

Theoretical Studies of Aqueous Systems
above 25°C. 1. Fundamental Concepts for
Equilibrium Diagrams and some General
Features of the Water System.

Derek Lewis

This report is intended for publication in a periodical. References may not be published prior to such publication without the consent of the author.



AKTIEBOLAGET ATOMENERGI

STUDSVIK, NYKÖPING, SWEDEN 1971

THEORETICAL STUDIES OF AQUEOUS SYSTEMS ABOVE 25°C.
1. FUNDAMENTAL CONCEPTS FOR EQUILIBRIUM DIAGRAMS
AND SOME GENERAL FEATURES OF THE WATER SYSTEM.

Derek Lewis

SUMMARY

The illustration of thermodynamic data on aqueous systems is discussed and diagrams are described that are useful for bringing together the large numbers of data that are relevant to technological problems such as corrosion, mass-transport and deposition.

Two kinds of logarithmic equilibrium diagram are particularly useful, namely, diagrams depicting the variation with pH or p_e of the concentrations of ionic species relative to that of a chosen reference ion and diagrams depicting the fields of conditions of pH and p_e in which the various species in any given system predominate or are stable. Such diagrams clearly and concisely illustrate the data and greatly simplify the comparison of the states of a system at different temperatures.

Estimates of the equilibrium constants for the redox and the acid-base dissociation of water up to 375°C are reported and some general features of aqueous systems at elevated temperatures are discussed

LIST OF CONTENTS

	<u>Page</u>
Introduction	3
1. Fundamental concepts for equilibrium diagrams for aqueous systems	5
1.1. Tension - concentration diagrams	5
1.2. Relative concentration diagrams	6
1.3. Approximations in logarithmic diagrams	7
2. The water system up to 374 ^o C	9
2.1. The stability domain of water	9
2.2. The acid - base dissociation of water	11
2.3. The redox dissociation of water	12
2.4. Absolute neutrality in water	13
2.5. The principle features of the system	14
Conclusion	15
Acknowledgements	16
References	17
Tables	21
Figures	

INTRODUCTION

Only slow progress is being made in the experimental study of aqueous systems at elevated temperatures, partly because of difficulties that arise in the construction of apparatus such as autoclaves and electrode systems. For this reason, and because it is probably not practicable to study experimentally each of the very large number of systems and reactions of practical interest, it is important to develop theoretical methods for characterizing these systems.

A method has been described elsewhere [1] which enables reasonable estimates to be made of the equilibrium constants for reactions in aqueous systems at temperatures up to close to the critical temperature. It is based on the relations of classical thermodynamics and empirical equations for the variation with temperature of ionic heat capacity, derived from those for ionic entropy obtained by Criss and Cobble [2, 3]. The data that are needed are the standard entropies of the constituents at the reference temperature, the coefficients in the equations for their molar heats, and the value of the equilibrium constant at the reference temperature. These quantities have been determined experimentally for many species and reactions. Those that have not yet been so determined can often be estimated by means of thermodynamic or quasi-thermodynamic relationships [1, 4, 5].

Large numbers of equilibrium data must be considered together in the characterisation of most chemical systems and, especially in the definition of the conditions for the stability or the corrosion of different materials in various milieu, increasing attention is being paid to the construction of diagrams that concisely and clearly illustrate them [6 - 14]. The concept of the potential - pH diagram developed by Pourbaix [6] forms the basis of most of this work but other kinds of diagram, especially the logarithmic (double) activity or concentration diagrams extensively treated by Sillén [7] are also very useful, especially when the primary interest is in the relative concentrations of dissolved species. Only a little of the work on equilibrium diagrams for aqueous systems so far reported has related to temperatures above 100°C.

In the studies to be described in this series of reports, work on the estimation of thermodynamic quantities for a number of aqueous systems at elevated temperatures and on their representation has been brought together and further developed. Diagrams are presented that clearly illustrate the equilibrium characteristics of the systems in a way that is useful in investigations of corrosion, mass-transport and deposition in power-plant working on the water-cycle. In this first report, the fundamental concepts used in the series are described and equilibrium data and diagrams for water up to 350°C are presented.

1. FUNDAMENTAL CONCEPTS FOR EQUILIBRIUM DIAGRAMS FOR AQUEOUS SYSTEMS.

Equilibria in aqueous media involving an oxidised species, A, and the conjugate reduced species, B, may be described generally by the formula:



and the equilibrium constant at T°K:

$${}_T K_r = \{B\}^b \{H_2O\}^w \{A\}^{-a} \{H^+\}^{-h} \{e^-\}^{-1}$$

For dilute solutions in which the activity of water is likely to be close to unity a reasonable approximation is obtained when the concentrations of ionic species, [], are substituted for their activities, { }, so that

$$\log_T k_r = pe + hpH - \log [A]^a \cdot [B]^{-b} \quad (1.1)$$

The quantity pe, a measure of "tension" [8], may conveniently be defined by means of the standard hydrogen electrode, like pH.

It follows from equation (1.1) that if the activities or concentrations of two of the species are fixed then a graph of corresponding values of the logarithms of the activities or concentrations of the other two species will describe a straight line. Quite generally, the several chemical equilibria in which a metal or other central species may be involved can be represented by a system of lines on one or another kind of logarithmic diagram [7].

1.1. Tension - concentration diagrams.

The tension - pH diagrams developed on the basis of the work of Pourbaix [6] on the illustration of equilibrium data relating to corrosion have hitherto been constructed with redox potential (volt) or some partial pressure parameter such as rH or P(O₂) as the ordinate. A better method, particularly for treating and comparing systems at widely different temperatures, is to use pe as the conjugate of pH.

A number of benefits are obtained when chemical equilibria are formulated in terms of electron activity [15, 16, 17] instead of an electrical volt. Thus, for example, the elimination of the factor $RTF^{-1} \ln 10$ appearing in the Nernst relation simplifies equilibrium calculations and

permits the construction of equilibrium diagrams in which the slopes of the lines depend only on the stoichiometry of the reactions they represent, and not also on the temperature. When it is necessary to evaluate the voltage, on any one of the several scales of potential now commonly used, that corresponds to a given value of pe use may be made of the relation

$${}_T\epsilon = RTF^{-1} \ln 10 \cdot pe$$

where ${}_T\epsilon$ is the potential (volt) relative to the standard hydrogen electrode. Some values for the factor $RTF^{-1} \ln 10$ in the range of temperature of concern here are given in the table below.

$t^{\circ}\text{C}$	50	100	150	200	250	300	350
$(RTF^{-1} \ln 10)\text{mV}$	64.12	74.04	83.96	93.88	103.8	113.7	123.6

Because of these benefits, and because the usage may assist in the development of a uniform description of electrochemical equilibria in media varying from dilute aqueous solution to molten salts [14], here, and in the similar publications that follow, tension - pH diagrams are constructed with pe as the ordinate. The diagrams so obtained are otherwise similar in principle to those first introduced by Pourbaix and his name is used to designate them. Thus, the field of the diagram is divided by lines describing equilibria into areas corresponding to the fields of conditions (domains) in which the several species in question are stable or otherwise, such as those in which a metal is immune or passive or subject to corrosion. A diagram of this kind illustrating data for the iron - water system at 25°C [15] is shown in figure 1.

1.2. Relative concentration diagrams.

Other kinds of diagrams, such as those illustrating the concentrations of ionic species as a function of pH or pe , may often be a valuable complement to the Pourbaix diagram. Each such diagram might be regarded as a section of a three-dimensional figure showing the relations between the log concentrations of the species concerned, say $\log [i]$, and pe and pH, in a plane parallel to that containing the axes of $\log [i]$ and pH and intersecting the line $pe = 0$. The Pourbaix diagram then corresponds to the section $(pe, \text{pH})_{\log [i] = -6}$. Clearly this concept is

of only limited usefulness in studies of systems at more than one temperature.

In the present work particular use will be made of relative concentration diagrams showing the variation with pH or pe of the concentrations of ions relative to that of a given reference species, $\log [i]/[\text{ref}]$. Figure 2. shows one such relative concentration diagram for the characterised species of iron in dilute aqueous solution at 25°C. It illustrates the variation with pH of the log ratio of the concentrations relative to that of $\text{Fe}(\text{OH})^+$ of $\text{Fe}(\text{VI})$, $\text{Fe}(\text{III})$ and $\text{Fe}(\text{II})$ species in oxidising milieu, under conditions of redox neutrality, and in reducing milieu.

1.3. Approximations in equilibrium diagrams.

In parts of the fields represented in equilibrium diagrams for a given system several aqueous species may coexist in similar concentrations. This has the result that ion-solid and ion-ion equilibria in these parts cannot strictly be represented by straight lines on the Pourbaix diagram or other logarithmic equilibrium diagram. Rectilinearity depends on the assumption that the total concentration of dissolved metal is the same as the concentration of the reacting ion, $[\text{M}]_{\text{tot}} = [i]$. When several mononuclear species coexist, as in a simple alternative to the presence of only a single ion, the total concentration of metal will be given by an expression of the form [7]:-

$$[\text{M}]_{\text{tot}} = [i](1 + \sum \beta_p [\text{H}^+]^{-p})$$

It seems likely that the application of corrections for the presence of more than one species in solution would make the construction of Pourbaix diagrams very much more complicated; the more so because the concentrations of individual ions in a mixture usually cannot be expressed explicitly in terms of total concentration and must be evaluated by iterative procedures.

One reasonable solution to this difficulty is to construct the Pourbaix diagram on the assumption that the concentration of the predominant species is equal to the conventional corrosion limit,

10^{-6} molal, and then to complement the Pourbaix diagram with a relative concentration diagram constructed assuming linearity. This scheme has been followed here.

Another usual assumption in the construction of equilibrium diagrams is that, as in the derivation of equation (1.1), the concentrations of ions can be taken instead of their activities. Clearly this is invalid for concentrated solutions such as those to which very high or very low pH numbers are assigned. In such solutions activity coefficients are likely to be so large, and to change so rapidly with pH, that concentration quotients will differ greatly from the corresponding equilibrium constants. For this reason no significance is attached here to lines in equilibrium diagrams based on concentration quotients when these lines extend beyond the limits $\text{pH} = 1$ and $\text{pH} = 13$. In the diagrams presented in this work such parts of lines beyond these limits as may be included for construction purposes are drawn dotted.

2. THE WATER SYSTEM UP TO 375°C.

2.1. The stability domain of water.

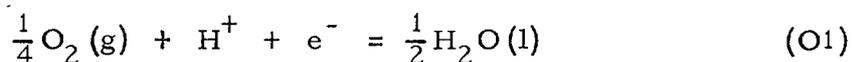
The thermodynamic stability of aqueous systems is limited by the dissociation of water and by its reduction and its oxidation according to the reactions



$$\log_{298} k_{\text{W3}} = -14.00 \quad [15]$$



$$\log_{298} k_{\text{H1}} = \text{zero}$$



$$\log_{298} k_{\text{O1}} = 20.79 \quad [15]$$

Thus, for example, in a system containing no other oxidising agent the introduction of a metal with an equilibrium potential below that corresponding to a reversible hydrogen electrode in the same system leads to the reduction of water (and the oxidation of the metal) according to W3 and H1.

Corresponding to the reactions H1 and O1 the stability domain of water on a Pourbaix diagram is bounded by the lines

$$pe = \log_T k_{\text{H1}} - pH - \frac{1}{2} \log P(\text{H}_2) \quad (\text{a})$$

$$pe = \log_T k_{\text{O1}} - pH + \frac{1}{4} \log P(\text{O}_2) \quad (\text{b})$$

where $P(\text{H}_2)$ and $P(\text{O}_2)$ are the partial pressures of hydrogen and of oxygen, respectively. Thus the stability domain of water at 25°C corresponding to an equilibrium pressure of hydrogen or of oxygen of one atmosphere extends between the lines

$$pe = -pH \quad \text{and} \quad pe = 20.79 - pH$$

At any other temperature than 25°C, for a given equilibrium

pressure of hydrogen and of oxygen, the extent of the stability domain is determined by the magnitudes of k_{H1} and k_{O1} . Estimates of these quantities for temperatures up to 375°C have been obtained in this study from the data in table 1 by the method described previously [1]. They are given in tables 2 and 3. Table 4 gives estimates of $\log_T k_{W3}$ obtained in the same way (GIBBS K), together with estimates of this quantity obtained by interpolation between the values reported by Noyes [31]. The Pourbaix diagrams (incomplete) for the oxygen - water - hydrogen system illustrating the results for 50°, 150°, 250° and 350°C are shown in figure 3.

The calculations leading to the estimates of equilibrium constants given here and in the following publications in this series have been performed by a computer with a simple program (TEMCON) giving tabulations of related equilibrium quantities for the reaction in question such as those reproduced in tables 2 and 3. The quantities under the column headings are:-

$$10 E 3 = 10^3 T^{-1},$$

VHOFF K = estimate of $\log_T k$ formed using the Van't Hoff isobar,

$$HEAT H = 10^{-3} \cdot \int_{298}^T \Delta_T C_P^{\circ} \cdot dT,$$

$$SIG TH = 10^{-3} (\Delta_{298} H^{\circ} + \int_{298}^T \Delta_T C_P^{\circ} \cdot dT),$$

$$HEAT S = \int_{298}^T \Delta_T C_P^{\circ} d \ln T,$$

$$TSIG TS = 10^{-3} T (\Delta_{298} S^{\circ} + \int_{298}^T \Delta_T C_P^{\circ} d \ln T),$$

GIBBS K = estimate of $\log_T k$ formed using equation (1.1)

E ZERO = $RF^{-1} \ln_T k$ (GIBBS K) x number of electrons involved

When the standard heat of formation has not been known for all the constituents the data for one constituent (usually $\Delta_{298} H_f^{\circ}(e^-)$) have been adjusted so that $\Delta_T H_r^{\circ} = 0$. In such cases a single value, $\log_{298} k$, appears repeatedly under VHOFF K.

For a partial pressure of one atmosphere of hydrogen or oxygen, the results obtained in this study indicate that the limits of the domain of stability of water are as follows

t ^o C	50	150	250	350
	pe + pH			
<u>reduction</u>	0.33	1.00	1.06	0.80
<u>oxidation</u>	19.18	14.43	11.18	8.70

Clearly, any physically significant partial pressure may be chosen in this connection and lower values than one atmosphere may be more relevant to discussions of corrosion in high-temperature systems such as, for example, those existing in water-cycle power-plant. Here, partial pressures of hydrogen and of oxygen have been chosen that, according to recently published solubility data [18], correspond to mole fractions of gas in the aqueous phase of, respectively, 0.8×10^{-6} and 8.0×10^{-6} . These concentrations represent the conditions that might exist in a 500 MWt boiler. For the temperatures here taken in illustration, the limiting partial pressures corresponding to the boundaries of the water domain, indicated by the broken lines on the Pourbaix diagrams in figure 2 and the similar figures that follow, are:

t ^o C	50	150	250	350
P(H ₂)	0.727	0.384	0.172	0.028
P(O ₂)	0.885	0.468	0.211	0.035

2.2. The acid - base dissociation of water.

Regardless of the differences between the numerical values in table 4 for the dissociation constant of water, T^k_{W3} , obtained experimentally (Noyes) and theoretically (GIBBS K), it is well-established that this constant, like the dissociation constants of many weak acids and bases, passes through a maximum as the temperature increases. To the extent that the temperature coefficient of the dissociation constant differs for different substances the orders of acid and base strengths may change with temperature.

The condition for acid - base neutrality in aqueous solution, defined by equal concentrations of H⁺ - ion and OH⁻ - ion, changes with temperature in accordance with the dissociation of water. In the Pourbaix

diagram it corresponds to the line

$$\text{pH}_n = -\frac{1}{2} \log_T k_{W3} \quad (\text{d})$$

which, according to the data used here (GIBBS K), moves from pH 7.00 at 25°C through pH 5.57 at 275°C to pH 5.65 at 375°C.

Gurney [19] and, more recently, Helgeson [20] have shown how such maxima might arise as the resultant of opposed electrostatic and non-electrostatic contributions to the free-energy of dissociation. The electrostatic contribution may be related to the dielectric constant of water on the basis of the Born equation, and this constant decreases non-linearly with increasing temperature. Dissociation constants must then have a maximum value if, as is assumed, the non-electrostatic contribution does not vary with temperature or increases nearly linearly. The maximum would be expected to occur at different temperatures for different acids or bases, depending on the different relative magnitudes of the two contributions in different substances. For the dissociation of water the maximum might be expected to occur about 250°C because the temperature coefficient of the dielectric constant begins to increase rapidly above this temperature. Because of, among other things, the inadequacies of the Born model of ionic free energy [cf., 21, 22 and the references therein] it is not clear to what extent this quasi-thermodynamic approach to dissociation in aqueous systems at elevated temperatures is valid.

2.3. The redox dissociation of water.

In some contexts it may be convenient to consider the conditions for redox neutrality as well as dissociative neutrality. For any system at equilibrium the pe of a reversible hydrogen electrode in the system is the same as that of a reversible oxygen electrode. Thus, from equations (a) and (b).

$$\log_T k_{O1} + \frac{1}{4} \log P(\text{O}_2) = \log_T k_{H1} - \frac{1}{2} \log P(\text{H}_2)$$

and so, with the stoichiometric condition for redox neutrality
 $P(\text{H}_2) = 2 P(\text{O}_2)$,

$$\log P(\text{O}_2) = \frac{4}{3}(\log {}_T k_{\text{H}1} - \log {}_T k_{\text{O}1}) - \frac{2}{3} \log 2$$

Substitution for $\log P(\text{O}_2)$ in equation (b) leads to the line described by pe at redox neutrality, viz,

$$\text{pe} = \frac{2}{3} \log {}_T k_{\text{O}1} + \frac{1}{3} \log {}_T k_{\text{H}1} - 0.05 - \text{pH} \quad (\text{c})$$

Thus, according to the values for $k_{\text{H}1}$ and $k_{\text{O}1}$ obtained here, redox neutrality in dilute aqueous solutions corresponds to the conditions

t °C	25	50	150	250	350
pe + pH	13.80	12.85	9.90	7.75	6.02

Both tension (pe) and hydrogen-ion activity (pH) must usually be specified in comparisons of redox systems. In an attempt to simplify these comparisons Clarke and his coworkers introduced a single parameter, rH = -log P(H₂), as a measure of relative redox activity. It was intended that each and every potential on the line € vs pH (cf. (a)) defined by the reversible hydrogen electrode should be designated by the single value of rH corresponding to the partial pressure of hydrogen determining the intercept of the line on the potential axis. Subsequently, other authors, recently including Robins [23], have more often used rH as a symbol for -log P(H₂) analogous to pH (and similarly rO for -log P(O₂)). Clarke has himself pointed out the several undesirable consequences to which this misunderstanding leads, and has concluded [24] "In brief, rH has become an unmitigated nuisance".

2.4. Absolute neutrality in water.

Complete electrochemical neutrality or absolute neutrality in water corresponds to the point of intersection of the lines, (d) and

(c), describing acid - base neutrality and redox neutrality at the temperature in question. According to the results presented here, absolute neutrality prevails at the points

$t^{\circ}\text{C}$	25	50	150	250	350
pH_n	7.00	6.64	5.83	5.58	5.62
pe_n	6.80	6.21	4.07	2.17	0.40

As Pourbaix has pointed out, the lines describing acid - base and redox neutrality divide the field of the general Pourbaix diagram into four regions corresponding to

- I. Oxidising acid media.
- II. Reducing acid media
- III. Reducing alkaline media.
- IV. Oxidising alkaline media

2.5. The principle features of the system.

For the present purpose it has not been necessary to consider the formation of other species in the oxygen - water - hydrogen system than H_2O , H^+ and OH^- , and such species as $\text{O}_3(\text{aq})$, $\text{H}_2\text{O}_2(\text{aq})$ and HO_2^- have been neglected.

The analysis presented here, although incomplete, gives useful information on the extent of the stability domain of H_2O , as well as on the conditions for acid - base dissociation and redox neutrality. As seen from figure 3., the extent of this domain decreases rapidly with temperature, being at 50° , 150° , 250° and 350°C , respectively, about 90%, 60%, 50% and 35% of its extent at 25°C . Clearly the stability domains of other substances in aqueous systems, such as metals and metal oxides, must decrease correspondingly.

CONCLUSION

Data on equilibria in aqueous systems at elevated temperatures, such as estimates of equilibrium constants obtained by a method based on the Criss and Cobble correspondence principle, can conveniently be illustrated by diagrams showing the relations between p_e and pH , and between relative ionic concentration and pH , obtaining at equilibrium.

A marked feature of the oxygen - water - hydrogen system is the rapid decrease in the extent of the stability domain of liquid water with increasing temperature.

ACKNOWLEDGEMENTS

Much of the work presented here has followed from suggestions made by the late Professor Lars Gunnar Sillén. I am also indebted to Dr. Marcel Pourbaix whom I thank for his helpful interest and advice, as well as for kindly making an opportunity for a presentation of some of this work at a C. I. T. C. E. Colloquium in Istanbul. I also thank my colleagues Walter Hübner, Stig Johansson, Georg Neumann and Tom Wallin for many fruitful discussions about redox diagrams and p_e .

REFERENCES

1. LEWIS, D.,
Studies of redox equilibria at elevated temperatures. I. The estimation of equilibrium constants and standard potentials for aqueous systems up to 374°C.
Ark. Kemi 32(1971) p. 385.
2. CRISS, C.M. and COBBLE, J.W.,
The thermodynamic properties of high temperature aqueous solutions. IV. Entropies of the ions up to 200° and the correspondence principle.
J. Amer. Chem. Soc. 86(1964) p. 5385.
3. CRISS, C.M. and COBBLE, J.W.,
The thermodynamic properties of high temperature aqueous solutions. V. The calculation of ionic heat capacities up to, 200°. Entropies and heat capacities above 200°.
Ibid, p. 5390.
4. KUBASCHEWSKI, O. and EVANS, E.LI.,
Metallurgical Thermochemistry.
Pergamon, London 1956.
5. LATIMER, W.M.,
The oxidation states of the elements and their potentials in aqueous solutions. 2nd Ed.
Prentice Hall, Englewood Cliffs, New Jersey 1952.
6. POURBAIX, M.J.N.,
Thermodynamics of dilute aqueous solutions with applications to electrochemistry and corrosion.
Edward Arnold & Co, London 1949.
7. SILLÉN, L.,
Graphic presentation of equilibrium data.
LEE, T.S.,
Chemical equilibrium and the thermodynamics of reactions.
in: Treatise on analytical chemistry. Ed. by I.M. Kolthoff and P.J. Elving. Pt. 1. Theory and Practice. Vol. 1, p. 277 and 185.
8. POURBAIX, M.,
Atlas of electrochemical equilibria in aqueous solutions.
Pergamon Press, Oxford 1966.
9. GARRELS, R.M. and CHRIST, C.L.,
Solutions, minerals and equilibria.
Harper, New York 1965.
10. MATTSSON, E.,
Potential - pH diagram för korrosionsstudier. Med beräknings-exempel avseende systemet Cu - Cl - H₂O.
Svensk Kemisk Tidskrift 74(1962) p. 76 (in Swedish).
11. LITTLEWOOD, R.,
Diagrammatic representation of the thermodynamics of metal-fused chloride systems.
J. Electrochem. Soc. 109(1962) p. 525.

12. INGRAM, M.D. and JANZ, G.J.,
The thermodynamics of corrosion in molten carbonates:
Application of E/pCO₂ diagrams.
Electrochim. Acta 10(1965) p. 783.
13. BOMBARA, G., BAUDO, G. and TAMBA, A.,
Thermodynamics of corrosion in fused sulphates.
Corros. Sci. 8(1968) p. 393.
14. LEWIS, D.,
Some aspects of electrochemical thermodynamics and
equilibrium diagrams for aqueous systems at elevated
temperatures and for simple molten salt systems.
J. Inorg. Nucl. Chem. 33(1971) p. 2121.
15. Stability constants of metal-ion complexes 2 ed. Section I:
Inorganic ligands. Comp by L.G. Sillén.
(The Chemical Society. Spec. publ. No 17).
London 1964.
16. JOHANSSON, S.,
Elektronens särställning i kemin. I. Redoxreaktioner och
elektrokemi i ny belysning.
Elementa 49(1966) p. 3, 95 (in Swedish).
17. JOHANSSON, S.,
Elektronens särställning i kemin. II. Logaritmiska
redoxdiagram.
Ibid, p. 183, 283 (in Swedish).
18. BRUHN, G.,
Untersuchungen über die Lösungen von Salzen und Gasen
in Wasser und wässrigeren Lösung bei Temperaturen oberhalb
100°C.
Diss. Technischen Universität, Berlin 1964 (in German).
19. GURNEY, R.W.,
Ionic processes in solution.
McGraw Hill, London 1953.
20. HELGESON, C.,
Thermodynamics of complex dissociation in aqueous solution
at elevated temperatures.
J. Phys. Chem. 71(1967) p. 3121.
21. IRVING H.M.N.H. and LEWIS, D.,
The extraction of indium halides into organic solvents. VIII.
A theoretical approach to the partition of solvated ion-pairs.
Ark. Kemi 32(1970) p. 121.
22. IRVING, H.M.N.H. and LEWIS, D.,
The extraction of indium halides into organic solvents. IX.
The relative efficiencies of different organic solvents.
Ibid, p. 131.
23. EDENBOROUGH, B.W. and ROBINS, R.G.,
High temperature rH/pH diagrams for the system uranium (IV) -
nitrate - water.
Electrochim. Acta 14(1969) p. 1285.

24. CLARK, W.M.,
Oxidation-reduction potentials of organic systems.
Williams and Wilkins, Baltimore 1960.
25. Selected values of chemical thermodynamic properties,
Pt. 1. Tables. Pt. 2. References. Washington D.C. 1952.
(Nat. Bur. Standards Circular No. 500).
26. COUTURE, A.M. and LAIDLER, K.J.,
The entropies of ions in aqueous solution. II. An
empirical equation for oxy-anions.
Canad. J. Chem. 35(1957). p. 202.
27. POWELL, R.E. and LATIMER, W.M.,
The entropy of aqueous solutes.
J. Chem. Phys. 19(1951) p. 1139.
28. LATIMER, W.M.,
Methods of estimating the entropies of solid compounds.
J. Amer. Chem. Soc. 73(1951) p. 1480.
29. COBBLE, J.W.,
Empirical considerations of entropy. II. The entropies of
inorganic complex ions.
J. Chem. Phys. 21(1953) p. 1446.
30. PITZER, K.S.,
The heats of ionization of water, ammonium hydroxide,
carbonic, phosphoric and sulphuric acids. The variation
of ionization constants with temperature and the entropy
change with ionization.
J. Amer. Chem. Soc. 59(1937) p. 2365.
31. NOYES, A.A.
The electrical conductivity of aqueous solutions. Wash. 1907.
(Carnegie Inst. Washington, Publ. No: 63).

Table 1. Thermodynamic constants and heat capacity parameters for species in the oxygen - water - hydrogen system.

Species	$-\Delta_{298}G_f^{\circ}$ cal. mol ⁻¹ x 10 ⁻³	$-\Delta_{298}H_f^{\circ}$ x 10 ⁻³	$_{298}S^{\circ}$	a	b x 10 ³	c x 10 ⁻⁴
				cal. mol ⁻¹ . deg ⁻¹		
H ₂ (g)	0	0	31.2	6.52	0.8	1.2
H ⁺	0	0	-5.0	0	92.25	0
OH ⁻	37.6	55.0	2.5	0	-172.7	-
H ₂ O (l)	56.7	68.3	16.7	18.03	-	-
H ₂ O ₂ (aq)	31.5	45.7	41.3 ^f	12.50	2.84	-2.84 [†]
HO ₂ ⁻	15.6	-	25.3 [*]	-	-114.4	-
O ₂ (aq)	0	3.8	-	-	-	-
O ₂ (g)	0	0	49.0	7.16	1.0	-4.0
O ₃ (aq)	-	32.2	-	-	-	-
O ₃ (g)	39.1	34.0	56.8	-	-	-

In this and the similar tables in following reports in the series, data for gases and solids have been taken from Kubaschewski and Evans [4] and for dissolved species from Latimer [5]. Exceptions are the b - parameters for ions which have been estimated as described in [1], and those indicated as follows:

- a. From N. B. S. 500 [25].
 - b. From Latimer [5].
 - c. Estimated using the equation of Couture and Laidler [26].
 - d. Estimated using the equation of Powell and Latimer [27].
 - e. Estimated using the equation of Latimer [28].
 - f. Estimated using the equation of Cobble [29].
 - g. From Pourbaix et al. [8].
 - h. Estimated from the corresponding equilibrium constant and ΔG .
- † Data for H₂O₂ (g).
 * Estimated from $_{298}S^{\circ}(\text{H}_2\text{O}_2)$ by Pitzer's rule [5, 30].

REDN HYDROGEN ION

$H+1 + E-1 = 0.5H_2(9)$

LOG298K = 0.0 SIGMA298S = 20.60 SIGMA298H = 0.0

TEMP C	TEMP K	10E3/T	VHCF K	HEAT H	SIG TH	HEAT S	T*SIGTS	GIBBS K	E ZERO
50.00	323.15	3.0945	0.0	-0.630	-0.630	-2.029	6.003	0.331	0.0212
75.00	348.15	2.8723	0.0	-1.318	-1.318	-4.079	5.754	0.583	0.0403
100.00	373.15	2.6799	0.0	-2.064	-2.064	-6.146	5.395	0.771	0.0571
125.00	398.15	2.5116	0.0	-2.867	-2.867	-8.228	4.928	0.906	0.0716
150.00	423.15	2.3632	0.0	-3.728	-3.728	-10.324	4.350	0.999	0.0839
175.00	448.15	2.2314	0.0	-4.646	-4.646	-12.432	3.663	1.056	0.0939
200.00	473.15	2.1135	0.0	-5.622	-5.622	-14.550	2.865	1.082	0.1016
225.00	498.15	2.0074	0.0	-6.655	-6.655	-16.677	1.957	1.083	0.1070
250.00	523.15	1.9115	0.0	-7.745	-7.745	-18.813	0.938	1.061	0.1101
275.00	548.15	1.8243	0.0	-8.893	-8.893	-20.956	-0.192	1.020	0.1109
300.00	573.15	1.7447	0.0	-10.099	-10.099	-23.106	-1.434	0.962	0.1094
325.00	598.15	1.6718	0.0	-11.362	-11.362	-25.263	-2.786	0.889	0.1055
350.00	623.15	1.6047	0.0	-12.682	-12.682	-27.425	-4.250	0.803	0.0993
375.00	648.15	1.5429	0.0	-14.060	-14.060	-29.593	-5.825	0.705	0.0907

Table 2. TEMCON output. Estimates of the equilibrium constant and standard potential for the reduction of hydrogen-ion.

REDN OXYGEN



LOG298K = 20.788 SIGMA298S = 1.10 SIGMA298H = -34160.00

TEMP C	TEMP K	10E3/T	VHCF K	HEAT H	SIG TH	HEAT S	T*SIGTS	GIBBS K	E ZERO
50.00	323.15	3.0945	18.851	-0.535	-34.695	-1.722	-0.200	19.184	1.2300
75.00	348.15	2.8723	17.192	-1.128	-35.288	-3.490	-0.830	17.783	1.2284
100.00	373.15	2.6799	15.755	-1.780	-35.940	-5.296	-1.564	16.543	1.2248
125.00	398.15	2.5116	14.499	-2.489	-36.649	-7.136	-2.401	15.435	1.2193
150.00	423.15	2.3632	13.391	-3.257	-37.417	-9.004	-3.343	14.433	1.2117
175.00	448.15	2.2314	12.407	-4.082	-38.242	-10.899	-4.389	13.520	1.2021
200.00	473.15	2.1135	11.527	-4.966	-39.126	-12.817	-5.542	12.681	1.1905
225.00	498.15	2.0074	10.735	-5.907	-40.067	-14.755	-6.800	11.906	1.1767
250.00	523.15	1.9115	10.019	-6.907	-41.067	-16.712	-8.165	11.184	1.1609
275.00	548.15	1.8243	9.368	-7.964	-42.124	-18.686	-9.637	10.509	1.1429
300.00	573.15	1.7447	8.774	-9.079	-43.239	-20.675	-11.216	9.873	1.1228
325.00	598.15	1.6718	8.230	-10.252	-44.412	-22.677	-12.903	9.273	1.1005
350.00	623.15	1.6047	7.729	-11.483	-45.643	-24.693	-14.699	8.703	1.0760
375.00	648.15	1.5429	7.267	-12.771	-46.931	-26.720	-16.602	8.160	1.0493

Table 3. TEMCON output. Estimates of the equilibrium constant and standard potential for the reduction of oxygen.

Table 4. Values for the dissociation constant of water obtained experimentally (Noyes) and by calculations (GIBBS K) using thermodynamic data.

t°C	25	50	150	250	350
			- log T^k_{W3}		
Noyes	14.09	13.25	11.82	11.32	12.38
GIBBS K	14.00	13.27	11.65	11.16	11.23

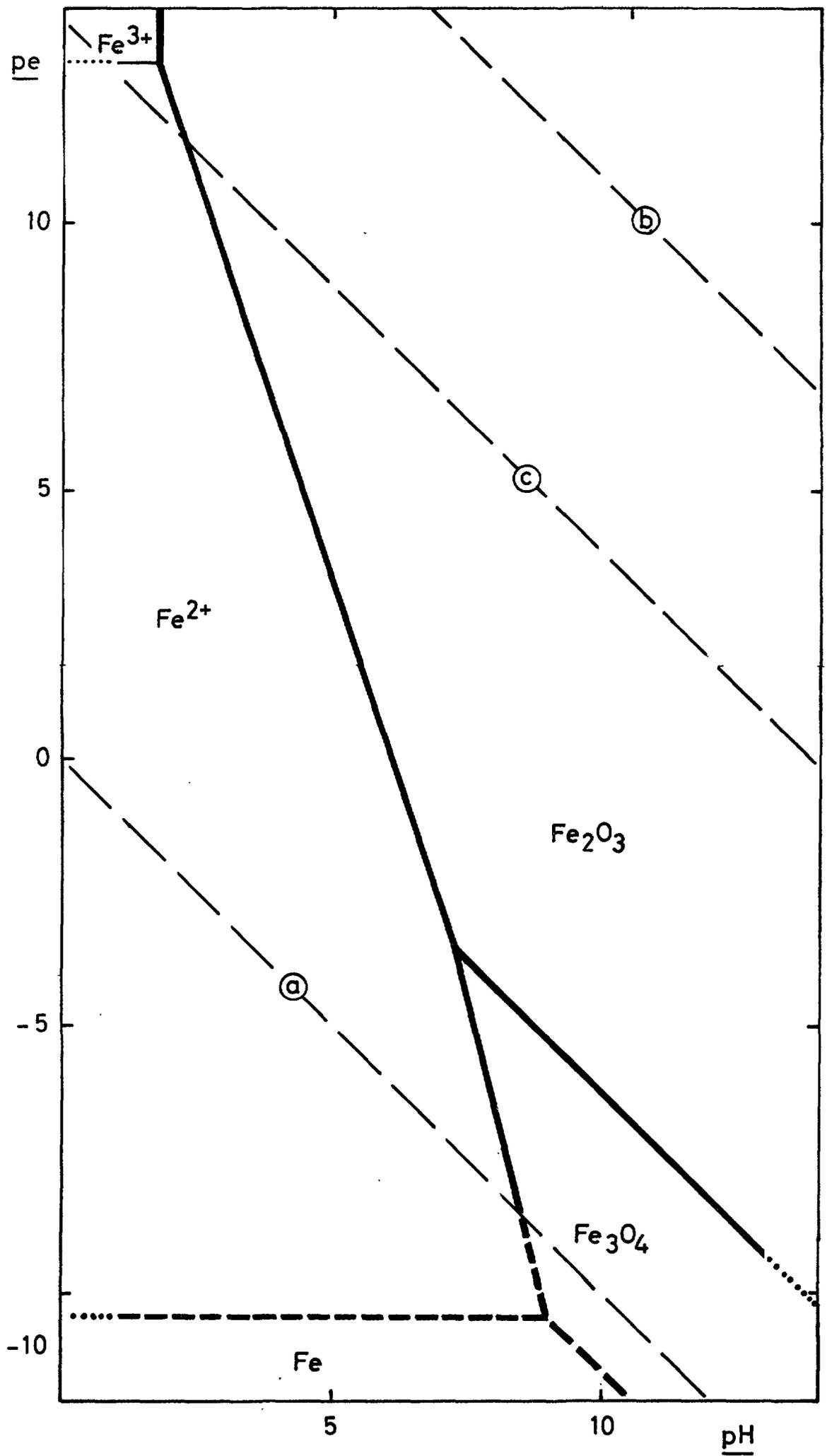


Figure 1. Tension - pH diagram for the Fe - H₂O system at 25°C.

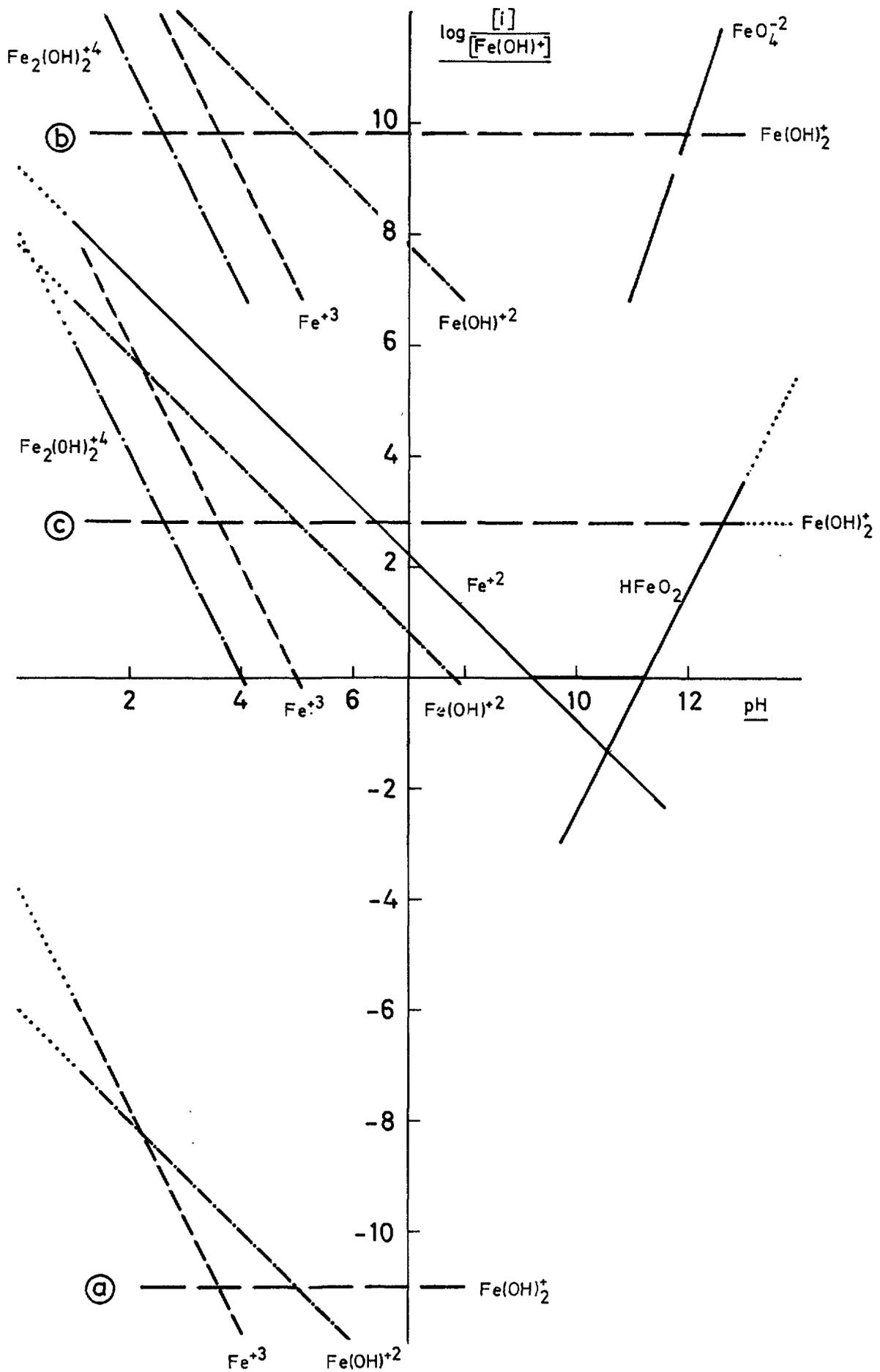


Figure 2. Relative concentration diagram showing the concentrations relative to Fe(OH)_2^+ of aqueous Fe(II), Fe(III) and Fe(VI) species in oxidising, redox neutral and reducing media at 25°C .

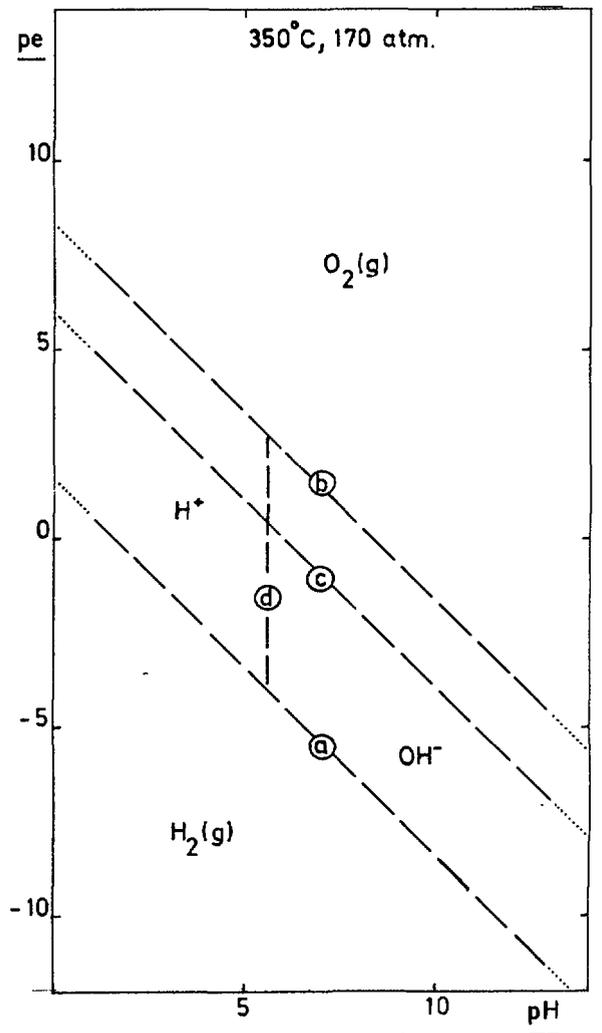
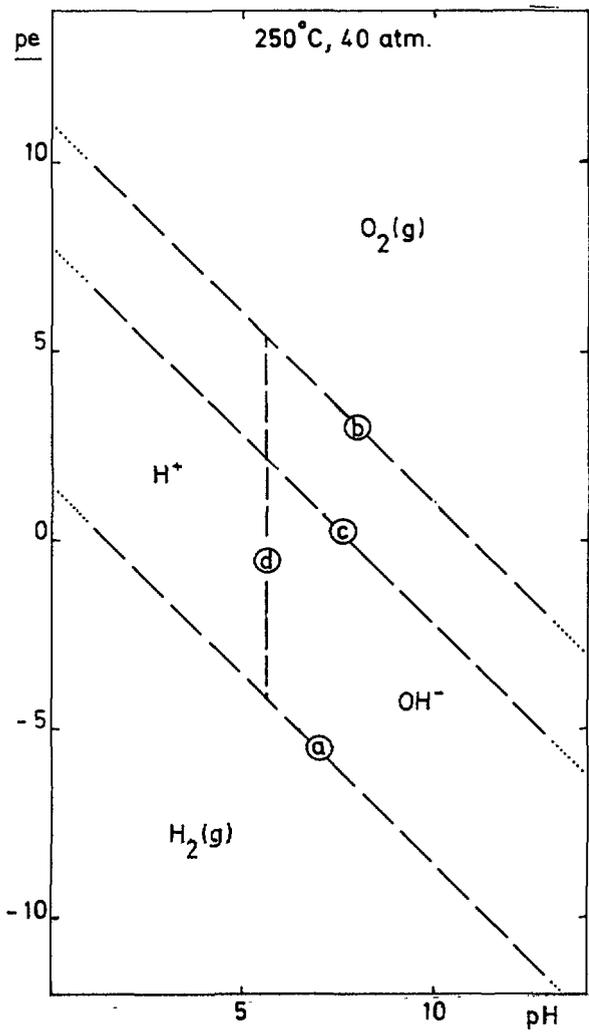
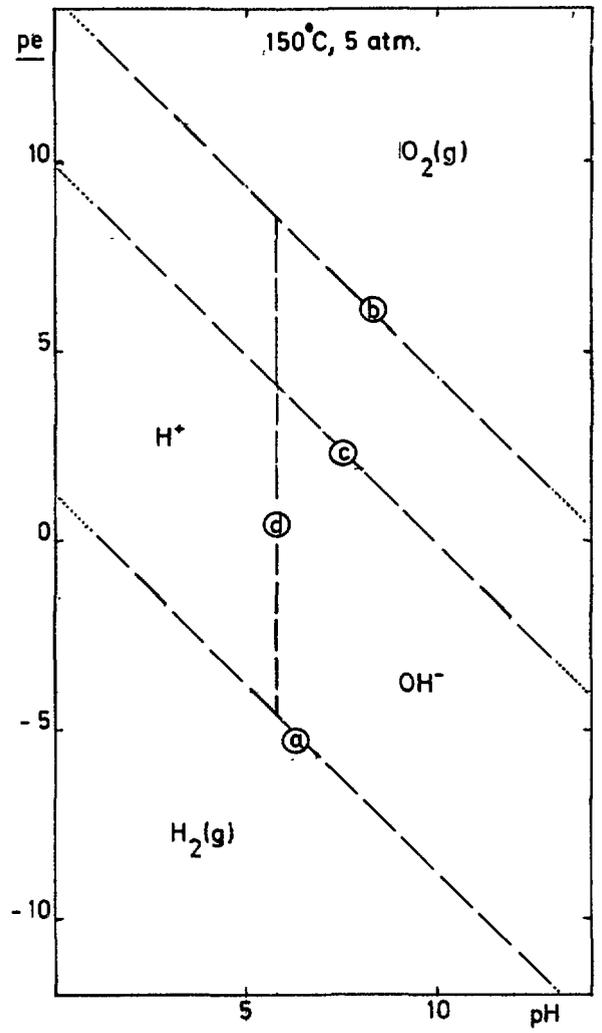
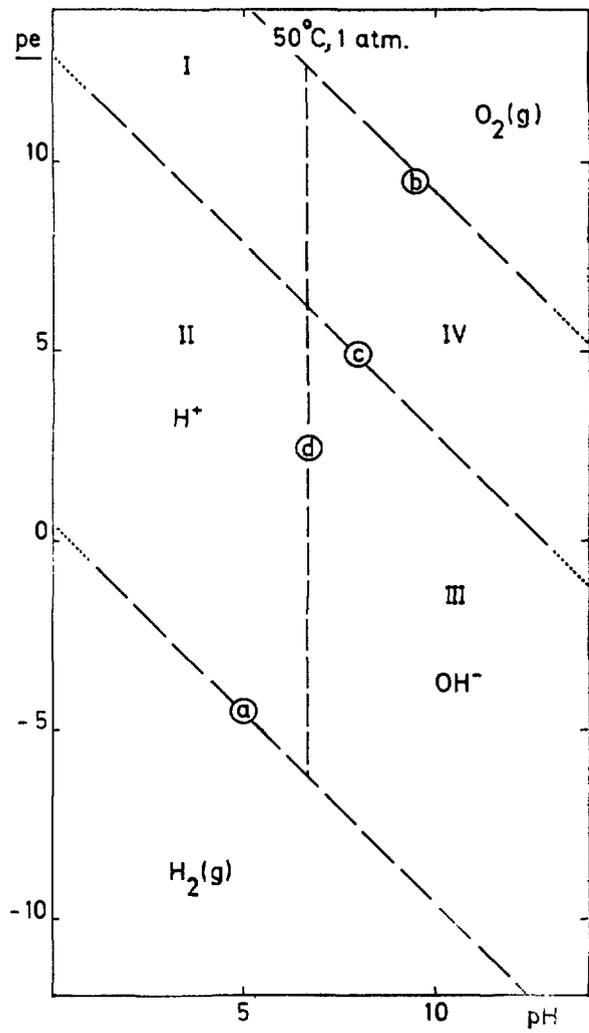


Figure 3. Pourbaix diagrams for the water system above 25°C.

LIST OF PUBLISHED AE-REPORTS

1-360 (See back cover earlier reports.)

361. A half-life measurement of the 343.4 keV level in ¹⁷⁵Lu. By M. Höjberg and S. G. Malmkog. 1969. 10 p. Sw. cr. 10:--.
362. The application of thermoluminescence dosimeters to studies of released activity distributions. By B.-I. Rudén. 1969. 36 p. Sw. cr. 10:--.
363. Transition rates in ¹⁶¹Dy. By V. Berg and S. G. Malmkog. 1969. 32 p. Sw. cr. 10:--.
364. Control rod reactivity measurements in the Ågesta reactor with the pulsed neutron method. By K. Björus. 1969. 44 p. Sw. cr. 10:--.
365. On phonons in simple metals II. Calculated dispersion curves in aluminium. By R. Johnson and A. Westin. 1969. 124 p. Sw. cr. 10:--.
366. Neutron elastic scattering cross sections. Experimental data and optical model cross section calculations. A compilation of neutron data from the Studsvik neutron physics laboratory. By B. Holmqvist and T. Wiedling. 1969. 212 p. Sw. cr. 10:--.
367. Gamma radiation from fission fragments. Experimental apparatus - mass spectrum resolution. By J. Higbie. 1969. 50 p. Sw. cr. 10:--.
368. Scandinavian radiation chemistry meeting, Studsvik and Stockholm. September 17-19, 1969. By H. Christensen. 1969. 34 p. Sw. cr. 10:--.
369. Report on the personnel dosimetry at AB Atomenergi during 1968. By J. Carlsson and T. Wahlberg. 1969. 10 p. Sw. cr. 10:--.
370. Absolute transition rates in ¹⁰⁴Ir. By S. G. Malmkog and V. Berg. 1969. 16 p. Sw. cr. 10:--.
371. Transition probabilities in the 1/2+(631) Band in ²³⁵U. By M. Höjberg and S. G. Malmkog. 1969. 18 p. Sw. cr. 10:--.
372. E2 and M1 transition probabilities in odd mass Hg nuclei. By V. Berg, A. Bäcklin, B. Fogelberg and S. G. Malmkog. 1969. 19 p. Sw. cr. 10:--.
373. An experimental study of the accuracy of compensation in lithium drifted germanium detectors. By A. Lauber and B. Malmsten. 1969. 25 p. Sw. cr. 10:--.
374. Gamma radiation from fission fragments. By J. Higbie. 1969. 22 p. Sw. cr. 10:--.
375. Fast neutron elastic and inelastic scattering of vanadium. By B. Holmqvist, S. G. Johansson, G. Lodin and T. Wiedling. 1969. 48 p. Sw. cr. 10:--.
376. Experimental and theoretical dynamic study of the Ågesta nuclear power station. By P.-Å. Bliselius, H. Vollmer and F. Åkerhielm. 1969. 39 p. Sw. cr. 10:--.
377. Studies of Redox equilibria at elevated temperatures 1. The estimation of equilibrium constants and standard potentials for aqueous systems up to 374°C. By D. Lewis. 1969. 47 p. Sw. cr. 10:--.
378. The whole body monitor HUGO II at Studsvik. Design and operation. By L. Devell, I. Nilsson and L. Venner. 1970. 26 p. Sw. cr. 10:--.
379. ATMOSPHERIC DIFFUSION. Investigations at Studsvik and Ågesta 1960-1963. By L.-E. Hægglom, Ch. Gyllander and U. Widemo. 1969. 91 p. Sw. cr. 10:--.
380. An expansion method to unfold proton recoil spectra. By J. Kockum. 1970. 20 p. Sw. cr. 10:--.
381. The 93.54 keV level ¹¹⁸Sr, and evidence for 3-neutron states above N=50. By S. G. Malmkog and J. McDonald. 1970. 24 p. Sw. cr. 10:--.
382. The low energy level structure of ²⁰¹Ir. By S. G. Malmkog, V. Berg, A. Bäcklin and G. Hedin. 1970. 24 p. Sw. cr. 10:--.
383. The drinking rate of fish in the Skagerack and the Baltic. By J. E. Larsson. 1970. 16 p. Sw. cr. 10:--.
384. Lattice dynamics of NaCl, KCl, RbCl and RbF. By G. Raunio and S. Rolandson. 1970. 26 p. Sw. cr. 10:--.
385. A neutron elastic scattering study of chromium, iron and nickel in the energy region 1.77 to 2.76 MeV. By B. Holmqvist, S. G. Johansson, G. Lodin, M. Salama and T. Wiedling. 1970. 26 p. Sw. cr. 10:--.
386. The decay of bound isobaric analogue states in ²⁸Si and ³²Si using (d, n) reactions. By L. Nilsson, A. Nilsson and I. Bergqvist. 1970. 34 p. Sw. cr. 10:--.
387. Transition probabilities in ¹⁹⁹Os. By S. G. Malmkog, V. Berg and A. Bäcklin. 1970. 40 p. Sw. cr. 10:--.
388. Cross sections for high-energy gamma transition from MeV neutron capture in ²⁰⁸Pb. By I. Bergqvist, B. Lundberg and L. Nilsson. 1970. 16 p. Sw. cr. 10:--.
389. High-speed, automatic radiochemical separations for activation analysis in the biological and medical research laboratory. By K. Samsahl. 1970. 18 p. Sw. cr. 10:--.
390. Use of fission product Ru-106 gamma activity as a method for estimating the relative number of fission events in U-235 and Pu-239 in low-enriched fuel elements. By R. S. Forsyth and W. H. Blackadder. 1970. 25 p. Sw. cr. 10:--.
391. Half-life measurements in ¹⁴¹I. By V. Berg and A. Höglund. 1970. 16 p. Sw. cr. 10:--.
392. Measurement of the neutron spectra in FRO cores 5, 9 and PuB-5 using resonance sandwich detectors. By T. L. Andersson and M. N. Qazi. 1970. 30 p. Sw. cr. 10:--.
393. A gamma scanner using a Ge(Li) semi-conductor detector with the possibility of operation in anti-coincidence mode. By R. S. Forsyth and W. H. Blackadder. 1970. 22 p. Sw. cr. 10:--.
394. A study of the 190 keV transition in ¹⁴¹La. By B. Berg, A. Höglund and B. Fogelberg. 1970. 22 p. Sw. cr. 10:--.
395. Magnetoacoustic waves and instabilities in a Hall-effect-dominated plasma. By S. Palmgren. 1970. 20 p. Sw. cr. 10:--.
396. A new boron analysis method. By J. Weitman, N. Däverhög and S. Färvolden. 1970. 26 p. Sw. cr. 10:--.
397. Progress report 1969. Nuclear chemistry. 1970. 39 p. Sw. cr. 10:--.
398. Prompt gamma radiation from fragments in the thermal fission of ²³⁵U. By H. Albinsson and L. Lindow. 1970. 48 p. Sw. cr. 10:--.
399. Analysis of pulsed source experiments performed in copper-reflected fast assemblies. By J. Kockum. 1970. 32 p. Sw. cr. 10:--.
400. Table of half-lives for excited nuclear levels. By S. G. Malmkog. 1970. 33 p. Sw. cr. 10:--.
401. Needle type solid state detectors for in vivo measurement of trace activity. By A. Lauber, M. Wolgast. 1970. 43 p. Sw. cr. 10:--.
402. Application of pseudo-random signals to the Ågesta nuclear power station. By P.-Å. Bliselius. 1970. 30 p. Sw. cr. 10:--.
403. Studies of redox equilibria at elevated temperatures 2. An automatic divided-function autoclave and cell with flowing liquid junction for electrochemical measurements on aqueous systems. By K. Johnsson, D. Lewis and M. de Pourbaix. 1970. 38 p. Sw. cr. 10:--.
404. Reduction of noise in closed loop servo systems. By K. Nygaard. 1970. 23 p. Sw. cr. 10:--.
405. Spectral parameters in water-moderated lattices. A survey of experimental data with the aid of two-group formulae. By E. K. Sokolowski. 1970. 22 p. Sw. cr. 10:--.
406. The decay of optically thick helium plasmas, taking into account ionizing collisions between metastable atoms or molecules. By J. Stevefelt. 1970. 18 p. Sw. cr. 10:--.
407. Zooplankton from Lake Magelungen, Central Sweden 1960-63. By E. Almqvist. 1970. 62 p. Sw. cr. 10:--.
408. A method for calculating the washout of elemental iodine by water sprays. By E. Bachofner and R. Hesböl. 1970. 24 p. Sw. cr. 10:--.
409. X-ray powder diffraction with Guinier-Hägg focusing cameras. By A. Brown. 1970. 102 p. Sw. cr. 10:--.
410. General phys'c section. Progress report. Fiscal year 1969/70. By J. Braun. 1970. 92 p. Sw. cr. 10:--.
411. In-nile determination of the thermal conductivity of UO₂ in the range 500-2 500 degrees centigrade. By J.-Å. Gyllander. 1971. 70 p. Sw. cr. 10:--.
412. A study of the ring test for determination of transverse ductility of fuel element casing. By G. Anevi and G. Östberg. 1971. 17 p. Sw. cr. 15:--.
413. Pulse radiolysis of Aqueous Solutions of aniline and substituted anilines. By H. C. Christensen. 1971. 40 p. Sw. cr. 15:--.
414. Radiolysis of aqueous toluene solutions. By H. C. Christensen and R. Gustafson. 1971. 20 p. Sw. cr. 15:--.
415. The influence of powder characteristics on process and product parameters in UO₂ pelletization. By U. Runfors. 1971. 32 p. Sw. cr. 15:--.
416. Quantitative assay of Pu239 and Pu240 by neutron transmission measurements. By E. Johansson. 1971. 26 p. Sw. cr. 15:--.
417. Yield of prompt gamma radiation in slow-neutron induced fission of ²³⁵U as a function of the total fragment kinetic energy. By H. Albinsson. 1971. 38 p. Sw. cr. 15:--.
418. Measurements of the spectral light emission from decaying high pressure helium plasmas. By J. Stevefelt and J. Johansson. 1971. 48 p. Sw. cr. 15:--.
419. Progress report 1970. Nuclear chemistry. 1971. 32 p. Sw. cr. 15:--.
420. Energies and yields of prompt gamma rays from fragments in slow-neutron induced fission of ²³⁵U. By H. Albinsson. 1971. 56 p. Sw. cr. 15:--.
421. Decay curves and half-lives of gamma-emitting states from a study of prompt fission gamma radiation. By H. Albinsson. 1971. 28 p. Sw. cr. 15:--.
422. Adjustment of neutron cross section data by a least square fit of calculated quantities to experimental results. Part 1. Theory. By H. Hægglom. 1971. 28 p. Sw. cr. 15:--.
423. Personnel dosimetry at AB Atomenergi during 1969. By J. Carlsson and T. Wahlberg. 1971. 10 p. Sw. cr. 15:--.
424. Some elements of equilibrium diagrams for systems of iron with water above 100°C and with simple chloride, carbonate and sulfate melts. By D. Lewis. 1971. 40 p. Sw. cr. 15:--.
425. A study of material buckling in uranium-loaded assemblies of the fast reactor FRO. By R. Håkansson and L. I. Tirén. 1971. 32 p. Sw. cr. 15:--.
426. Dislocation line tensions in the noble metals, the alkali metals and β-Brass. By B. Pettersson and K. Malén. 1971. 14 p. Sw. cr. 15:--.
427. Studies of fine structure in the flux distribution due to the heterogeneity in some FRO cores. By T. L. Andersson and H. Hægglom. 1971. 32 p. Sw. cr. 15:--.
428. Integral measurement of fission-product reactivity worths in some fast reactor spectra. By T. L. Andersson. 1971. 36 p. Sw. cr. 15:--.
429. Neutron energy spectra from neutron induced fission of ²³⁵U at 0.95 MeV and of ²³⁸U at 1.35 and 2.02 MeV. By E. Almén, B. Holmqvist and T. Wiedling. 1971. 16 p. Sw. cr. 15:--.
430. Optical model analyses of experimental fast neutron elastic scattering data. By B. Holmqvist and T. Wiedling. 1971. 238 p. Sw. cr. 20:--.
431. Theoretical studies of aqueous systems above 25°C. 1. Fundamental concepts for equilibrium diagrams and some general features of the water system. By Derek Lewis. 1971. 27 p. Sw. cr. 15:--.

List of published AES-reports (In Swedish)

1. Analysis by means of gamma spectrometry. By D. Brune. 1961. 10 p. Sw. cr. 6:--.
 2. Irradiation changes and neutron atmosphere in reactor pressure vessels-some points of view. By M. Grounes. 1962. 33 p. Sw. cr. 6:--.
 3. Study of the elongation limit in mild steel. By G. Östberg and R. Attermo. 1963. 17 p. Sw. cr. 6:--.
 4. Technical purchasing in the reactor field. By Erik Jonson. 1963. 64 p. Sw. cr. 8:--.
 5. Ågesta nuclear power station. Summary of technical data, descriptions, etc. for the reactor. By B. Lilliehöök. 1964. 336 p. Sw. cr. 15:--.
 6. Atom Day 1965. Summary of lectures and discussions. By S. Sandström. 1966. 321 p. Sw. cr. 15:--.
 7. Building materials containing radium considered from the radiation protection point of view. By Stig O. W. Bergström and Tor Wahlberg. 1937. 26 p. Sw. cr. 10:--.
 8. Uranium market. 1971. 30 p. Sw. cr. 15:--.
- Additional copies available from the Library of AB Atomenergi, Fack, S-611 01 Nyköping 1, Sweden.