,600
Beryllium	
[Be]	0
Be^{++}aq.	− 90,500
Bromine	
Br_2	0
(Br)	+ 19,680
(Br_2)	+ 755
Br_2aq.	+ 977
(HBr)	− 12,540
Br^-aq.	− 24,595
Br_3^-aq.	− 25,230
BrOHaq.	− 19,680
BrO_3^-aq.	+ 2,300
(BrCl)	− 250
Cadmium	
[Cd]	0
Cd	+ 563
(Cd)	+ 18,616
Cd amalg.	− 2,330
Cd^{++}aq.	− 18,348
[CdO]	− 55,064
$[Cd(OH)_2]$	−112,178
$[CdCl_2]$	− 81,860
$[CdBr_2]$	− 70,100
$[CdSO_4]$	−194,710

* Landolt-Börnstein,[66] 2. Ergänzungsband, 1931, pp. 1593 ff., 3. Ergänzungsband, 1936, pp. 2836 ff.

‡ *Chemiker Taschenbuch*,[128] 1939, part 3, pp. 237–9.

Calcium

[Ca]	0
Ca^{++}aq.	−133,600
[CaO]	−145,300
$[Ca(OH)_2]$	−214,600
$[CaCO_3]$ calc.	−270,390
$[CaCO_3]$ arag.	−270,200
$[CaF_2]$	−276,800
[CaS]	−109,800
$[CaSO_4]$	−311,470

Carbon

[C] graphite	0
[C] diamond	+ 390
(CO)	− 32,510
(CO_2)	− 94,260
H_2CO_3aq.	−148,810
HCO_3^-aq.	−140,000
CO_3^{--}aq.	−125,760
(COS)	− 39,600
CCl_4	− 15,400
$(COCl_2)$	− 48,770
(CS_2)	+ 17,600
HCN	+ 29,660
CN^-aq.	+ 39,370
(C_2N_2)	+ 92,000
HCNO aq.	− 28,980
CNO^-aq.	− 23,750
[ICN]	+ 42,790

Chlorine

(Cl_2)	0
(Cl)	+ 25,900
Cl_2	+ 1,146
Cl_2aq.	+ 1,650
(HCl)	− 22,740
Cl^-aq.	− 31,345
HOCl aq.	− 19,018
ClO^-aq.	− 6,500
ClO_3^-aq.	− 250
ClO_4^-aq.	− 10,937
(Cl_2O)	+ 21,210

Chromium

[Cr]	0
Cr^{++}aq.	− 25,670†?
Cr^{+++}aq.	− 35,220†?
$CrOH^{++}$aq.	− 86,040†?
$Cr(OH)_2^+$aq.	−134,120†?
H_2CrO_4aq.	−172,569†?
$HCrO_4^-$aq.	−171,560†?
CrO_4^{--}aq.	−162,700†?
CrO_2^-aq.	−111,260†?
$[Cr(OH)_2]$	−127,440†?
$[Cr(OH)_3]$	−188,260†?

Cobalt

[Co]	0
[CoO]	− 50,630
$[Co_3O_4]$	−181,355

Copper

[Cu]	0
Cu	+ 2,280
(Cu)	+ 78,940
(Cu_2)	+ 82,565
Cu amalg.	− 240
Cu^+aq.	+ 12,050
Cu^{++}aq.	+ 15,912
CuO_2H^-aq.	− 60,960†
CuO_2^{--}aq.	− 43,100†
$[Cu_2O]$	− 34,990
Cu_2O	− 20,230
[CuO]	− 30,300
CuO	− 19,470
$[Cu(OH)_2]$	− 84,900†
$[Cu_2S]$	− 20,640
[CuS]	− 11,720
[CuCl]	− 28,490
$CuCl_2^-$aq.	− 58,222
$[CuCl_2 . 2H_2O]$	−157,220
$[CuSO_4]$	−156,200
$[CuO . CuSO_4]$	−186,570

Fluorine

(F_2)	0
F^-aq.	− 65,600
(HF)	− 65,000
$(HF)_6$	−371,100

Gallium

[Ga]	0
Ga^{+++}aq.	− 36,000

Gold

[Au]	0
$[Au_2O_3]$	+ 18,810

Hydrogen

(H_2)	0
(H)	+ 48,300
H_2aq.	+ 4,180
H^+aq.	0
(HD)	− 351

Iodine

[I]	0
I_2	+ 920
(I)	+ 14,400
(I_2)	+ 4,630
I_2aq.	+ 3,926
I^-aq.	− 12,361
I_3^-aq.	− 12,315
(HI)	+ 315
HIO aq.	− 23,170
IO_3^-aq.	− 31,580
IO_4^-aq.	− 18,500
(ICl)	− 1,370
$[ICl_3]$	− 5,410
(IBr)	+ 970

Iron

$[Fe]\alpha$	0
$[Fe]\gamma$	64
Fe^{++}aq.	− 20,310
FeO_2H^-aq.	− 90,250†?
Fe^{+++}aq.	− 3,120
$FeOH^{++}$aq.	− 56,650†
FeO_4^{--}aq.	−111,760†?
$[Fe(OH)_2]$	−115,200
$[Fe(OH)_3]$	−167,640†?
[FeO]	− 58,720
$[Fe_3O_4]$	−241,820
$[Fe_2O_3]$	−176,100?
[FeS]	− 23,100
$[FeS_2]$	− 32,780

Lead

[Pb]	0
Pb	+ 530
(Pb)	+ 41,760
Pb amalg.	− 270
Pb^{++}aq.	− 5,551
$PbOH^+$aq.	− 53,440
$Pb(OH)_2$aq.	− 96,870
PbO_2H^-aq.	− 80,600
[PbO] yellow	− 44,887
[PbO] red	− 45,050
$[Pb_3O_4]$	−147,270
$[PbO_2]$	− 52,010
$[PbCl_2]$	− 74,990
$PbCl_2$	− 58,700
$PbCl_5^-$aq.	−104,700
$[PbBr_2]$	− 62,065
$[PbI_2]$	− 41,501
[PbS]	− 22,220
$[PbSO_4]$	−192,160
$[PbCO_3]$	−149,000
$[2PbCO_3 . Pb(OH)_2]$	−407,070

Lithium

[Li]	0
Li^+aq.	− 68,248
[LiOH]	−105,130
[LiCl]	− 91,610
$[Li_2SO_4]$	−313,610

Magnesium

[Mg]	0
Mg^{++}aq.	−108,500
$[Mg(OH)_2]$	−168,440†
[MgO]	−138,690
$[MgCO_3]$	−227,990†
$[MgCl_2]$	−140,890
$[MgBr_2]$	−144,000

Manganese

[Mn]	0
[MnO]	− 90,240
$[Mn_3O_4]$	−320,000
$[MnO_2]$	−112,600
[MnS]	− 64,000?

Mercury

Hg	0
[Hg]	+ 149
(Hg)	+ 7,630
Hg_2^{++}aq.	+ 37,240
Hg^{++}aq.	+ 39,680
[HgO] yellow	− 13,850
[HgO] red	− 13,940
[HgCl]	− 25,163
$[HgCl_2]$	− 43,550
$HgCl_2$	− 41,930
$(HgCl_2)$	− 34,570
[HgBr]	− 21,350
[HgI]	− 13,290
$[Hg_2SO_4]$	−147,830

Nickel

[Ni]	0
[NiO]	− 56,497

Nitrogen

(N_2)	0
(N)	+102,500
N_2aq.	+ 4,360
(N_2O)	+ 24,770
(NO)	+ 20,850
(NO_2)	+ 11,920
(N_2O_4)	+ 22,640
HNO_2aq.	− 13,070
NO_2^-aq.	− 8,500
NO_3^-aq.	− 26,500
(NH_3)	− 3,910
NH_3	− 2,620
NH_4OH aq.	− 62,860
NH_4^+aq.	− 18,930
$[NH_4Cl]$	− 47,810
(NOCl)	+ 16,010
(NOBr)	+ 19,260

Oxygen

(O_2)	0
(O)	+ 57,500
(O_3)	+ 38,850
O_2aq.	+ 3,900
$[H_2O]$	− 56,420
H_2O	− 56,560
(H_2O)	− 54,507
(OH)	+ 4,850
OH^-aq.	− 37,455
$[H_2O_2]$	− 27,980
H_2O_2	− 28,230
(H_2O_2)	− 24,730
H_2O_2aq.	− 31,470
HO_2^-aq.	− 15,610

Phosphorus

[P] white	0
(P_2)	+ 16,070
(P_4)	+ 5,850
(PH_3)	− 3,296
PCl_3	− 63,300
(PCl_3)	− 62,220

Potassium

[K]	0
K^+aq.	− 67,477
[KOH]	− 92,950
[KCl]	− 97,700
[KBr]	− 90,455
[KI]	− 77,520
$[KClO_3]$	− 69,250
$[KClO_4]$	− 73,650
$[KNO_3]$	− 95,000
$[K_2SO_4]$	−313,520
$[KHg_{12}]$	− 23,430

Rubidium

[Rb]	0
Rb^+aq.	− 67,473

Selenium

[Se]	0
H_2SeO_3aq.	−101,360
$HSeO_3^-$aq.	− 97,850
$HSeO_4^-$aq.	−107,710

Silicon

[Si]	0
$SiCl_4$	−135,600?

Silver

[Ag]	0
Ag^+aq.	+ 18,448
$[Ag_2O]$	− 2,395
[AgCl]	− 26,220
[AgBr]	− 22,910
[AgI] hex.	− 16,356
[AgI] precip.	− 15,825
$[Ag_2S]$	− 9,770
$[AgNO_3]$	+ 4,900
$[Ag_2SO_4]$	−145,950
$[Ag_2CO_3]$	−103,910
$Ag(SO_3)_2^{---}$aq.	−226,345
$Ag(NH_3)_2^+$aq.	− 4,003
[AgCN]	+ 38,499
$Ag(CN)_2^-$aq.	+ 72,047

Sodium

[Na]	0
Na^+aq.	− 62,588
[NaOH]	− 90,760
[NaF]	−129,500
[NaCl]	− 91,792
[NaBr]	− 83,105
[NaI]	− 68,465
$[NaNO_3]$	− 88,300
$[Na_2SO_4]$	−301,670

Strontium

[Sr]	0
Sr^{++}aq.	−135,900

Sulphur	
[S] rhomb.	0
[S] monoclin.	+ 18
Sλ	+ 94
(S_2)	+ 18,280
(S_6)	+ 11,900
(S_8)	+ 10,000
(H_2S)	− 7,840
H_2S aq.	− 6,490
SH^- aq.	+ 2,980
S^{--} aq.	+ 23,450
(SO_2)	− 69,660
H_2SO_3 aq.	−126,330
HSO_3^- aq.	−123,920
SO_3^{--} aq.	−116,680
$S_2O_3^{--}$ aq.	−125,110
(SO_3)	− 85,890
SO_4^{--} aq.	−176,540
SF_6	−238,000
(SO_2Cl_2)	− 71,560

Tellurium	
[Te]	0
Te^{++++} aq.	− 52,430
$[TeO_2]$	− 64,320

Thallium	
[Tl]	0
Tl amalg.	− 55
Tl^+ aq.	− 7,760
$[Tl_2O]$	− 32,410
[TlOH]	− 45,400
[TlCl]	− 44,164
[TlBr]	− 39,740
[TlI]	− 30,020
$[Tl_2SO_4]$	−196,740

Tin	
[Sn] white	0
[Sn] grey	+ 9
Sn^{++} aq.	− 6,276
[SnO]	− 61,332
$[SnO_2]$	−123,200
$[SnCl_4]$	−113,210?
$[Sn(OH)Cl.H_2O]$	−154,490

Vanadium	
[V]	0
$[V_2O_2]$	−216,510
$[V_2O_3]$	−299,280
$[V_2O_4]$	−345,850

Zinc	
[Zn]	0
Zn	+ 998
(Zn)	+ 22,885
Zn^{++} aq.	− 34,984
$[Zn(OH)_2]$	−132,220
[ZnO]	− 75,930
$[ZnCl_2]$	− 87,800
$[ZnBr_2]$	− 74,140
$[ZnCO_3]$	−175,500
$[ZnSO_4]$	−204,350
$[3ZnO.2SO_3]$	−474,300

Abbreviations:

amalg.: 2 phase amalgam
calc.: calcite
arag.: aragonite

APPENDIX B

METHODS OF CONSTRUCTING CURVES

(1) *Solubility of Hydroxides*

Inscribed curves of the type mentioned in connexion with $Al(OH)_3$ can be drawn by use of the following rules.

At the pH at which the two straight lines enclosing the curve intersect, the ordinate of the curve lies 0·301 unit above the ordinate of the point of intersection. At pH's 0·5 unit below or above the pH of intersection, the ordinate of the curve is 0·119, 0·040 or 0·014 unit above the higher of the two straight lines, according as the slopes of these lines differ by 1, 2 or 3 units. The difference in the slopes, without regard to sign, is equal to the difference in the valencies of the corresponding solute ions.

As an example, consider the solubility of $Zn(OH)_2$. The three straight lines intersect at $\mathrm{pH} = 13{\cdot}3$, $\log C = -2{\cdot}40$ and at $\mathrm{pH} = 10{\cdot}0$, $\log C = -5{\cdot}65$; the curve of log (total solubility) thus passes through the points:

$$\mathrm{pH} = 13{\cdot}3;\ \log C = -2{\cdot}40 + 0{\cdot}30 = -2{\cdot}10;$$
$$\mathrm{pH} = 10{\cdot}0;\ \log C = -5{\cdot}65 + 0{\cdot}30 = -5{\cdot}35.$$

The valency differences are:

For ZnO_2^{--} and ZnO_2H^-: valency change 1;
ZnO_2H^- and Zn^{++}: valency change 3;

and consequently:

at $\mathrm{pH} = 13{\cdot}8$: $\log C = -1{\cdot}40 + 0{\cdot}12 = -1{\cdot}28$;
$12{\cdot}8$: $-2{\cdot}90 + 0{\cdot}12 = -2{\cdot}78$;
$10{\cdot}5$: $-5{\cdot}15 + 0{\cdot}01 = -5{\cdot}14$;
$9{\cdot}5$: $-4{\cdot}65 + 0{\cdot}01 = -4{\cdot}64$.

The values 0·119, 0·041 and 0·014, quoted above and used in the example, can be determined as follows.

The equations of the two straight lines under consideration are of the form

$$\log C_1 = a_1 + m_1\mathrm{pH},$$

and

$$\log C_2 = a_2 + m_2\mathrm{pH}.$$

They intersect at

$$\mathrm{pH} = \frac{a_1 - a_2}{m_2 - m_1}.$$

At a pH 0·5 unit higher, i.e. at

$$\mathrm{pH} = \frac{a_1 - a_2}{m_2 - m_1} + 0{\cdot}5,$$

the ordinates of the two lines are respectively

$$\log C_1 = a_1 + m_1\left[\frac{a_1 - a_2}{m_2 - m_1} + 0{\cdot}5\right] = \frac{a_1m_2 - a_2m_1}{m_2 - m_1} + 0{\cdot}5m_1,$$

and

$$\log C_2 = a_2 + m_2\left[\frac{a_1 - a_2}{m_2 - m_1} + 0{\cdot}5\right] = \frac{a_1m_2 - a_2m_1}{m_2 - m_1} + 0{\cdot}5m_2,$$

from which it follows that

$$\log C_1 - \log C_2 = \log \frac{C_1}{C_2} = 0{\cdot}5(m_1 - m_2).$$

The ordinate for *total* concentration $C_1 + C_2$ can now be calculated:

$$\log (C_1 + C_2) = \log C_1\left(1 + \frac{C_2}{C_1}\right) = \log C_1 + \log\left(1 + \frac{C_2}{C_1}\right).$$

If $m_1 > m_2$, we have $C_1 > C_2$, since $\log \frac{C_1}{C_2} = 0{\cdot}5(m_1 - m_2)$; the difference between the ordinate of the total solubility $(C_1 + C_2)$ curve, and that of the higher curve (C_1) of the two components, is then

$$\log (C_1 + C_2) - \log C_1 = \log\left(1 + \frac{C_2}{C_1}\right),$$

and has the following values for various values of the valency difference $(m_1 - m_2)$:

$m_1 - m_2$	1	2	3
$\log \frac{C_1}{C_2}$	0·5	1·0	1·5
$\frac{C_2}{C_1}$	0·316	0·100	0·0316
$1+\frac{C_2}{C_1}$	1·316	1·100	1·0316
$\log\left(1 + \frac{C_2}{C_1}\right)$	0·119	0·041	0·014

(2) *Equilibria in the N-H_2O system*

The conditions of equilibrium between the total solute $HNO_2 + NO_2^-$ on the one hand and the gases NO_2, N_2O_4 and NO on the other can be established as follows:

1. The conditions of equilibrium between a given gas and the two solutes HNO_2 and NO_2^- considered separately are of the form

$$E_1 = E_1^0 - \frac{0{\cdot}0591 m_1}{n}\text{pH} + \frac{0{\cdot}0591}{n}\chi_1, \qquad \ldots (a)$$

and

$$E_2 = E_2^0 - \frac{0{\cdot}0591 m_2}{n}\text{pH} + \frac{0{\cdot}0591}{n}\chi_2, \qquad \ldots (b)$$

where χ_1 and χ_2 represent the logarithms of a function of the concentration of the solute HNO_2 or NO_2^- and the pressure of the gas; for example, for reactions (15) and (16) we have

$$\chi_1 = \log \frac{p_{NO_2}}{(HNO_2)},$$

and

$$\chi_2 = \log \frac{p_{NO_2}}{(NO_2^-)}.$$

The analogous reactions in other cases are (17) and (18) for N_2O_4 and (19) and (20) for NO (see p. 106); the coefficient n has the same value for each of the two reactions in a given group. When plotted on a pH-potential diagram such as fig. 27, equations (*a*) and (*b*) give rise to two families of straight lines, each line relating to a particular value of χ_1 or χ_2, shown on the diagram by the index.

It follows from equations (*a*) and (*b*) that the difference in χ_1 and χ_2 at any given point on the diagram is

$$\chi_1 - \chi_2 = \frac{n(E_1 - E_2)}{0{\cdot}0591} + (m_1 - m_2)\text{pH}. \qquad \ldots (c)$$

Putting $\chi_1 = \chi_2$ in this equation, we obtain the pH of the point of intersection of the two straight lines of the same index

$$\text{pH}_i = -\frac{n(E_1 - E_2)}{0{\cdot}0591(m_1 - m_2)}. \qquad \ldots (d)$$

By combining (*c*) and (*d*) we thus obtain

$$\chi_1 - \chi_2 = (m_1 - m_2)(\text{pH} - \text{pH}_i). \qquad \ldots (e)$$

2. The condition of equilibrium between a given gas and the two solutes $HNO_2 + NO_2^-$ taken together will be of the form

$$E_s = f(\text{pH}, \chi_s), \qquad \ldots (f)$$

where χ_s is the logarithm of a function of the combined concentration of the two solutes and the pressure of the gas, this function being of the same form as that occurring in the corresponding χ_1 and χ_2 defined above. The relation between χ_s, χ_1 and χ_2 varies with the form of this function:

(*a*) In reactions (19) and (20) the terms (HNO_2) and (NO_2^-) occur in χ_1 and χ_2 with exponents $+1$, and we have

$$\chi_1 = \log \frac{(HNO_2)}{p_{NO}}, \quad \chi_2 = \log \frac{(NO_2^-)}{p_{NO}}, \quad \chi_s = \log \frac{(HNO_2) + (NO_2^-)}{p_{NO}},$$

and

$$\frac{(HNO_2) + (NO_2^-)}{p_{NO}} = \frac{(HNO_2)}{p_{NO}} + \frac{(NO_2^-)}{p_{NO}};$$

whence

$$10^{\chi_s} = 10^{\chi_1} + 10^{\chi_2}. \qquad \ldots (g)$$

(*b*) In reactions (15) and (16), the exponents of (HNO_2) and (NO_2^-) are -1, and we thus have

$$\chi_1 = \log \frac{p_{NO_2}}{(HNO_2)}, \quad \chi_2 = \log \frac{p_{NO_2}}{(NO_2^-)}, \quad \chi_s = \log \frac{p_{NO_2}}{(HNO_2) + (NO_2^-)};$$

whence

$$10^{-\chi_s} = 10^{-\chi_1} + 10^{-\chi_2}. \qquad \ldots (h)$$

(*c*) Finally, for reactions (17) and (18) the exponent is -2, and we have

$$\chi_1 = \log \frac{p_{N_2O_4}}{(HNO_2)^2}, \quad \chi_2 = \log \frac{p_{N_2O_4}}{(NO_2^-)^2}, \quad \chi_s = \log \frac{p_{N_2O_4}}{[(HNO_2) + (NO_2^-)^2]};$$

whence

$$10^{-0{\cdot}5\chi_s} = 10^{-0{\cdot}5\chi_1} + 10^{-0{\cdot}5\chi_2}. \qquad \ldots (j)$$

The required equations, ((15) (16)), ((17) (18)) and ((19) (20)), can now be obtained by eliminating χ_1 and χ_2 from (*g*), (*h*) and (*j*) respectively with the aid of (*e*) and (*a*) or (*b*).

3. $NO_2/HNO_2 + NO_2^-$ equilibrium (equations (15) and (16)). We have (equation (*h*))

$$10^{-\chi_s} = 10^{-\chi_1} + 10^{-\chi_2},$$

or

$$10^{-\chi_s} = 10^{-\chi_1}(1 + 10^{\chi_1-\chi_2}).$$

In view of (*e*), this can be written

$$10^{-\chi_s} = 10^{-\chi_1}[1 + 10^{(m_1-m_2)(pH-pH_i)}];$$

whence

$$\chi_1 = \chi_s + \log[1 + 10^{(m_1-m_2)(pH-pH_i)}].$$

Introducing this value of χ_1 into (*a*), we obtain the equation of the required curve

$$E_s = E_1^0 - \frac{0{\cdot}0591 m_1}{n} \text{pH} + \frac{0{\cdot}0591}{n}[\chi_s + \log\{1 + 10^{(m_1-m_2)(pH-pH_i)}\}].$$

Alternatively, χ_s may be expressed in terms of χ_2, and with the aid of equation (*b*) we then obtain

$$E_s = E_2^0 - \frac{0{\cdot}0591 m_2}{n} \text{pH} + \frac{0{\cdot}0591}{n}[\chi_s + \log\{1 + 10^{(m_1-m_2)(pH_i-pH)}\}].$$

Introducing the numerical values of E_1^0, E_2^0, m_1, m_2 and n (see (15) and (16) on pp. 105–6), and putting $pH_i = 3{\cdot}35$ (equation (*d*)) we find

$$\left.\begin{aligned} E_s &= 1{\cdot}084 - 0{\cdot}0591\text{pH} + 0{\cdot}0591[\chi_s + \log(1 + 10^{pH-3{\cdot}35})], \\ &\text{and} \\ E_s &= 0{\cdot}886 \qquad\qquad + 0{\cdot}0591[\chi_s + \log(1 + 10^{3{\cdot}35-pH})]. \end{aligned}\right\}\ldots((15)(16))$$

These equations constitute two equivalent formulations of the curve ((15) (16)). Both of them are most convenient for computation when the exponent of 10 is negative; the first should thus be used for pH's less than 3·35 and the second for pH's above this value.

4. $N_2O_4/HNO_2 + NO_2^-$ equilibrium (equations (17) and (18)). The procedure is closely similar to that just described, and leads to two equivalent equations for the curve ((17) (18))

$$\left.\begin{aligned} E_s &= 1{\cdot}057 - 0{\cdot}0591\text{pH} + 0{\cdot}0295[\chi_s + 2\log(1 + 10^{pH-3{\cdot}35})], \\ &\text{and} \\ E_s &= 0{\cdot}859 \qquad\qquad + 0{\cdot}0295[\chi_s + 2\log(1 + 10^{3{\cdot}35-pH})]. \end{aligned}\right\}\ldots((17)(18))$$

5. $NO/HNO_2 + NO_2^-$ equilibrium (equations (19) and (20)). In this case, the two equivalent equations for curve ((19) (20)) are

$$\left.\begin{aligned} E_s &= 0{\cdot}982 - 0{\cdot}0591\text{pH} + 0{\cdot}0591[\chi_s - \log(1 + 10^{pH-3{\cdot}35})], \\ &\text{and} \\ E_s &= 1{\cdot}180 - 0{\cdot}1182\text{pH} + 0{\cdot}0591[\chi_s - \log(1 + 10^{3{\cdot}35-pH})]. \end{aligned}\right\}\ldots((19)(20))$$

6. A simple practical method of constructing these curves was mentioned on p. 110; a proof will now be given. As an example, consider the curve ((15) (16)), which is defined by equations ((15) (16)). The separate straight lines (15) and (16) are defined respectively by the equations

$$E_1 = 1{\cdot}084 - 0{\cdot}0591\text{pH} + 0{\cdot}0591\chi_1, \qquad \ldots (15)$$

$$E_2 = 0{\cdot}886 \qquad\qquad + 0{\cdot}0591\chi_2. \qquad \ldots (16)$$

Considering a curve of the family ((15) (16)) and two straight lines (15) and (16), having the same index, so that $\chi_s = \chi_1$ or $\chi_s = \chi_2$, the differences in the ordinates E at a given pH must be

$$E_s - E_1 = 0{\cdot}0591 \log(1 + 10^{pH-3{\cdot}35}) \qquad \text{for ((15) (16)) and (15),}$$

and

$$E_s - E_1 = 0{\cdot}0591 \log(1 + 10^{3{\cdot}35-pH}) \qquad \text{for ((15) (16)) and (16),}$$

which give the following values:

(pH − 3·35)	$E_s - E_1$	$E_s - E_2$
− 1·0	0·0024 V.	—
− 0·5	0·0070	—
0·0	0·0178	0·0178 V.
+ 0·5	—	0·0070
+ 1·0	—	0·0024

It can easily be shown that $E_s - E_1$ and $E_s - E_2$ have these same values for the curve ((17) (18)); for ((19) (20)) the potential differences have the same magnitudes but opposite signs. This result agrees with the rule already stated; the curve lies above or below the two corresponding straight lines according as the solute (HNO_2 or NO_2^-) is the compound of lower or higher degree of oxidation in the equilibrium.

APPENDIX C

SYMBOLS

(Symbols marked † are used in De Donder and Van Rysselberghe's *Affinity*.[19])

†A	Chemical affinity.
Ā	Electrochemical affinity.
a_γ	Activity of dissolved constituent γ (corrected molar concentration: $a_\gamma \equiv C_\gamma f_\gamma$).
†C_γ	Concentration of dissolved constituent γ (in g. mol. per litre).
E	"Electrical equilibrium potential" (in volts), measured with respect to the standard hydrogen electrode. This is the potential taken up by an electrode in equilibrium with the oxidized and reduced substances taking part in a reaction. When the oxidized and reduced substances are both in solution (e.g. a platinum electrode in a solution of Cu^{++} and Cu^{+} ions), E is a "redox" potential; when one of the substances is a solid (e.g. a copper electrode in a solution of Cu^{++} and Cu^{+} ions), E is a "solution" potential; when one of the substances is a gas (e.g. a hydrogen electrode), E is a "gas electrode" potential.[*]
E^0	"Standard electrode potential", or equilibrium potential E when the reactants are all in the "standard state" (i.e. all gases have a fugacity of 1 atm. and all solutes have an activity of 1 g. mol. per litre, the temperature being 25·0° C.).
f_γ	Activity or fugacity coefficient of the constituent γ.
†K	Equilibrium constant (see p. 9).
†M_γ	Chemical symbol of reactant γ.
(M_γ)	Fugacity of a gaseous constituent γ (in atmospheres), or activity of a solute γ (g. mol. per litre).
m	Stoichiometric coefficient of H^+ ion (i.e. ν_γ for H^+).
n	Stoichiometric coefficient of electrons, e^- (i.e. ν_γ for e^-).
†n_γ	Number of g. mol. of constituent γ.
†p	Pressure (in atmospheres).
†R	Gas constant (1·98 cal./° C.).
rH	Cologarithm of hydrogen pressure (atm.) ($rH = -\log p_{H_2}$).
rO	Cologarithm of oxygen pressure (atm.) ($rO = -\log p_{O_2}$).
†T	Absolute temperature.
†γ	Any reacting species.
†φ_γ	Fugacity of a gaseous constituent γ (corrected partial pressure: $\varphi_\gamma = p_\gamma f_\gamma$).
†μ_γ	Molar chemical potential of constituent γ. μ_γ is defined by the equations: $\mu_\gamma = \left(\frac{\partial E}{\partial n_\gamma}\right)_{S,V} = \left(\frac{\partial H}{\partial n_\gamma}\right)_{S,p} = \left(\frac{\partial F}{\partial n_\gamma}\right)_{V,T} = \left(\frac{\partial G}{\partial n_\gamma}\right)_{p,T}$ (see De Donder[19] (p. 34, equation 5.32)), where E = Internal energy, F = Helmholtz free energy, G = Gibbs's function $\zeta = E - TS + PV$, H = Heat content (enthalpy), S = Entropy, V = Volume. μ_γ is related to the partial molar heat content $\overline{H}_\gamma$ and to the partial molar entropy $\overline{S}_\gamma$ by the equation: $\mu_\gamma = \overline{H}_\gamma - T\overline{S}_\gamma$.
μ'_γ	Molar chemical potential of constituent γ when the constituent is in a standard state (fugacity = 1 atm. for gases; activity = 1 g. mol. per litre for solutes) at a temperature T.
μ^0_γ	Standard molar chemical potential of constituent γ at 25·0° C., i.e. the value of μ'_γ when T = 298·1° K. μ^0_γ has a definite value (apart from an arbitrary constant) for every substance. These values are tabulated in several specialized works, under different names, which are equivalent to one another except for sign (*Affinité*, *Free Energy* (Lewis), *Standardbildungsarbeit*, etc.). A table showing values of μ^0 for a number of substances will be found in Appendix A.
ν_γ	Molar or stoichiometric coefficient of constituent γ.

---

[*] Cf. Pourbaix.[98]

REFERENCES

1. Bauer, Kröhnke and Masing, "Die Korrosion metallischer Werkstoffe", Vol. **1** (Leipzig, 1936).
2. Bawn and Evans, *Trans. Faraday Soc.*, 1935, **31**, 1392.
3. Bennett, *Trans. Faraday Soc.*, 1932, **28**, 889.
3*a*. Bézier, Thesis (série A, no. 2100, Paris, 1945).
4. Bjerrum, *Z. physikal. Chem.*, 1910, **73**, 724.
5. Brandsma, *Rec. Trav. Chim.*, 1928, **47**, 94.
6. Brandsma, *Rec. Trav. Chim.*, 1929, **48**, 1205.
7. Bray and Hershey, *J. Am. Chem. Soc.*, 1934, **56**, 1889.
8. Burgers, *Chem. Weekblad*, 1942, **39**, 198, 215.
9. Buydens, *J. Pharm. Belg.*, 1941, nos. 6, 7, 8.
9*a*. Charlot, "Théorie et méthode nouvelle d'analyse qualitative," 3ème edn. (Paris 1949).
9*b*. Charlot and Bézier, "Méthodes modernes d'analyse quantitative", 2ème edn. (Paris 1949).
10. Chaudron, Personal communication (29th October 1938).
11. Chaudron, *Chim. et Ind.*, 1931, **26**, 273.
12. Chipman and Murphy, *Trans. Am. Soc. Met.*, 1933, **25**, 319.
13. Clark, "The Determination of Hydrogen Ions" (London, 1928).
14. Coin, *Ann. Hygiène*, 1942, **20**, 145.
15. Colombier, "L'état passif des métaux. Étude de la passivité du nickel" (Thesis, Nancy, 1936).
16. Cooper, *Proc. Roy. Soc.*, B, 1937, **124**, 299.
17. Debye and Hückel, *Physikal Z.*, 1923, **24**, 185, 334; 1924, **25**, 97.
18. De Donder, "L'affinité" (Paris, 1927).
19. De Donder and Van Rysselberghe, "Affinity" (Stanford, 1936); (Van Rysselberghe, *Chem. Reviews*, 1935, **16**, 29, 37.
20. De Donder, *Bull. Acad. Roy. Belg.*, 1942, **28**, 626.
21. Déribéré, "Les Applications Industrielles du rH" (Paris, 1937).
22. Dony-Hénault, *Bull. Soc. Chim. Belg.*, 1910, **24**, 56.
23. Erculisse, Course in Analytical Chemistry at the University of Brussels (unpublished).
24. Erculisse, "Les bases théoriques de la corrosion", Association Belge pour l'Étude, l'Essai et l'Emploi des Matériaux, Report no. 8 (1937).
25. Erculisse, "Considérations générales sur les méthodes d'Epuration des Eaux d'alimentation des chaudières", *Bulletin Sofina*, December 1939.
26. Evans, A. G., and Evans, M. G., *Trans. Faraday Soc.*, 1935, **31**, 1400.
27. Evans, M. G., and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875.
28. Evans, U. R., *J. Inst. Metals*, 1923, **30**, 267.
29. Evans, U. R., *J. Chem. Soc.*, 1930, 478.
30. Evans, U. R., *Metals and Alloys*, 1931, 2 (February).
31. Evans, U. R., and Hoar, *Trans. Faraday Soc.*, 1934, **30**, 424.
32. Evans, U. R., "Metallic Corrosion, Passivity and Protection" (London, 2nd edn., 1946).
33. Eyring, *J. Chem. Phys.*, 1935, **3**, 107.
34. Fenwick, *J. Am. Chem. Soc.*, 1926, **48**, 860.
35. Franquin and Marécaux, *Chim. et Ind.*, special no., 1938, **40**, 1224.
36. Fricke and Hüttig, "Hydroxyde und Oxydhydrate" in P. Walden, "Handbuch der allgemeinen Chemie", Bd. IX (Leipzig).
37. Fricke and Meyring, *Z. anorg. allg. Chem.*, 1933, **214**, 269.
38. Gatty and Spooner, "The Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions" (Oxford, 1938).
38*a*. Gillet, "Leçons sur l'Electrolyse" (Université de Liége).
39. Glasstone, "Electrochemistry of Solutions" (London, 1937).
40. Gmelin, "Handbuch der anorganischen Chemie", "Stickstoff", 8th edn. (Berlin, 1935–6).
41. Gmelin, "Handbuch der anorganischen Chemie", "Eisen B" (Berlin, 1932).
42. Groesbeck and Waldron, *Proc. Am. Soc. Test. Mat.*, 1931, **31**, 286.
43. Grube and Breitinger, *Z. Elektrochem.*, 1927, **33**, 112.
44. Grübe and Gmelin, *Z. Elektrochem.*, 1920, **26**, 459.
45. Guillerd, *Ann. Hygiène*, 1941, no. 5.
46. Haber, *Z. Elektrochem.*, 1898, **4**, 506.

47. Haber, *Z. physikal. Chem.*, 1900, **32**, 193.
48. Herzog and Chaudron, *Bull. Soc. Chim.*, 1931, **49**, 702.
49. Herzog and Chaudron, *C.R.*, 1931, **192**, 837.
50. Heyrovsky, *J. Chem. Soc.*, 1920, **117**, 20.
51. Heyrovsky, *Trans. Faraday Soc.*, 1930, **26**, 341.
52. Heyrovsky, "Polarographie" (Vienna, 1941).
53. Hoar, *Chim. et Ind.*, special no., 1939, **41**, 118c.
54. Hoar, *Trans. Faraday Soc.*, 1937, **33**, 1152.
55. Hoar and Evans, U. R., *J. Chem. Soc.*, 1932, 2476.
56. Latimer and Hildebrand, "Reference Book of Inorganic Chemistry" (New York, 1929).
57. Hoover, *J. Am. Waterworks Ass.*, 1938, 1891.
58. Huybrechts, "Le pH et sa mesure—Le potential d'oxydo-réduction" (Liége, 1932).
59. Jolibois, "Les méthodes actuelles de la Chimie" (Paris, 1938).
60. Jolibois, *Berichte*, 1938, **71**, 73.
61. Karschulin, *Z. Elektrochem.*, 1937, **43**, 588, 591.
62. Kassel, *J. Chem. Phys.*, 1933, **1**, 414.
63. Kassel, *J. Am. Chem. Soc.*, 1943, **56**, 1838.
64. Kolthoff and Furman, "Indicators" (New York and London, 1926).
65. Krause, *Z. anorg. allg. Chem.*, 1928, **174**, 145.
66. Landolt-Börnstein, *Physikalische-chemische Tabellen*, II and III Ergänzungsbände.
67. Lange and Nagel, *Z. Elektrochem.*, 1938, **44**, 637.
68. Lange and Nagel, *Z. Elektrochem.*, 1938, **44**, 792.
69. Lange and Nagel, *Z. Elektrochem.*, 1938, **44**, 856.
70. Langelier, *J. Am. Waterworks Ass.*, 1936, **28**, 1500.
71. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions (New York, 1938).
72. Léonet, *Bull. Assoc. Gaziers Belges*, 1936 (December).
73. Léonet, *Bull. Assoc. Gaziers Belges*, 1938 (December).
74. Lewis, *Z. physikal. Chem.*, 1908, **61**, 129.
75. Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances" (New York, 1923).
76. McAulay and White, *J. Chem. Soc.*, 1930, 194.
77. McBain and Van Rysselberghe, *J. Am. Chem. Soc.*, 1928, **50**, 3009.
78. McDowell and Johnston, *J. Am. Chem. Soc.*, 1936, **58**, 2009.
79. Marcelin, *Ann. Physique*, 1915, (9) III, 120.
80. Meunier, *J. Chim. phys.*, 1925, **22**, 595.
81. Meunier and Bihet, *Chim. et Ind.*, special no., 1934, **31**, 444.
82. Meyer, *Bull. Soc. Chim. Belg.*, 1908, **22**, 259.
83. Michaelis, "Hydrogen Ion Concentration" (London, 1926).
84. Michaelis, "Oxidation-reduction Potentials" (Philadelphia, 1930).
85. Müller, E., "Das Eisen und seine Verbindungen" (Dresden and Leipzig, 1917).
86. Müller, W. J., *Z. Elektrochem.*, 1924, **30**, 405.
87. Müller, W. J., and Löwy, *Wiener Monatshefte*, 1928, **49**, 64.
88. Müller, W. J., "Die Bedeckungstheorie des Passivität der Metalle und ihre experimentalle Begründung" (Berlin, 1933).
89. Müller, W. J., *Trans. Am. Electrochem. Soc.*, 1939.
90. Noyes and Chow, *J. Am. Chem. Soc.*, 1918, **40**, 739.
91. Palmaer, "The Corrosion of Metals" (Svenska Bokhandelscentralen, 1929–31).
92. Peters, *Z. physikal. Chem.*, 1898, **26**, 193.
93. Pick, *Z. Elektrochem.*, 1920, **26**, 193.
94. Pourbaix, *Bull. Soc. Belg. Ing. Ind.*, 1934, 671 and 783.
95. Pourbaix, *Rev. Univ. Mines*, 1935, **11**, 367.
96. Pourbaix, *Bull. Soc. Chim. Belg.*, 1938, **47**, xlviii.
97. Pourbaix, *Métaux et Corrosion*, 1938, **14**, 189.
98. Pourbaix, *Chim. et Ind.*, special no., 1939, **41**, 110c.
99. Randall and Frandsen, *J. Am. Chem. Soc.*, 1932, **54**, 40 and 47.
100. Randall and Young, *J. Am. Chem. Soc.*, 1928, **50**, 989.
101. Randall, Nielsen and West, *Ind. Eng. Chem.*, 1931, **23**, 388.
102. Reiller, "Evolution du Potentiel du fer dans la corrosion par effet Evans" (Publ. sci. tech. Secr. Etat Aviation no. 180, Paris, 1942).
103. Reiller, *Métaux Corrosion Usure*, 1942, **17**, 19 and 42.
104. Scheffer and Kohnstamm, *Versl. Ak. Wetensch. Amsterdam*, 1911, **19**, 878 (in Dutch).
105. Scheffer and Kohnstamm, *Versl. Ak. Wetensch. Amsterdam*, 1911, **13**, 789 (in English).
106. Scheffer, *Versl. Ak. Wetensch. Amsterdam*, 1913, **21**, 1134 (in Dutch).
107. Scheffer, *Versl. Ak. Wetensch. Amsterdam*, 1913, **15**, 1109 (in English).

108. Scheffer and Brandsma, *Rec. Trav. Chim.*, 1926, **45**, 522.
109. Schenk, *Z. angew. Chem.*, 1936, **49**, 649.
110. Schrager, *Chem. News*, 1929, **138**, 354.
111. Sörensen, *Biochem. Zeitschrift*, 1909, **21**, 131 and 200.
112. Spitzer, *Z. Elektrochem.*, 1905, **11**, 345.
113. Tafel, *Z. anorg. allg. Chem.*, 1902, **31**, 289.
114. Taylor, H. S., *Proc. Roy. Soc.*, A, 1925, **108**, 105.
115. Thiel and Strohecker, *Berichte*, 1914, **47**, 945.
116. Thiesse, Thesis (Nancy, 1937).
117. Tillmans and Heublein, *Gesundh. Ing.*, 1912, **34**, 669.
118. Tillmans and Heckman, *Z. f. Untres. Lebensmitteln*, 1929, **58**, 33.
119. Travers, *Métaux et Corrosion*, 1938, **13**, 194.
120. Treadwell, "Analytical Chemistry", Vol. II, p. 151 (7th edn., New York and London 1930).
121. Ulich, "Chemische Thermodynamik" (Dresden and Leipzig, 1930).
122. Van Bohnson and Robertson, *J. Am. Chem. Soc.*, 1923, **45**, 2493.
123. Van Rysselberghe, *Bull. Acad. Belgique*, 1938, 353.
124. Von Euler, *Z. anorg. allg. Chem.*, 1922, **124**, 70.
125. Wagner and Traud, *Z. Elektrochem.*, 1938, **44**, 391.
126. Wanatabe, *Sci. Rep. Tôhoku Univ.*, 1934, **23**, 115.
127. Whitby, *Trans. Faraday Soc.*, 1933, **29**, 1322.
128. Wohl, "Chemiker-Taschenbuch", 1939, **59**, III, 208–41.
129. Wurmser, "Oxydations et Réductions" (Paris, 1930).
130. Wurmser, *Bull. Soc. Chim. France*, 1937, 1942.
131. Pourbaix, *Bull. Soc. Chim. Belg.*, 1945, **54**, 10.
132. Pourbaix, *Métaux et Corrosion*, 1946, **21**, 121.
133. Pourbaix, *Journées des États de Surface*—Paris, Oct. 1945. (Ed. Office Professionel général de la Transformation des Métaux, 16 Ave. Hoche, Paris 8) pp. 251–65.
134. Pourbaix, *Corrosion*, 1949, **5**, 121. *Bulletin Technique A.I.Br.*, (Bruxelles) 1946, (3), 167; 1947, (1), 109.
135. Pourbaix, *Bulletin Soc. Belge Ingénieurs et Industriels*, 1948, 97.
136. Pourbaix, *J. Chimie Physique*, N° spécial, Colloquium de Thermodynamique. (Brussels, January 1948.) *La Metallurgia Italiana*, 2° Convegno dell' Associazione Italiana de Metallurgia, Milan, 1948.
137. Pourbaix, *Chimie et Industrie*, N° spécial, XXI^{e} Congrès de Chimie Industrielle, Brussels, 1948.

INDEX