AE-424
UDC 541.48.143:
621.039.522
620.193.431.8
541.135.3

AE-424

Some Elements of Equilibrium Diagrams for Systems of Iron with Water above 100°C and with Simple Chloride, Carbonate and Sulfate Melts

Derek. Lewis

AKTIEBOLAGET ATOMENERGI

STUDSVIK, NYKÖPING, SWEDEN 1971

SOME ELEMENTS OF EQUILIBRIUM DIAGRAMS FOR SYSTEMS OF IRON WITH WATER ABOVE 100°C, AND WITH SIMPLE CHLORIDE, CARBONATE AND SULFATE MELTS.

Derek Lewis

SUMMARY

This report is based on the text of one of a number of papers published together by former pupils of Professor H. M. N. H. Irving in commemoration of his retirement. In it some aspects of molten salts relevant to the nuclear power industry are discussed briefly and an approach is presented to the theoretical description of the electrochemical thermodynamics of corrosion, mass-transport and deposition processes in power-plant working on the water-cycle, and in homogenous molten-salt reactors. Diagrams are introduced, based on the parameter pe instead of the usual redox potential, that are useful for illustrating equilibrium data for aqueous systems at elevated temperatures and for molten salts. Systems including iron in water and in the eutectic mixtures of lithium and sodium chloride, carbonate and sulfate, are taken as examples.

Printed and distributed in May 1971.

LIST OF CONTENTS

INTRODUCTION

A number of years ago, in connection with a study of the relative efficiences of organic solvents as extractants [1, 2, 3, 4], Harry Irving taught me that even when gross approximations are necessary useful answers to complicated problems can often be obtained by a quasi-thermodynamic approach. This paper briefly summarizes attempts to apply that lesson to the technological problems of less-leisured times.

The subcritical water-cycle power-plant now most used consists essentially of a heat source from which energy is transfered directly or indirectly by steam to a turbine backed by a condenser. In the various parts of such plant foreign deposits are likely to be formed as a result of mass-transport phenomena like those illustrated in figure 1 [5, 6]. Particularly important among these phenomena, because of the introduction of anions such as chloride and sulfate, is likely to be the inevitable leakage of coolant into the working fluid in the condenser.

The deposits may be formed in various parts of the plant but usually they can be placed in one or other of three classes, namely: (a) water-side deposits of corrosion products, (b) water-side deposits of impurities contained in the boiler feed-water, and (c) fire-side deposits of impurities derived from the fuel. In contemporary nuclear power-plant only the first two of these classes are important.

The exact nature of the deposits that may be formed will vary from plant to plant. The feed-water of open cycle plant and the condenser coolant of closed cycle systems contain residual salts that vary with location, and different stations contain different materials that release corrosion products into the boiler. However, at first it can be supposed that we are largely concerned with mixtures of iron and nickel oxides from corrosion [7] and sodium chloride together with a little magnesium chloride and sulfate from sea-water.

The effects of such deposits may also be expected to vary from plant to plant, although they are likely always to be deleterious. Among the effects that have been observed are localised changes in heat-transfer properties leading to rapid thermal-mechanical failure, and accelerated local corrosion leading to stress-corrosion cracking.

In a first attempt to treat them systematically the water-side deposits of (a) corrosion products, and (b) impurities, may be supposed to form separately and to resemble, respectively, mixtures of metal oxides in equilibrium with the corresponding solutions, and either mixtures of molten salts or the very concentrated solutions like hydrate melts [8], that may be produced in crevices by wick-boiling [9]. It is then a natural step to start by considering the electrochemical thermodynamics of aqueous solutions.

1. ELECTROCHEMICAL EQUILIBRIA IN AQUEOUS SYSTEMS AT ELEVATED TEMPERATURES.

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

$$aA + hH^+ + e^- = bB + wH_2O \qquad (r)$$

and the equilibrium constant at temperature T°K

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

For dilute solutions a reasonable approximation is obtained when concentration, [ ], is substituted for activity, { }, so that the concentration quotient, $_Tk_r$, is given by

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

where p denotes the operator - log.

It has been shown elsewhere [10] that, on the basis of the relations of classical thermodynamics and by means of the empirical equations describing the variation of ionic entropy with temperature obtained by Criss and Cobble [11, 12], reasonable estimates can be made of the equilibrium constants for reactions in aqueous systems at temperatures up to the critical temperature.

For largely historical reasons the free energy changes accompanying reactions in electrochemical cells have usually been expressed in terms of the Nernst relation. Thus, for the half-cell (electrode) reaction (r)

$$_T\varepsilon = {}_T\varepsilon^o + RTF^{-1} \ln 10 . \log [H^+] + RTF^{-1} \ln 10 . \log [A]^a [B]^{-b}$$

Here ϵ represents electrode potential (volt), otherwise the symbols have their conventional meanings [13].

An often more advantageous formulation of electrochemical phenomena, consistent with the general treatment of chemical equilibria and comparable with that of the (hydrated) proton, is obtained when the electron is treated like any other anion. Thus, from (1.1),

$$pe = pe^{o} - hpH + \log[A]^{a}\,[B]^{-b}$$

where

$$pe = (RTF^{-1}.\ \ln 10)^{-1} \cdot {}_{T}\epsilon$$

$$pe^{o} = (RTF^{-1}.\ \ln 10)^{-1}\,{}_{T}\epsilon$$

1.1. The stability domain of water.

The simplest redox reactions in aqueous systems are those that lead to the oxidation and to the reduction of the solvent itself, namely,

$$\frac{1}{4}\,O_2\,(g) + H^{+} + e^{-} = \frac{1}{2}\,H_2O\,(l) \tag{O1}$$

$$pe = \log {}_{T}K_{O1} - pH + \frac{1}{4}\log P(O_2)$$

$$H^{+} + e^{-} = \frac{1}{2}\,H_2(g) \tag{H1}$$

$$pe = \log {}_{T}K_{H1} - pH - \frac{1}{2}\log P(H_2)$$

A scale of pe is defined according to equation (H1) with ${}_{298}K_{H1} = 1$.

Clearly, water is thermodynamically stable only between those limits of pe corresponding to its oxidation and its reduction. The numerical values of these limits, which are dependent on pH, are determined by the conventional hydrogen scale of potential and the magnitude of the equilibrium constant for the oxidation. At 25°C and 1 atm pressure $\log {}_{298}K_{O1} = 83.16/4$, and the stability domain of water at 25°C under partial pressures of hydrogen or of oxygen of 1 atm extends between the lines:

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

If a metal more electropositive than hydrogen is immersed in water then, provided that the reaction products are not continuously removed or access of water to the metal surface is prevented, it will be oxidised until the redox equilibria that are possible have been established. The nature of the principle reaction products and of the predominant equilibria will depend on the properties of the metal and its compounds, and on the conditions such as temperature, pH and pe. Usually, a great number of variables must be taken into account in a theoretical analysis of such systems.

1.2. Equilibrium diagrams for aqueous systems.

When many data must be made available quickly and in an easily digestable form it is often most convenient to represent them diagrammatically. It follows from equation (1.1) that for a given ratio of concentrations (activities) of A and B in equilibrium a graph of corresponding values of pe and pH will describe a straight line. Quite generally, the several 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.

Several different kinds of diagram have been used for aqueous redox systems but the most valuable in connection with corrosion problems is that which was developed by Marcel Pourbaix [14]. Hitherto, Pourbaix diagrams have been constructed with redox potential (volt) as the ordinate. However, as noted above, a number of advantages are gained when electrochemical equilibria are instead formulated in terms of electron activity. Consequently, in the following equilibrium diagrams will be constructed with pe as the ordinate. The diagrams so obtained are essentially similar to those developed by Pourbaix and his name is retained to designate them.

1.3. The stability domains of iron species in aqueous systems at elevated temperatures.

The application of these principles to aqueous systems may be illustrated with the iron-water system at elevated temperatures. A Pourbaix diagram for this system at 250°C is shown in figure 2. The field of the diagram, like that of the classical Pourbaix diagram for the system at 25°C [14], is divided by lines representing various equilibria into a number of areas corresponding to fields of conditions (domains). Within the limits of pe and pH corresponding to the domain boundaries the species indicated is the sole or primary thermodynamically stable form of iron. In the construction of this diagram Pourbaix' practice has been followed and the corrosion limit has been taken as 10^{-6} molal metal ion. The domain of stability of the solvent is defined by the broken lines on the diagram. Just as in the classical diagrams, the extent to which any of the several species of iron shares its domain of stability with water describes the extent to which it is thermodynamically stable in water

It is seen that the predominent form of iron (III) in solution at 250°C is the hydrolysed species $Fe(OH)_2^+$. The ion Fe^{+3} does not exist in appreciable amounts. Depending on the conditions of pe and pH, the predominent form of iron (II) in solution may be Fe^{+2}, or $Fe(OH)^+$, or $HFeO_2^-$. By far the most widely stable solid species in the system is iron (III) oxide and deposits of α-Fe_2O_3 can be expected to form over wide ranges of conditions.

2. ELECTROCHEMICAL EQUILIBRIA IN MOLTEN CHLORIDES

Except for the use of pe in this connection, and the methods for estimating equilibrium constants for aqueous systems at elevated temperatures, the approach to the description of equilibria in aqueous systems summarised here has been well-established for about twenty-five years. The development of analogous methods for molten salt systems, however, seems to have started only about ten years ago. Consequently they are less well-established. Despite this an approach to the description of the effects of salt-like deposits in water-cycle power-plant can usefully be started by considering the thermodynamics of simple molten salt systems.

If molten salts are regarded as infinitely concentrated aqueous solutions it is a natural step to try to formulate a description of redox equilibria and corrosion in them on the basis of concepts like those that have been developed for aqueous solutions. A relatively simple system which can be examined first is the chloride mixture that may often be a predominent part of the deposits of impurities in water-cycle plant.

The first thermodynamic treatment of molten salt systems like Pourbaix' treatment of aqueous systems seems to be that published by Edeleanu and Littlewood [15]. Although there seems to be some confusion between thermodynamic and kinetic arguments in this work, and some weaknesses in its basic assumptions have subsequently become apparent, it provides a basis for a description of the electrochemical thermodynamics of molten chloride systems.

2.1. The stability range of the solvent.

The stability of a metal chloride as a solvent, like the solvent water, is limited by the redox processes corresponding to its oxidation and its reduction. In pure chlorides, however, unlike aqueous solutions, there will usually be no acid-base process which, coupled with the redox process, permits the definition of a two-dimensional domain of stability.

Oxidation of the metal chloride MCl_m may be described by

$$\frac{1}{2}Cl_2\,(g) + e^- = Cl^-$$

$$pe = \log {}_TK_{Cl1} - \log \{Cl^-\} + \frac{1}{2}\log P(Cl_2) \qquad (Cl1)$$

By the convention ${}_TK_{Cl1} = 1$ a scale of pe may be defined according to (Cl1) with zero when the partial pressure of chlorine is unity.

Reduction may be described by

$$\frac{1}{m} M^{+m} + e^- = \frac{1}{m} \overline{M}$$

$$pe = \log {}_T K_{M1} - \frac{1}{m} \log \{\overline{M}\} \{M^{+m}\}^{-1} . \qquad (M1)$$

and at equilibrium

$$\log {}_T K_{Cl1} - \log {}_T K_{M1} = \frac{1}{m} \log \{M^{+m}\} \{\overline{M}\}^{-1} + \log \{Cl^-\} - \frac{1}{2} \log P(Cl_2)$$

c. f. ,

$$\frac{1}{m} MCl_m(s) = \frac{1}{m} M(s) + \frac{1}{2} Cl_2 (g)$$

$$\log {}_T K_{Cl/Cl_2} = \frac{1}{2} \log P(Cl_2)$$

If pure MCl_m is taken as the standard state of M^{+m}, ${}_T K_{M1}$ is equal to the dissociation constant of the salt, account being taken of the changes of free energy accompanying melting.

The analogy between the molten salt and an aqueous solution is disturbed by the term in $\overline{M}$ for the metal dissolved in the melt. For the present purpose it may be supposed that this term is constant so that it may be included in the equilibrium constant, but for some systems where the solubility of the metal is high [11] this assumption might lead to large errors.

2.2. Contamination of the solvent by oxides.

In practice very pure salts are often difficult to obtain. Oxide ion, for example, can be expected to be a common contaminant introduced into molten salts by interaction with oxygen or water vapour or oxides from container materials. Equilibria may then be supposed to exist such as, for example,

$$\frac{1}{4} O_2 (g) = \frac{1}{2} O^{-2} - e^-$$

$$pe = \log {}_T K_{Oi} + \frac{1}{2} pO^{-2} + \frac{1}{4} \log P(O_2) \qquad (Oi)$$

cf., for aqueous systems,

$$pe = \log {}_{T}K_{H1} - pH - \frac{1}{2}\log P(H_2) \qquad (H1)$$

Regarding $-e^{-}$ as an acid in the Lux-Flood sense [17, 18] it may be seen that acid-base equilibria involving the O^{-2}-ion provide a basis for Pourbaix diagrams for molten chloride systems, similar to those for aqueous systems. Each possible reaction may be represented by a straight line relating the concentrations of the reacting species at equilibrium and pe and pO^{-2}. The latter parameter is a measure of the acidity of the system, which increases with pO^{-2}.

In the absence of other redox couples the pe of the melt is determined by its own redox equilibrium, thermal dissociation of MCl_m leading to a fixed partial pressure of chlorine in the vapour phase, so that redox neutrality corresponds to the condition

$$pe = -\log {}_{T}K_{Cl/Cl_2}$$

Similarly, pO^{-2} is determined by the partial pressure of oxygen in the vapour phase and acid-base neutrality corresponds to the condition

$$pO^{-2} = -\frac{2}{3}(\log {}_{T}K_{Oi} + \frac{1}{4}\log P(O_2) - \log 2)$$

Clearly, in the same way that the pe of the system can be varied by adding a redox couple to it, so can pO^{-2} be varied by the addition of a sparingly soluble condensed oxide, such as V_2O_5 or MgO, as well as by changing the partial pressure of oxygen.

When the oxide of the solvent cation, $MO_{m/2}$, separates equilibrium will be established between O^{-2} and the cation so that

$$\log {}_{T}K_{Oi} - \log {}_{T}K_{M1} = \frac{1}{m}\log\{M^{+m}\}\{\bar{M}\}^{-1} + \frac{1}{2}\log\{O^{-2}\} - \frac{1}{4}\log P(O_2)$$

c.f.,

$$\frac{1}{m}M(s) + \frac{1}{4}O_2(g) \rightleftharpoons \frac{1}{m}MO_{m/2}(s)$$

$$\log {}_{T}K_{MO_{m/2}} = -\frac{1}{4}\log P(O_2)$$

Thus if the pure oxide is taken as the standard state of the oxide-ion then, in a working hypothesis, the formation constant of this ion,

${}_{T}K_{Oi}$, is equal to the ratio between the formation constant of the oxide and that of the chloride.

The validity and practical usefulness of these concepts clearly depends on the reversibility of the oxygen electrode, as defined by equation (Oi). One must note in this connection that, in a study of the oxygen electrode in molten salts [19], Wrench has found that the potential of this electrode in LiCl-KCl eutectic, at least, can be explained only by taking into account the formation of peroxide and other ions, as well as oxide ions. More recently similar results have been obtained for molten nitrates [20]. Nevertheless, in a first approximation it may be supposed to be sufficient to consider only the oxide ion.

2. 3. The oxidation of metals in molten chlorides.

If the metal N which forms the chloride NCl_n is immersed in molten MCl_m it will be oxidised according to

$$\frac{1}{n} N^{+n} + e^- \rightleftharpoons \frac{1}{n} N$$

$$pe = \log {}_{T}K_{N1} + \frac{1}{n} \log \{N^{+n}\} \tag{N1}$$

The standard state of N^{+n} is taken to be pure NCl_n so that, on the standard chlorine electrode scale of pe, ${}_{T}K_{N1}$ is equal to the dissociation constant of this salt, as follows:

$$\frac{1}{n} N^{+n} (MCl_m) + e^- = \frac{1}{n} N$$

$$\frac{1}{n} \Delta {}_{T}G^{o} (N) - \frac{1}{n} \Delta {}_{T}G^{o} (N^{+n}(MCl_m)) - \Delta {}_{T}G^{o}(e^-) = O$$

similarly,

$$\frac{1}{n} N^{+n} (NCl_n) + e^- = \frac{1}{n} N$$

$$\frac{1}{n} \Delta {}_{T}G^{o} (N) - \frac{1}{n} \Delta {}_{T}G^{o} (N^{+n}(NCl_n)) - \Delta_{T}G^{o} (e^-) = O$$

so that, for the same metallic state and redox potential,

$$\Delta_{T}G^{o} (N^{+n}(MCl_m)) = - RT\ln {}_{T}K_{N1} = \Delta_{T}G^{o} (N^{+n}(NCl_n))$$

In the absence of impurities the oxidation of N will be accompanied by the reduction of an equivalent amount of the solvent cation, and equilibrium will be established according to

$$\frac{1}{m} M^{+m} + \frac{1}{n} N = \frac{1}{m} M + \frac{1}{n} N^{+n}$$

so that, if the activity of the metals is unity,

$$\frac{1}{n} \log \{N^{+n}\} = \log {}_TK_{M1} - \log {}_TK_{N1} + \frac{1}{m} \log \{M^{+m}\}$$

Thus the overall reaction corresponds to a simple displacement equilibrium. If corrosion is to be negligable, say $\{N^{+n}\} < 10^{-6} \{M^{+m}\}$ then the dissociation constants of the metal chlorides must stand in the numerical relation

$$\log {}_TK_{M1} - \log {}_TK_{N1} < - \frac{6}{n}$$

In the presence of oxygen, water or other reducible oxides the cathodic reaction accompanying the oxidation of the metal N may be represented by

$$\frac{1}{4} O_2 (g) + e^- = \frac{1}{2} O^{-2}$$

$$pe = \log {}_TK_{Oi} + \frac{1}{2} pO^{-2} + \frac{1}{4} \log P(O_2) \qquad \text{(Oi)}$$

and, at equilibrium,

$$\frac{1}{n} \log \{N^{+n}\} = \log {}_TK_{Oi} - \log {}_TK_{N1} + \frac{1}{2} pO^{-2} + \frac{1}{4} \log P(O_2)$$

The activity of oxide ion in the melt, and hence the activity of N^{+n} at equilibrium, will be determined by the solubility of the least soluble of the oxides that may be present.

2.4. The solubility of metal oxides in molten chlorides.

Assuming ideal solution behaviour the solubility product of the metal oxide $NO_{n/2}$ in the solvent may be estimated from the dissociation constant of the oxide and the corresponding chloride NCl_n, and the value of $\log {}_TK_{Oi}$ for the solvent. Thus

$$\frac{1}{n}NO_{n/2}(s) = \frac{1}{n}N^{+n} + \frac{1}{2}O^{-2}$$

$$\log {}_TK_s = \frac{1}{n}\log\{N^{+n}\} - \frac{1}{2}pO^{-2} \qquad (s)$$

$$= \log {}_TK_{Oi} - \log {}_TK_{N1} + \frac{1}{4}\log P(O_2)$$

and

$$\frac{1}{n}N(s) + \frac{1}{4}O_2(g) = \frac{1}{n}NO_{n/2}(s)$$

$$\log {}_TK_{NO_{n/2}} = -\frac{1}{4}\log P(O_2)$$

so that,

$$\log {}_TK_s = \log {}_TK_{Oi} - \log {}_TK_{N1} - \log {}_TK_{NO_{n/2}}$$

For the construction of equilibrium diagrams it may be more convenient to suppose the reaction

$$\frac{1}{n}NO_{n/2}(s) + e^- = \frac{1}{n}N(s) + \frac{1}{2}O^{-2}$$

$$-\log {}_TK_{NO_{n/2}/N} = \log {}_TK_{NO_{n/2}} + \log {}_TK_{Oi}$$

2.5. Pourbaix diagrams for molten chloride systems.

In the construction of Pourbaix diagrams for aqueous systems a simple model (Debye-Hückel) of electrolyte solutions is assumed so that the activities of the dissolved species can be equated with their concentrations on one or another scale. The molal scale, which for low concentrations is little different from the mole fraction scale, is particularly convenient in this connection.

For molten salts no single, wholely-satisfactory theoretical model of ideal solutions seems yet to have been conceived or, otherwise, generally accepted. A reasonable approximation is obtained, however, if ideal behaviour in mixtures of salts is consistently defined in terms of the Temkin model of interpenetrating ionic lattices [see 21]. This model extended by Førland, leads to a relation between the chemical potential of any given component of a mixture and the concentration of its constituents expressed as cation or anion equivalent fractions, X. Thus

$$\mu\,(A_aC_c) = \mu^o\,(A_aC_c) + RT\ln\left(X^a(A)\cdot X^c(C)\right)$$

so that,

$$\{A\} = X(A) = \frac{\text{no. of equivalents of the cation A}}{\text{total no. of equivalents of all cations}}$$

and,

$$\{C\} = X(C) = \frac{\text{no. of equivalents of the anion C}}{\text{total no. of equivalents of all anions}}$$

For dilute solutions, concentrations of ions on the mole-fraction scale are proportional to the corresponding ion-equivalent fractions. However, the proportionality constant is related to the charge number and so the order of the series of standard potentials of different electrodes may be different for the two scales of concentration. This can be seen from the data in table 1.

The kind of Pourbaix diagram to which these considerations lead is exemplified by that for the iron - lithium chloride (27 mole%) - sodium chloride (63) system at 600°C shown in figure 3. For the construction of the diagram for this system it is supposed that (c.f., Flood, Førland and Grjøtheim, Z. anorg. allg. Chemie <u>276</u>(1964)289) the equilibrium constant for a reaction such as the formation of oxide ion in the mixture can be evaluated from the corresponding constants for the single salts according to:-

$$\log {}_TK_r(A, B, \ldots, Cl) = X(A)\log {}_TK_r(ACl_a) + X(B)\log {}_TK_r(BCl_b) + \ldots\ldots$$

The field of the diagram, as in the analogous diagrams for aqueous systems, is divided by lines representing equilibria into a number of areas corresponding to the domains of thermodynamic stability of the species indicated. The solvent, LiCl(27)-NaCl(63), has a domain of stability corresponding to the area bounded on the pe axis by the broken line describing the oxidation of Cl^--ion to chlorine gas with a partial pressure of one atmosphere, and that describing the reduction of Na^+ to liquid sodium. This domain is also limited by the formation of solid Li_2O, for which $pO^{-2} = 4.2$, and by whatever may be the practical limit of detection of the oxide ion.

Although the extent to which the stability domain of the solute coincides with that of the solvent describes the extent of their mutual compatibility, this is likely to be of less interest in discussions of molten salt systems than in those of aqueous systems. Few metals are likely to reduce the solvent sodium chloride, no matter what the temperature. Instead it may be more profitable to regard the molten solvent as a more or less inert medium that facilitates reaction between other components of the system. Thus figure 3 is best regarded as illustrating the equilibria that may be established between various iron species, and between these species and O^{-2}-ion derived from oxygen in a gaseous phase above the chloride melt.

From this point of view, iron in the system under consideration behaves as a noble metal over a wide range of pe and pO^{-2}. As in aqueous systems above about 200°C, Fe^{+2} is the stable simple ionic form of iron, and Fe^{+3} is not normally expected to occur. As might be expected from the phase diagram for the iron-oxygen system, FeO is barely stable in the solvent at 600°C and the predominent oxides are magnetite and hematite.

Whether or not a particular oxide will form a passivating film on a metal immersed in a molten salt, like in an aqueous solution, depends on other factors such as morphology, as well as on solubility. Thermodynamic data cannot directly give information about such factors although they can indicate the possibility of passivation in molten salts.

Following the work of Edeleanu and Littlewood on chloride systems treatments of electrochemical equilibria in mixtures of molten salts containing other anions have been described by a number of authors. A better understanding of the effects of deposits of impurities in power-plant may be obtained by extending these treatments in terms of the concepts applied here to chloride systems.

3. ELECTROCHEMICAL EQUILIBRIA IN MOLTEN CARBONATES.

A thermodynamic treatment of molten carbonate systems, closely resembling the earlier work by Pourbaix on aqueous systems and by Edeleanu and Littlewood on chloride systems, has been described by Ingram and Janz [22]. It may be reformulated as follows.

3.1. The stability range of the solvent.

The carbonate ion may be supposed to be formed according to

$$\frac{1}{2}CO_2(g) + \frac{1}{4}O_2(g) + e^- = \frac{1}{2}CO_3^{-2}$$

$$pe = \log {}_TK_{C1} - \frac{1}{2}\log\{CO_3^{-2}\} + \frac{1}{2}\log P(CO_2) + \frac{1}{4}\log P(O_2) \qquad (C1)$$

Experiments [18, 23] have shown conclusively that the $O_2(g) - CO_2(g)$ electrode in carbonate melts is reversible and that its pe (potential) is described by equation (C1). A practical scale of pe for carbonate systems can thus be defined according to this equation with zero when $CO_2(g)$ and $O_2(g)$ are present in the stoichiometric ratio and the total pressure is unity so that $P(CO_2) = 2P(O_2)$, and

$$\log {}_TK_{C1} = -\left(\frac{1}{2}\log\frac{2}{3} + \frac{1}{4}\log\frac{1}{3}\right) = +0.21$$

Two cathodic reactions seem to be feasible in carbonate "solvents", namely the reduction of the cation

$$\frac{1}{m}M^{+m} + e^- \rightleftharpoons \frac{1}{m}M \qquad (M1)$$

$$pe = \log {}_TK_{M1} + \frac{1}{m}\log\{M^{+m}\}$$

and the reduction of carbon dioxide

$$\frac{3}{4}CO_2(g) + e^- = \frac{1}{2}CO_3^{-2} + \frac{1}{4}C(s)$$

$$pe = \log {}_TK_{C2} - \frac{1}{2}\log\{CO_3^{-2}\} + \frac{3}{4}\log P(CO_2) \qquad (C2)$$

It is not yet clear for all common systems which of these is the limiting process. For the present purpose it is probably adequate to suppose that only the cation is reduced but, in a complete analysis the reduction of carbon dioxide and the possibility, pointed out by Rahmel [25], of the formation of metallic carbides in the domain of stability of graphite ought to be considered.

At redox equilibrium in the carbonate $M(CO_3)_{m/2}$

$$\log {}_TK_{C1} - \log {}_TK_{M1} = \frac{1}{m} \log \{M^{+m}\} + \frac{1}{2} \log \{CO_3^{-2}\}$$

$$- \frac{1}{2} \log P(CO_2) - \frac{1}{4} \log P(O_2)$$

c.f..

$$\frac{1}{m} M(CO_3)_{m/2} = \frac{1}{m} M + \frac{1}{2} CO_2(g) + \frac{1}{4} O_2(g)$$

$$\log {}_TK_{CO_3/CO_2} = \frac{1}{2} \log P(CO_2) + \frac{1}{4} \log P(O_2)$$

so that, if ${}_TK_{C1} = 10^{-0.2}$, and the pure carbonate is taken as the standard state of M^{+m}, ${}_TK_{M1}$ is given by 1.6 times the dissociation constant of the carbonate.

3.2. The fundamental acid-base equilibrium in molten carbonates.

It can be seen that the $O_2(g)$ - $CO_2(g)$ electrode reaction (C1) is equivalent to the resultant of the oxygen electrode reaction

$$\frac{1}{4} O_2(g) + e^- \rightleftharpoons \frac{1}{2} O^{-2}$$

$$\log {}_TK_{Oi} = pe - \frac{1}{2} pO^{-2} - \frac{1}{4} \log PO_2) \qquad (Oi)$$

and the fundamental Lux-Flood acid-base equilibrium in carbonate systems

$$\text{base } \frac{1}{2} CO_3^{-2} \rightleftharpoons \frac{1}{2} O^{-2} + \frac{1}{2} CO_2(g) \text{ oxide-ion + conjugate acid}$$

$$\log {}_TK_{CO_2} = \frac{1}{2} \log P(CO_2) - \frac{1}{2} pO^{-2}$$

$$\log {}_TK_{Oi} = \log {}_TK_{CO_2} + \log {}_TK_{C1}$$

Taking the standard state of the oxide-ion to be the pure oxide of the solvent cation, $MO_{m/2}$, as in the chloride system, then its formation constant, ${}_TK_{Oi}$, is equal to 1.6 times the ratio between the dissociation constant of the corresponding carbonate and that of the oxide.

3.3. Pourbaix diagrams for molten carbonate systems.

On the basis that the pe or redox potential and the pO^{-2} or acidity of a molten carbonate system are related to each other and to the partial pressure of oxygen and of carbon dioxide in the vapour phase, as shown above, Pourbaix diagrams for metal - molten carbonate systems may be constructed, analogous to those for aqueous systems and for chloride systems contaminated with oxides. Figure 4 shows such a diagram for the system iron - lithium carbonate (52 mole %) - sodium carbonate (48) at 600°C. As in the treatment of the analogous system of chlorides, equilibrium constants for reactions in the mixture have been evaluated from the corresponding constants for the single salts. This assumption of ideality inevitably leads to considerable similarities between the carbonate system and the chloride system.

4. ELECTROCHEMICAL EQUILIBRIA IN MOLTEN SULFATES

Recently, similar treatments of the electrochemical thermodynamics of molten sulfate systems have been published independently by Bombara, Baudo and Tamba [24] and by Rahmel [25]. These treatments, like the earlier treatments of chloride and carbonate systems, resemble Pourbaix' treatment of aqueous systems and may also usefully be reformulated in terms of the concepts previously described here.

4.1. The stability range of the solvent.

The sulfate ion may be supposed to be formed according to

$$\frac{1}{2}SO_3(g) + \frac{1}{4}O_2(g) + e^- = \frac{1}{2}SO_4^{-2}$$

$$pe = \log {}_TK_{S1} - \frac{1}{2}\log\left\{SO_4^{-2}\right\} + \frac{1}{2}\log P(SO_3)$$

$$+ \frac{1}{4}\log P(O_2) \qquad (S1)$$

The $O_2(g)$ - $SO_3(g)$ electrode in sulfate melts can be expected to be reversible [18, 26], as defined by equation (S1). A practical scale of pe for sulfate systems can thus be defined according to this equation with zero when $SO_3(g)$ and $O_2(g)$ are present in the stoichiometric ratio and the total pressure is unity so that $P(SO_3) = 2\,P(O_2)$, and

$$\log {}_TK_{S1} = -\left(\frac{1}{2}\log\frac{2}{3} + \frac{1}{4}\log\frac{1}{3}\right) = 0.21$$

A number of limiting cathodic processes are conceivable for sulfate "solvents", such as the reduction of the cation

$$\frac{1}{m}M^{+m} + e^- = \frac{1}{m}M\ (s) \qquad (M1)$$

$$pe = \log {}_TK_{M1} + \frac{1}{m}\log\left\{m^{+m}\right\}$$

or the reduction of sulfur trioxide to sulfur dioxide [24, 26]

$$\frac{1}{2}SO_3(g) + e^- = \frac{1}{2}SO_2(g) + \frac{1}{2}O^{-2}$$

$$pe = \log {}_TK_{S2} - \frac{1}{2}\log\left\{O^{-2}\right\} - \frac{1}{2}\log P(SO_2) + \frac{1}{2}\log P(SO_3) \qquad (S2)$$

or the reduction of sulfur dioxide to sulfide,

$$\frac{1}{2}SO_2(g) + e^- \rightleftharpoons \frac{1}{2}S^{-2} + \frac{1}{2}O_2(g)$$

$$pe = \log {}_TK_{S3} + \frac{1}{2}\log P(SO_2) - \frac{1}{2}\log \left\{S^{-2}\right\}$$

$$- \frac{1}{2}\log P(O_2) \qquad (S3)$$

The corresponding pure sulfate may be taken as the standard state of any dischargeable cation M^{+m}, so that with the convention ${}_TK_{S1} = 10^{0.2}$ the reduction constant ${}_TK_{M1}$ is given by 1.6 times the equilibrium constant for the dissociation of the sulfate to the metal

$$\log {}_TK_{S1} - \log {}_TK_{M1} = \frac{1}{m}\log \left\{M^{+m}\right\} + \frac{1}{2}\log \left\{SO_4^{-2}\right\} - \frac{1}{2}\log P(SO_3)$$

$$- \frac{1}{4}\log P(O_2)$$

c.f.,

$$\frac{1}{m}M(SO_4)_{m/2} = \frac{1}{m}M + \frac{1}{2}SO_3(g) + \frac{1}{4}O_2(g)$$

$$\log {}_TK_{SO_4/SO_3} = \frac{1}{2}\log P(SO_3) + \frac{1}{4}\log P(O_2)$$

Discharge of the alkali or alkaline earth cations is not to be expected to occur in sulfate systems and so the lower limit of stability of most common sulfate "solvents" may be supposed to be determined by the reduction of sulfur trioxide or of sulfate ion. The equilibrium constant for this limiting cathodic process may be obtained from:

$$\log {}_TK_{S1} - \log {}_TK_{S2} = \frac{1}{2}\log \left\{SO_4^{-2}\right\} - \frac{1}{2}\log \left\{O^{-2}\right\} - \frac{1}{2}\log P(SO_2)$$

$$- \frac{1}{4}\log P(O_2)$$

c.f.,

$$\frac{1}{m}M(SO_4)_{m/2} \rightleftharpoons \frac{1}{m}MO_{m/2} + \frac{1}{2}SO_2(g) + \frac{1}{4}O_2(g)$$

$$\log {}_TK_{SO_4/SO_2} = \frac{1}{2}\log P(SO_2) + \frac{1}{4}\log P(O_2)$$

and that for (S3) from

$$\log {}_{T}K_{S1} - \log {}_{T}K_{S3} = \frac{1}{2}\log \left\{SO_4^{-2}\right\} + \frac{1}{2}\log P(SO_2) - \frac{1}{2}\log \left\{S^{-2}\right\}$$

$$- \frac{1}{2}\log P(SO_3) - \frac{3}{4}\log P(O_2)$$

c.f.

$$\frac{1}{m} M(SO_4)_{m/2} \rightleftharpoons \frac{1}{m} MS_{m/2} + O_2(g)$$

and

$$\frac{1}{2} SO_3(g) \rightleftharpoons \frac{1}{2} SO_2(g) + \frac{1}{4} O_2(g)$$

4.2. The fundamental acid-base equilibrium in molten sulfates.

The $O_2(g)$ - $SO_3(g)$ electrode reaction (S1) may be seen to be the resultant of the oxygen electrode reaction

$$\frac{1}{4} O_2(g) + e^- \rightleftharpoons \frac{1}{2} O^{-2}$$

$$\log {}_{T}K_{Oi} = pe - \frac{1}{2} pO^{-2} - \frac{1}{4}\log P(O_2) \qquad \text{(Oi)}$$

and the fundamental Lux-Flood acid-base equilibrium in sulfate systems

$$\text{base } \frac{1}{2} SO_4^{-2} \qquad \frac{1}{2} O^{-2} + \frac{1}{2} SO_3(g) \text{ oxide-ion + acid}$$

$$\log {}_{T}K_{SO_3} = \frac{1}{2}\log P(SO_3) - \frac{1}{2} pO^{-2}$$

$$\log {}_{T}K_{Oi} = \log {}_{T}K_{SO_3} + \log {}_{T}K_{S1}$$

Taking the standard state of the oxide ion to be the pure oxide of the solvent cation, as in the chloride and the carbonate systems, then its formation constant, ${}_{T}K_{Oi}$, is equal to 1.6 times the ratio between the dissociation constant of the corresponding sulfate and that of the oxide.

4.3. Pourbaix diagrams for molten sulfate systems.

The relations between pe, pO^{-2} and the partial pressures of oxygen and of sulfur trioxide developed above provide a basis for

Pourbaix diagrams for metal - sulfate systems, analogous to those described for the other kinds of system discussed here. This is illustrated in figure 5 by a Pourbaix diagram for the system of iron - lithium sulfate (40 mole %) - sodium sulfate (60) at 600°C. The mixture is assumed to behave ideally, like the analogous chloride and carbonate systems.

As pointed out in connection with the carbonate system, in consequence of the assumption of ideality great similarities can be expected between the diagrams for similar systems with different anions. Sulfate systems, however, and nitrate systems, have the characteristic that the anion of the solvent can be reduced by some common metals. Thus corrosion in molten sulfates may procede by a process having no counterpart in chlorides nor, in many cases, in carbonates.

5. THE THERMODYNAMICS OF REACTOR MATERIALS IN MOLTEN CHLORIDES.

It is clear that much effort will be required for the extension of the work on the thermodynamics of simple model systems to the description of wet mixtures of salts and oxides like those that occur in the deposits in water-cycle power-plant. A more immediate application of this work to technological systems may be illustrated in connection with one of the newer and more imaginative of the uses proposed for molten salts, namely as media in homogenous reactors.

5.1. Molten salt homogenous reactors.

Reactor systems with continuously reprocessed fluid fuels have attracted attention since the start of the atomic energy industry. They offer considerable advantages, including reduced capital and running costs and improved control and neutron economy. Of all the homogenous reactor concepts so far advanced by far the most attractive are those based on systems of molten halides. Only either fluoride or chloride systems seem to be feasible for reactor purposes, the former having been chosen as the basis of the molten-fluoride thermal-breeder reactor (MFTBR) being developed in the U.S.A., while the latter is the basis of the design studies for a molten-chloride fast-breeder reactor (MCFBR) being carried out in Europe.

In molten salt reactors the fuel, instead of being in the form of a solid material enclosed in one or another kind of externally cooled cladding, is included in a mixture of fluid salts which can be used as the primary heat-transfer medium and which can be circulated so that the reaction products can be removed continuously and new fuel added without stopping the reactor. The practibility of such homogenous reactors has been clearly demonstrated by one american experimental system [29, 30] and various other types are being studied in England [31], West Germany [32] and Poland [33].

5.2. Corrosion problems in molten salt reactors.

Although in molten salt reactors there are no fuel cans that might swell, corrode or puncture, and the coolant is not very reactive chemically, it is obviously necessary to contain the salt. As the pressure in most such reactors is to be near atmospheric, the most important materials problems in them can be expected to be corrosion and radiation damage of the containing vessels and transfer plant (and of the moderator in the MFTBR). A preliminary examination of the corrosion problems that might occur in the MCFBR, for example, may be based on thermodynamic arguments such as those described here.

In the discussion of the oxidation of metals in molten chlorides it was shown that for a metal N that forms the salt NCl_n, the concentration of ions N^{+n} in equilibrium with the metal when immersed in another metal chloride varies with pe according to the equation

$$pe = \log {}_{T}K_{N1} + \frac{1}{n} \log \{N^{+n}\}$$

by convention the equilibrium constant ${}_{T}K_{N1}$ is equated with the dissociation constant of NCl_n. Thus, for ideal solutions, the variation with pe of the concentration of metal-ion in equilibrium with the solid metal can be represented by a straight line on a logarithmic diagram.

Figure 6 illustrates this approach with data for the common metals that might be considered in connection with the MCFBR which would probably have a charge consisting of UCl_3, $PuCl_3$ and NaCl. The broken vertical line corresponds to the conventional limit for corrosion, which has been taken to be a cation fraction of 10^{-6}. The broken horizontal line corresponds to the pe which would be maintained by the buffering action of U^{+4} in an arbitrary but likely ratio of $1 : 10^{-4}$ in a mixture of chlorides containing a large total concentration of uranium.

The data summarised in the figure can be seen to indicate that alloys containing iron, cobalt and nickel, should exhibit only limited general corrosion in contact with the charge of the MCFBR. By contrast, manganese and chromium can be expected to corrode so extensively that they ought to be excluded from the structural materials of the reactor.

Although these conclusions are probably valid, like those for the MFTBR reached in a similar way by Weinberg [29], it may be as well to point out that this simple treatment of the data is not wholely satisfactory. The point at issue is that in discussions of corrosion in molten salt systems the appropriate standard state of the solute ion N^{+n} is not the pure chloride NCl_n but a hypothetical solution in the solvent in question in which the activity of the ion is unity. Many mixtures of molten salts are non-ideal, particularly those containing lithium and, to a lesser extent, sodium. Thus in connection with corrosion in molten salts it is not directly relevant to compare the stabilities of metal salts as measured by their standard free energies of formation. Only experimentally determined equilibrium constants (standard potentials) for each system in question provide a wholely satisfactory basis. A change of medium, like a change of temperature, may lead to large changes in equilibrium constants that could be reflected in quite different orders for the galvanic series of the metals.

CONCLUSION

Although only a rudimentary treatment of simple model systems has been presented here it is clear from this work, and from analogous theoretical treatments of molten nitrates and of molten hydroxides that have been published recently [27, 28], that thermodynamic methods and equilibrium diagrams are widely applicable to the description of reactions in a variety of solvents. One may reasonably conclude that progress is being made in the development of a uniform and easily comprehensible treatment of corrosion in milieu varying from aqueous solution to molten salts.

ACKNOWLEDGEMENTS

The review presented here forms part of a study being carried out together with fil. mag. Birgit Svensson whose help is gratefully acknowledged. The work is financed by the Swedish Board for Technical Devlopment (STU).

REFERENCES

1. IRVING H. and LEWIS D. C.
The solvent extraction of solvated ion-pairs: A theoretical approach.
Proc. Chem. Soc. (1960)p. 222.

2. IRVING H. and LEWIS Derek
The extraction of indium halides into organic solvents. Part VII.
The distribution of indium between hydrochloric acid and binary solvent mixtures containing isobutyl methy ketone.
Arkiv Kemi 28(1967)p. 131.

3. IRVING H. M. N. H. and LEWIS Derek
The extraction of indium halides into organic solvents. Part VIII.
A theoretical approach to the partition of solvated ion-pairs.
Arkiv Kemi 32(1970)p. 121.

4. IRVING H. M. N. H. and LEWIS Derek
The extraction of indium halides into organic solvents. Part IX.
The relative efficiencies of different organic solvents.
Ibid. p. 131.

5. NICHOLS R. W. and TYZACK C.
Materials problems associated with the use of supercritical steam cycles. 1966.
(TRG Report 736 - C)

6. MANKINA N. N. and CHERNOVA L. A.
Deposits of readily soluble salts on the internal heating surfaces of drum boilers operating at high pressures
Teploenergetika 14 (1967) p. 35.

7. SWEETON F. H., BAES C. F. and RAY R. W.
Chemistry of pressurised-water reactor systems. 1965.
(ORNL - 3789, p. 113.)

8. ANGELL C. A.
A new class of molten salt mixtures - The hydrated dipositive ion as an independent cation species.
J. Electrochem. Soc. 112(1965)p. 1224.

9. HOLMES D. R. and MANN G. M. W.
A critical survey of possible factors contributing to internal boiler corrosion.
Corrosion 21(1965)p. 370.

10. LEWIS Derek
Studies of redox equilibria at elevated temperatures. 1. The estimation of equilibrium constants and standard potentials for aqueous systems up to 374°C.
To be published in Arkiv Kemi 1971.

11. CRISS C. M. and COBBLE J. W.
The thermodynamic properties of high temperature aqueous solutions. IV. Entropies of the ions up to 200°C and the correspondence principle.
J. Amer. Chem. Soc. 86(1964)p. 5385.

12. CRISS C. M. and COBBLE J. W.
The thermodynamic properties of high temperature aqueous solutions. V. The calculation of heat capacities up to 200°C.
Ibid. p. 5390.

13. SILLÉN L. G.
Stability constants of metal-ion complexes. Section 1.
The Chemical Society, London 1964

14. POURBAIX M.
Atlas of electrochemical equilibria in aqueous solutions.
Pergamon, Oxford 1966

15. EDELEANU C. and LITTLEWOOD R.
Thermodynamics of corrosion in fused chlorides.
Electrochim. Acta 3(1960) p. 195.

16. BREDIG M. A.
Mixtures of metals with molten salts
Molten salt chemistry. Ed. by M. Blander.
Interscience, New York 1964, p. 367.

17. LUX H.
"Säuren" und "Basen" im Schmelzfluss: Die Bestimmung der Sauerstoffionen-Koncentration.
Z. Elektrochem. 45(1939)p. 303.

18. FLOOD H., FØRLAND T. and MOTZFELDT K.
On the oxygen electrode in molten salts.
Acta Chem. Scand. 6(1952)p. 257.

19. WRENCH N. S.
Studies of the oxygen electrode in molten salts.
Thesis. University of London, 1967.

20. JORDAN J., McCARTHY W. B. and ZAMBONIN P. G.
Thermochemistry, complexation, electron and oxygen transfer in fused nitrates.
Molten Salts. Ed. by G. Mamantov.
Marcel Dekker, New York 1969, p. 127.

21. BLANDER M.
Thermodynamic properties of molten salt solutions.
Molten salt chemistry. Ed. by M. Blander.
Interscience, New York 1964, p. 127.

22. INGRAM M. D. and JANZ G. J.
The thermodynamics of corrosion in molten carbonates: Application of E/pCO_2 diagrams.
Electrochim. Acta 10(1965) p. 783.

23. BORUCKA A. and SUGIYAMA C. M.
Correlation of the equilibrium potentials, and micropolarisation characteristics of the O_2/CO_2 and CO/CO_2 gas electrodes in molten carbonates.
C. I. T. C. E. Colloquium, Istanbul, 12 - 16 Sept. 1967.

24. BOMBARA G., BAUDO G. and TAMBA A.
Thermodynamics of corrosion in fused sulphates.
Corros. Sci. 8(1968)p. 393.

25. RAHMEL A.
Thermodynamische Gesichtspunkte der Korrosion in Sulfatschmelzen: Die Konstruktion und Anwendung von $E/\log p_{SO_3}$ - Diagrammen.
Electrochim. Acta 13(1968)p. 495.

26. BURROWS B. W. and HILLS G. J.
The electrochemistry of deposits of inorganic constituents of fuels at high temperature.
J. Inst. Fuel 39(1966)p. 168.

27. CONTE A. and INGRAM M. D.
Corrosion of silver in fused nitrates: Applications of E/pO^{2-} diagrams.
Electrochim. Acta 13(1968)p. 1551.

28. KRÜGER H. J., RAHMEL A. and SCHWENK W.
Elektrochemische Messungen in NaOH-Schmelzen
Electrochim. Acta 13(1968)p. 625.

29. BRIANT R. C. and WEINBERG Alvin M.
Molten fluorides as power reactor fuels.
Nucl. Sci. and Engineering 2(1957)p. 797.

30. ROSENTHAL M. W., KASTEN P. R. and BRIGGS R. B.
Molten salt reactors - History, status and potential.
Nucl. Appl. and Technology 8(1970) p. 107.

31. LONG G.
Chemical aspects of a molten-chloride reactor concept.
Molten Salt Discussion Group Colloquium on Chemical Reactions in Melts. London, 19 Dec. 1967.

32. GAT U.
Cooling Concepts for a compact MOSEL (molten salt) reactor.
Nucl. Eng. and Des. 5(1967)p. 113

33. TAUBE M. et al.
New Boiling salt fast breeder reactor concepts.
Ibid., p. 109.

Table 1. The differences between the values of the standard potential for a couple M^{+m}/M in various chloride melts at 475°C calculated on the equivalent fraction scale, E^{o}_{if}, and on the mole fraction scale. E^{o}_{mf}.

m	Solvents containing:		
	$NaCl-MgCl_2$ 61:39 mol %	univalent cations	divalent cations
		$E^{o}_{if} - E^{o}_{mf}$, mV	
1	-26.6	0	-44.5
2	+ 9.1	+22.2	0
3	+14.7	+23.6	+ 8.0
4	+15.6	+22.4	+11.1

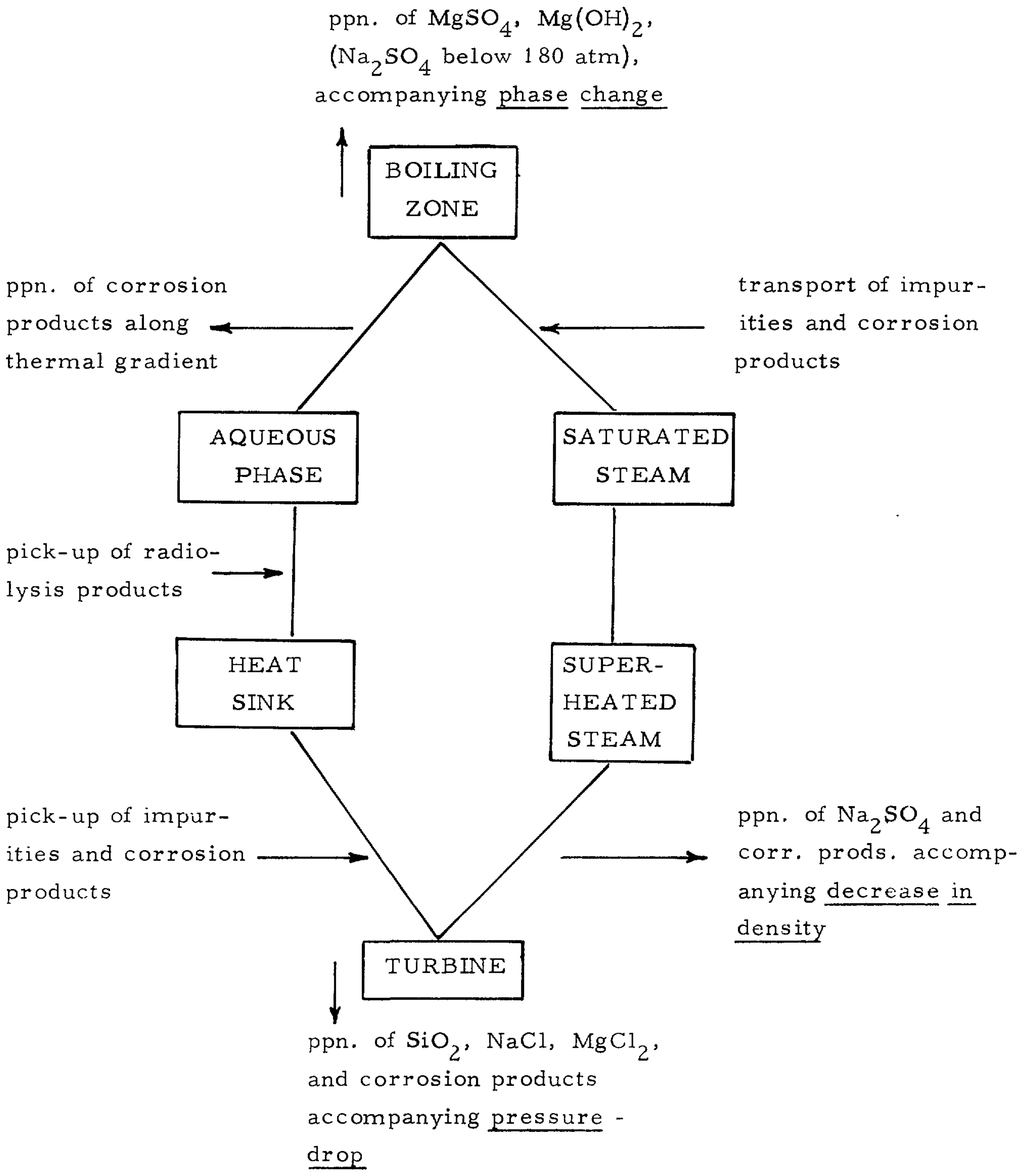

Figure 1. Transport phenomena in subcritical power cycles.

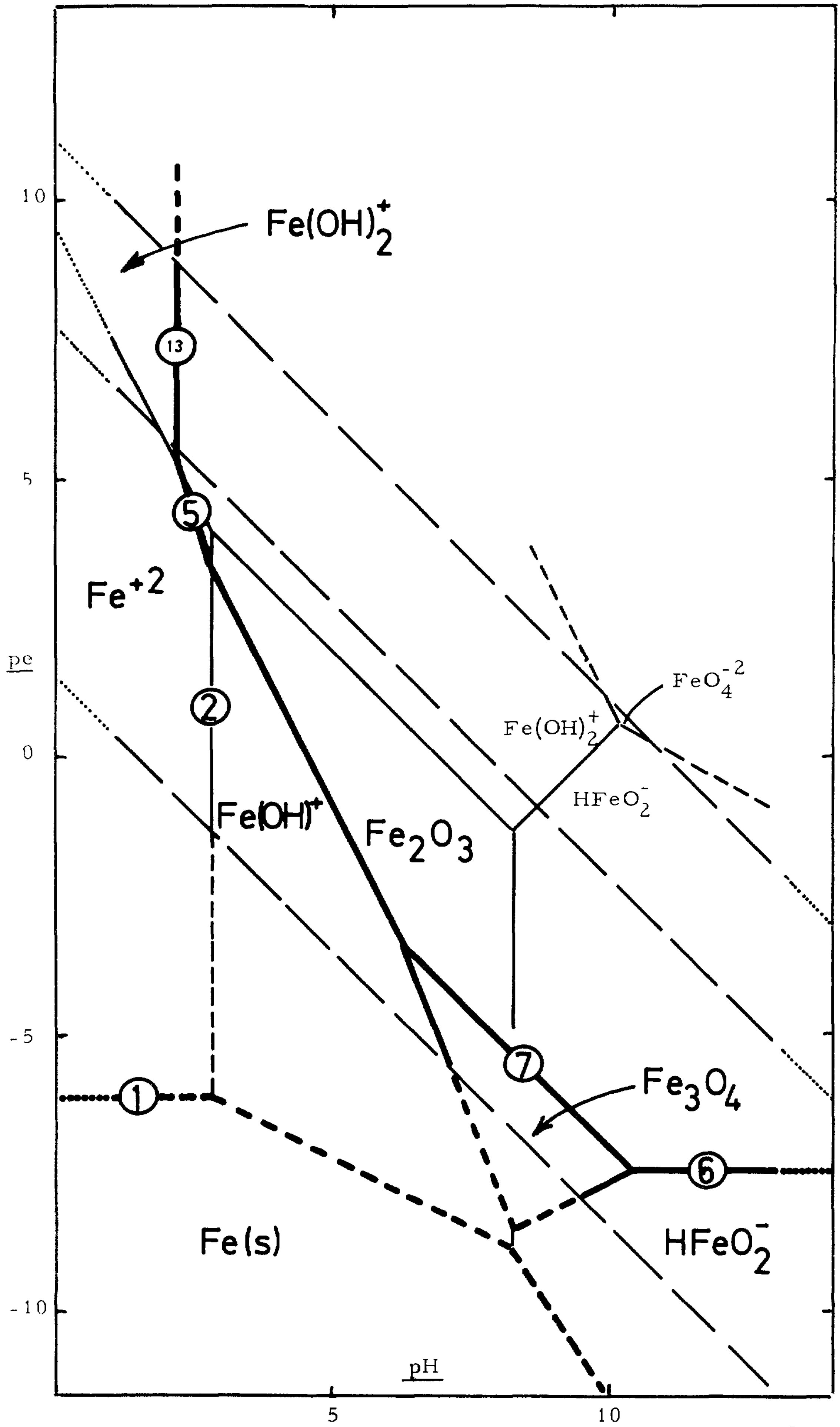

Figure 2. Pourbaix diagram for the iron-water system at 250°C

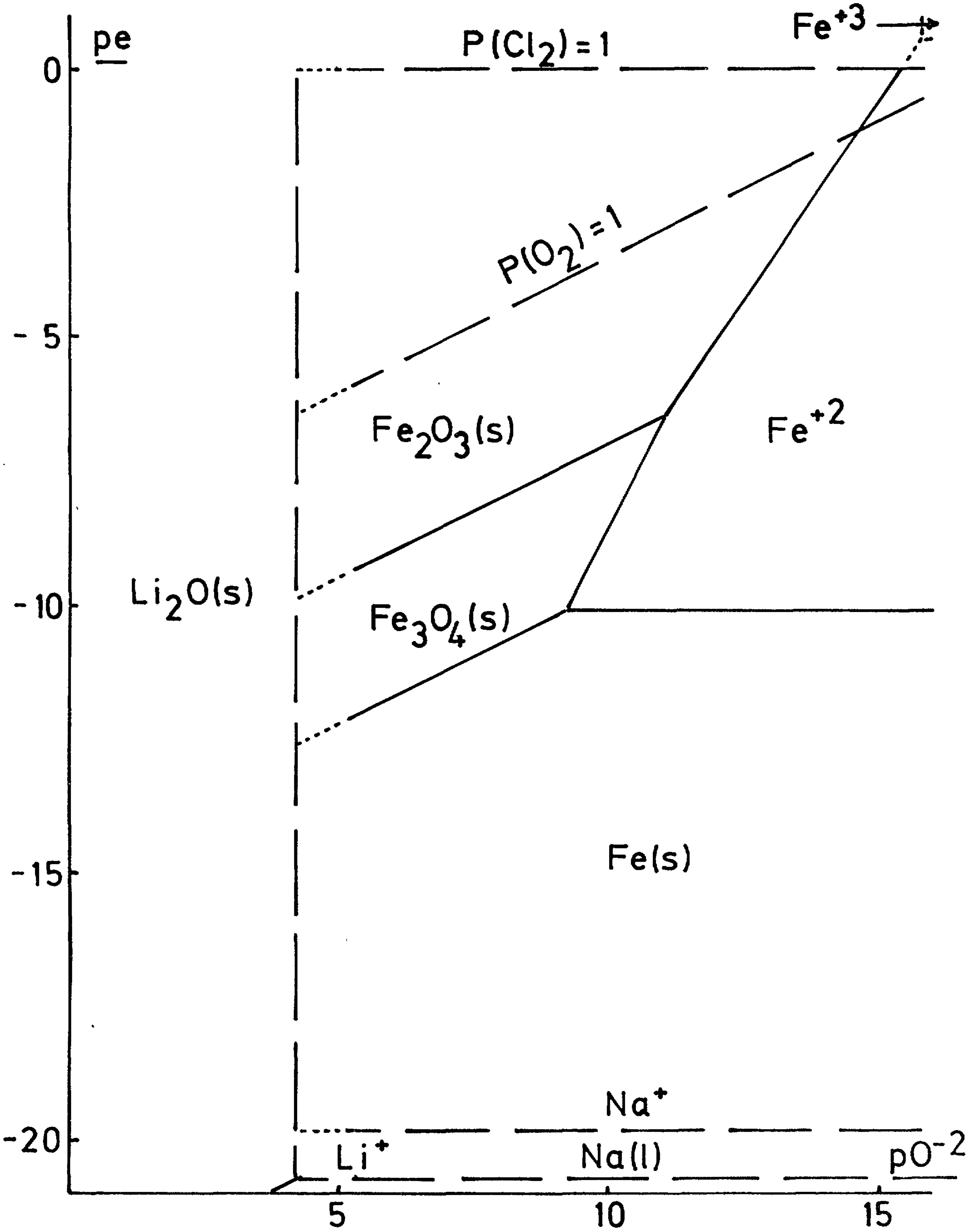

Figure 3. Pourbaix diagram for iron in LiCl (27 mole %) - NaCl (63) at 600°C.

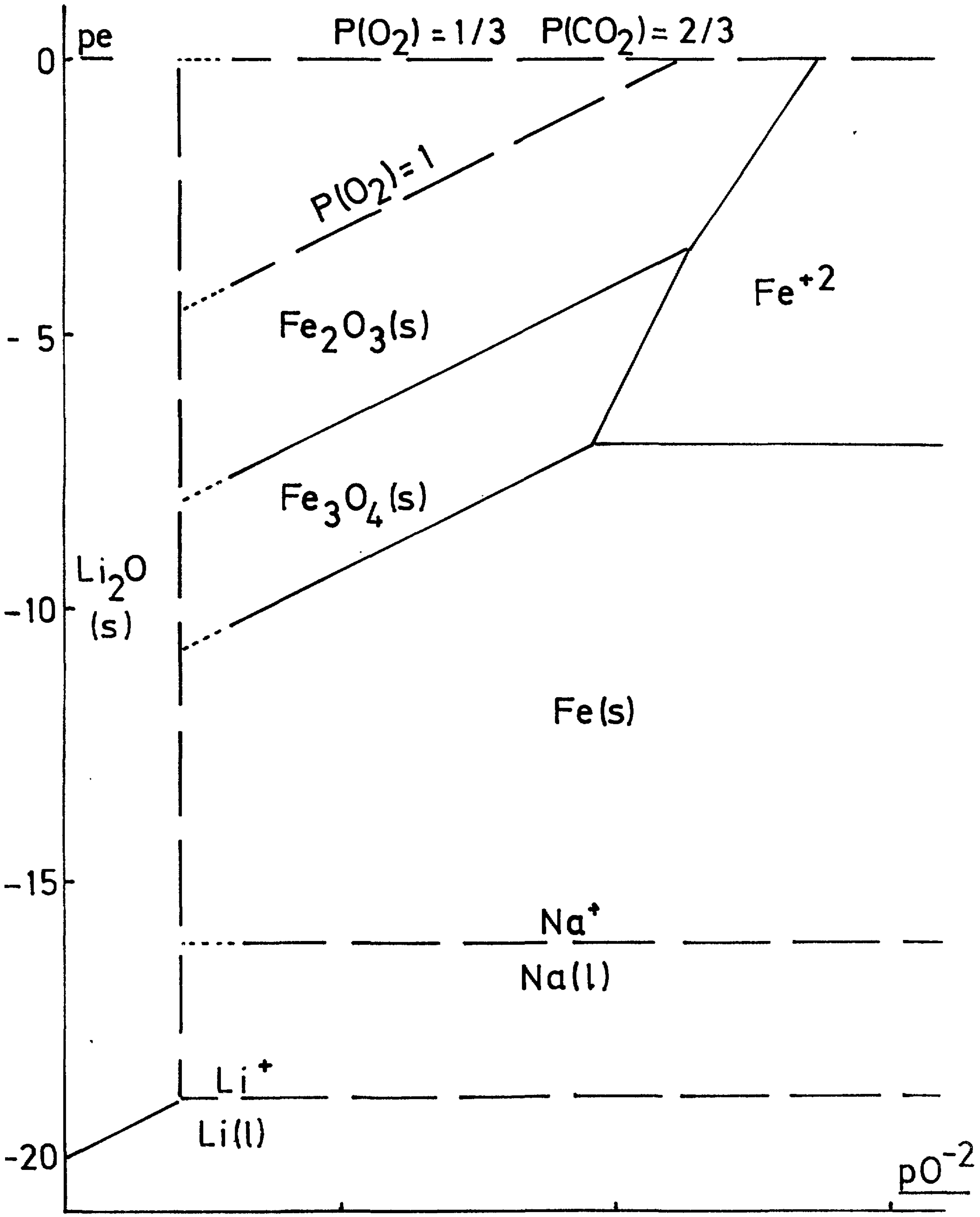

Figure 4. Pourbaix diagram for iron in Li_2CO_3 (52 mole %) - Na_2CO_3 (48) at 600°C.

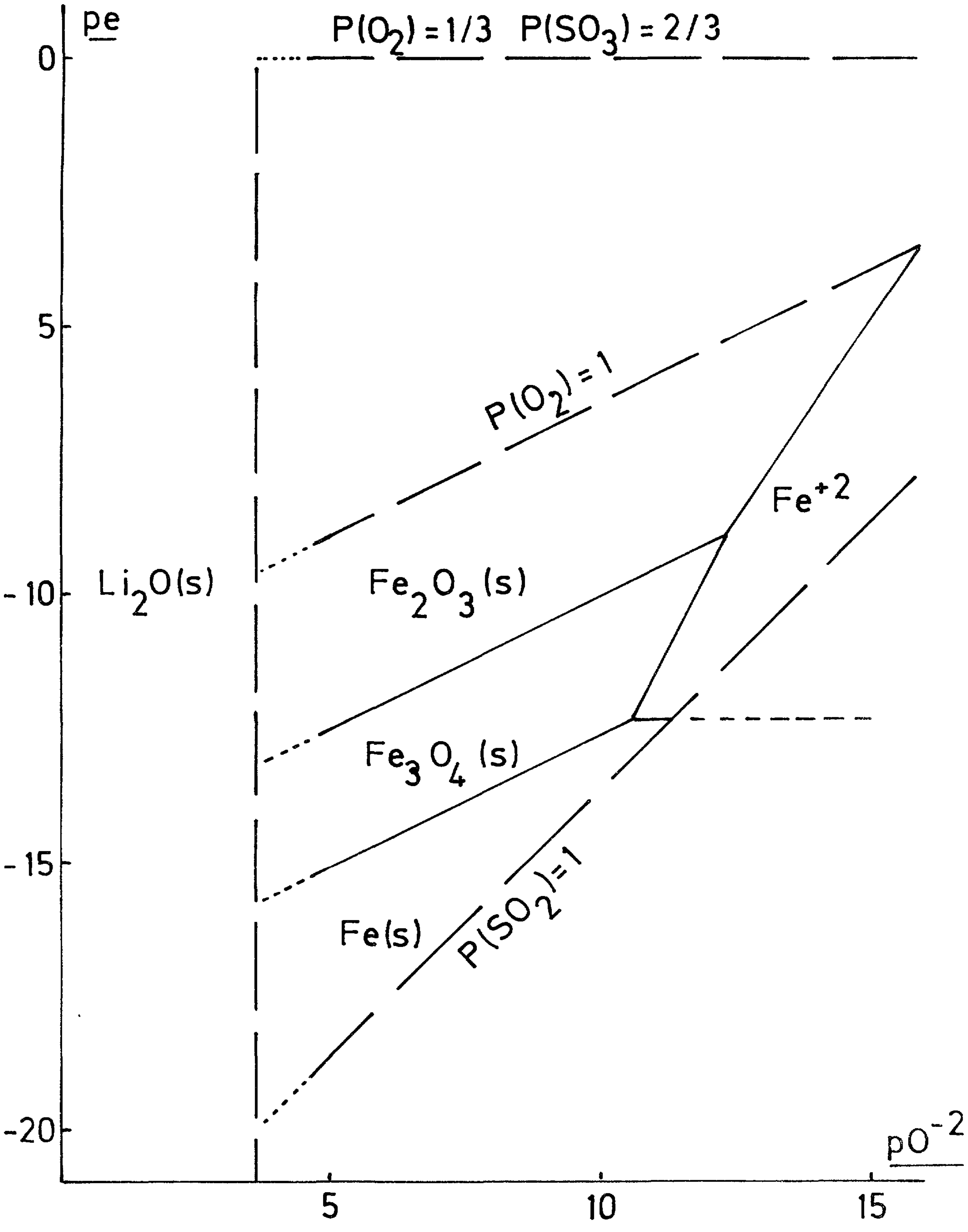

Figure 5. Pourbaix diagram for iron in Li_2SO_4 (40 mole %) - Na_2SO_4 (60) at 600°C.

$$pe = \log {}_T K + \frac{1}{n} \log N^{+n}$$

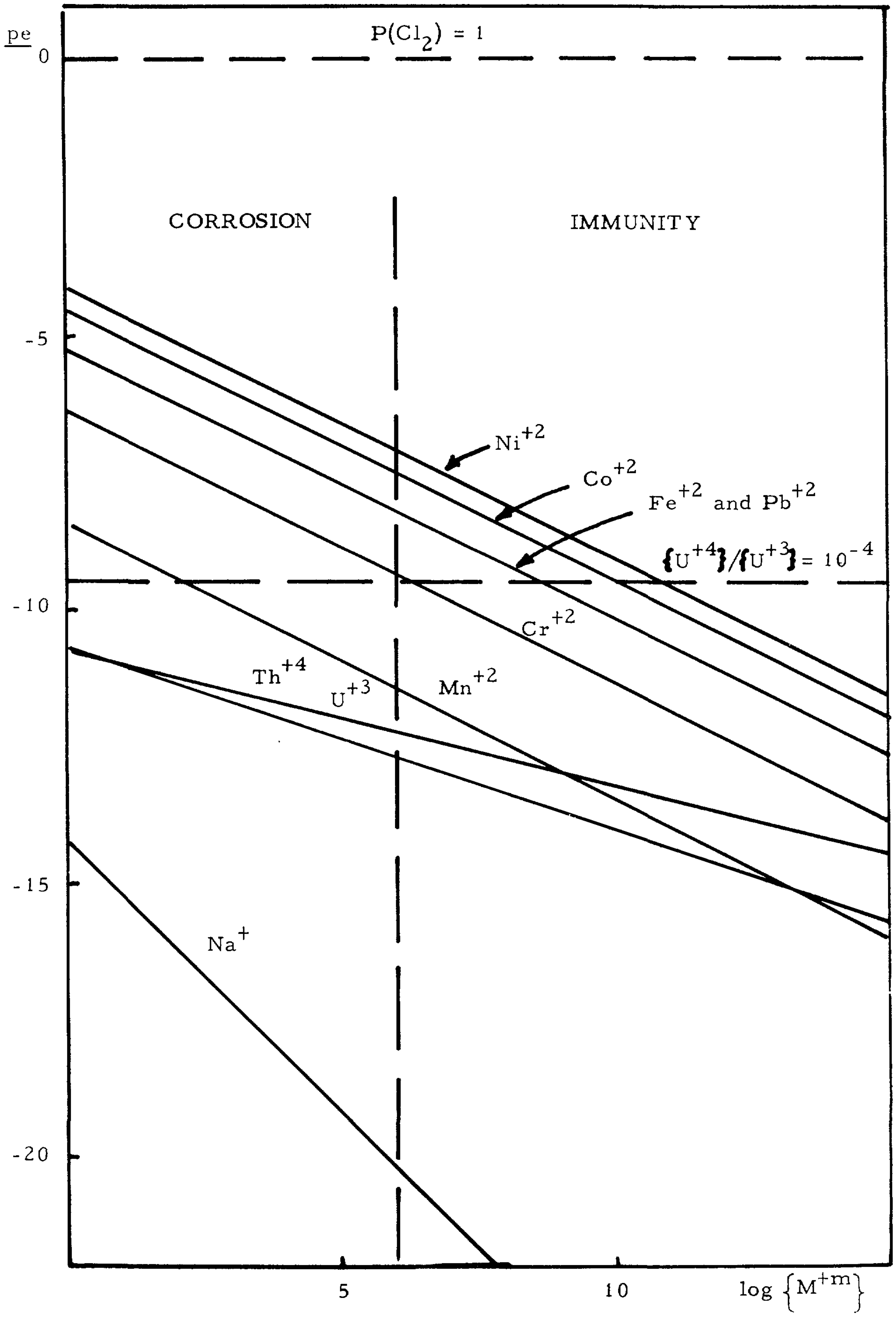

Figure 6. Redox equilibria of some metals in chloride media at 800°C.

LIST OF PUBLISHED AE-REPORTS

1–350 (See back cover earlier repports.)

351. A determination of the 2 200 m/s absorption cross section and resonance integral of arsenic by pile oscillator technique. By E. K. Sokolowski and R. Bladh. 1969. 14 p. Sw. cr. 10:–.

352. The decay of ^{191}Os. By S. G. Malmskog and A. Bäcklin. 1969. 24 p. Sw. cr. 10:–

353. Diffusion from a ground level point source experiment with thermoluminescence dosimeters and Kr 85 as tracer substance. By Ch. Gyllander, S. Hollman and U. Widemo. 1969. 23 p. Sw. cr. 10:–.

354. Progress report, FFN, October 1, – September 30, 1968. By T. Wiedling. 1969 35 p. Sw. cr. 10:–.

355. Thermodynamic analysis of a supercritical mercury power cycle. By A S. Roberts, Jr. 1969. 25 p. Sw. cr. 10:–.

356. On the theory of compensation in lithium drifted semiconductor detectors. By A. Lauber. 1969. 45 p. Sw. cr. 10:–.

357. Half-life measurements of levels in ^{75}As. By M. Höjeberg and S. G. Malmskog. 1969. 14 p. Sw. cr. 10:–.

358 A non-linear digital computer model requiring short computation time for studies concerning the hydrodynamics of the BWR. By F. Reisch and G. Vayssier. 1969. 38 p Sw. cr. 10:–.

359. Vanadium beta emission detectors for reactor in-core neutron monitoring. By I. Ö Andersson and B. Söderlund. 1969. 26 p Sw. cr. 10:–

360. Progress report 1968. Nuclear chemistry. 1969. 38 p. Sw. cr. 10:–.

361 A half-life measurement of the 343.4 keV level in ^{175}Lu. By M. Höjeberg and S. G. Maimskog. 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 ^{161}Dy. By V. Berg and S. G. Malmskog. 1969 32 p. Sw cr. 10:–.

364 Control rod reactivity measurements in the Ågesta reactor with the pulsed neutron method. By K. Björeus. 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 ^{188}Ir. By S. G. Malmskog and V. Berg. 1969. 16 p. Sw. cr. 10:–.

371. Transition probabilities in the 1/2+(631) Band in ^{235}U. By M. Höjeberg and S. G. Malmskog 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. Malmskog. 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 nucler power station. By P. Å. Bliselius, H. Vollmer and F. Akerhielm. 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:–.

279. ATOMSPHERIC DIFFUSION. Investigations at Studsvik and Agesta 1960–1963. By L-E. Hæggblom, 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 lever ^{91}Sr, and evidence for 3-neutron states above N=50. By S G Malmskog and J. McDonald 1970. 24 p. Sw. cr. 10:–.

382. The low energy level structure of ^{191}Ir. By S. G. Malmskog, 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 end 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 ^{28}Si and ^{32}Si using (d. nγ) reactions. By L. Nilsson, A Nilsson and I. Bergqvist. 1970. 34 p. Sw. cr. 10–.

387. Transition probabilities in ^{189}Os. By S G. Malmskog, V. Berg and A. Bäcklin. 1970 40 p Sw. cr. 10:–.

388. Cross sections for high-energy gamma transition from MeV neutron capture in ^{208}Pb. 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. 26 p. Sw. cr. 10:–.

391. Half-life measurements in ^{134}I. By V. Berg and Å. 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 ^{141}La. By B. Berg, Å. Höglund and B. Fogelberg. 1970 22 p. Sw cr. 10:–.

395 Magnetoacoustic waves and instabilities in a Hall-effect-dominiated plasma. By S. Palmgren 1970. 20 p Sw. cr. 10:–.

396. A new boron analysis method. By J. Weitman, N. Dåverhög and S. Farvolden. 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 ^{235}U. 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. Malmskog. 1970 33 p. Sw. cr. 10:–.

401. Needle type solid state detectors for in vivo measurement of tracer activity. By A. Lauber, M. Wolgast. 1970. 43 p. Sw. cr 10:–.

402. Application of pseudo-random signals to the Agesta 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. Almquist. 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 physic section Progress report. Fiscal year 1969/70. By J. Braun. 1970. 92 p. Sw. cr. 10:–.

411. In-pile determination of the thermal conductivity of UO_2 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 canning. 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 UO_2 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 ^{235}U 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 ^{235}U. 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. Häggblom. 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:–.

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 Agesta 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. 1967. 26 p Sw. cr. 10:–

Additional copies available from the Library of AB Atomenergi, Fack, S-611 01 Nyköping 1, Sweden.

EOS-tryckerierna, Stockholm 1971