

THE POWER OF THE CHEMICAL POTENTIAL – BEYOND TEXTBOOK WISDOM

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During corrosive reactions the chemical potential of hydrogen can be calculated. Examples will be presented for water reacting with iron or aluminum as well as H₂O and H₂S both reacting with iron. The chemical potential of hydrogen determines via Fermi-Dirac Statistics which of the sites within or near a crystal defect are occupied or trapped, respectively. The corresponding excess hydrogen Γ of a defect is the proportionality constant in the extended Gibbs Adsorption Isotherm

$$d\gamma = -\Gamma d\mu$$

describing how a positive excess decreases the formation energy γ of a defect, if the chemical potential μ is increased. Solutes decreasing surface energies by adsorption are called surfactants (surface active agents). In analogy defectants (defect active agents) are decreasing defect formation energies, a term not having entered textbooks yet. Thus in the presence of defectants more defects like vacancies, dislocations and grain boundaries are generated. Against textbook wisdom defectants may increase defect mobility despite the known solute drag. The accelerated motion occurs, if the defect moves via generation of secondary defects, i.e. kink pairs of dislocations or disclinations of grain boundaries. In this cases the formation energy of the secondary defects is decreased within the defectant concept. For dislocations the counteraction between defectant acceleration and solute drag leads to solute softening or solute hardening depending on which effect is dominant. Examples will be given for hydrogen in iron and consequences regarding hydrogen embrittlement will be discussed.

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