Pourbaix diagram

• summarizes the regions of immunity from corrosion, areas of active corrosion and passivity of any particular metal.

 diagrams derived by considering both chemical and electrochemical equilibria for a particular metal in contact with water in the absence of extraneous ions like the chloride and sulphate ions.

Pourbaix diagram

- metal ion concentrations of 10⁻⁶ mol dm ⁻³ and higher in a corroding system are regarded to be indicative of considerable corrosion.
- This is universally accepted although it was arbitrarily adopted. However, it is reasonable for all practical purposes

Limitations of E/pH diagram

• It considers only the thermodynamics of reactions.

For example, $1/2O_2 + H_2 \rightarrow H_2O$

 The ∆G for the above reaction in is negative. However, at room temperature the reaction will not proceed as written. Hence, kinetic factors should be considered.

Limitations

 consideration was not given to extraneous ions. K⁺ Na⁺ etc are not usually significant in any corroding system while SO_4^{2-} and NO_3^{-} are of limited importance because they do not form complexes. However, CN⁻, NH₄⁺ should be considered as very important because they do form complexes. Thus, they can stabilise, soluble species and destabilise solid species in any given corroding system. In effect they can extend the active corrosion zone and contract the passive zone of the metal under consideration

Limitations

- Most E/pH diagrams refer to reactions at 25^oC. others, considered at elevated temperatures are available in academic journals.
- The E/pH diagrams refer to pure metals. Derivation based on calculations cannot be obtained for alloys.
- Since the diagrams consider only thermodynamic factors, the rates of reactions considered may be very slow thus rendering boundary lines in the diagrams inadequate.

Limitations

 The pH considered when deriving the diagrams were the interfacial pH values of the metals/water system. The pH of the bulk of the solution must be different.

• Quality of the data used is poor.