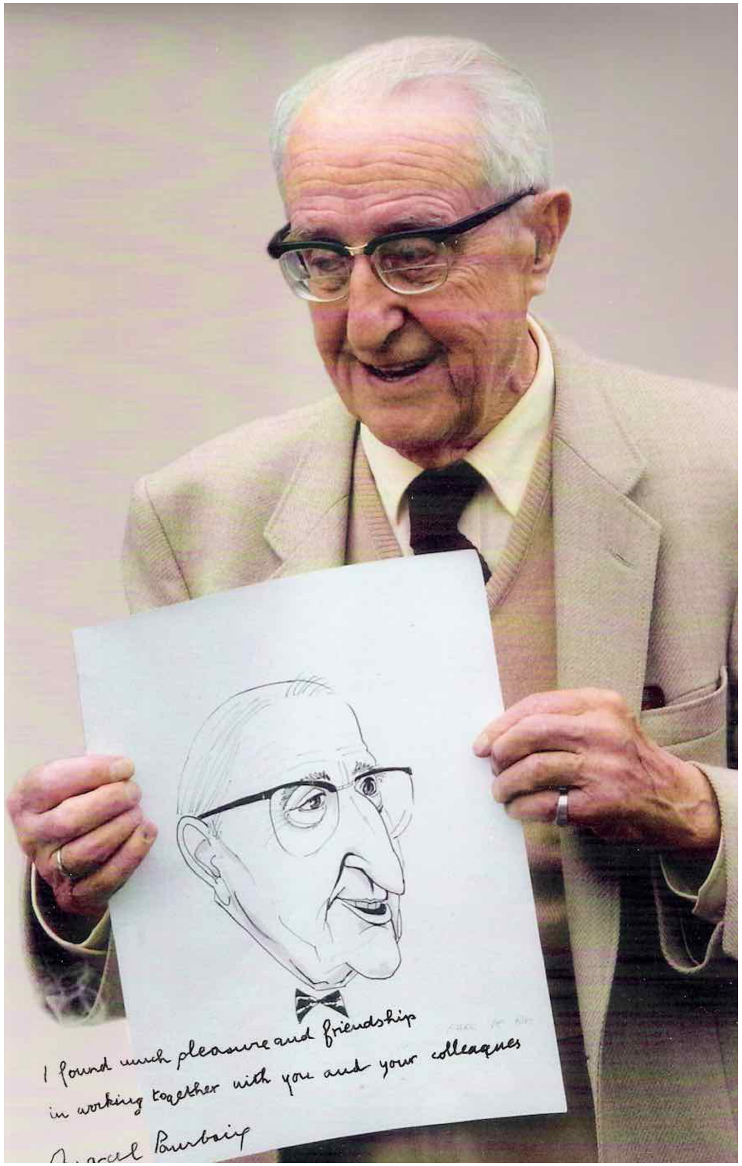
Thermo-Calc Software

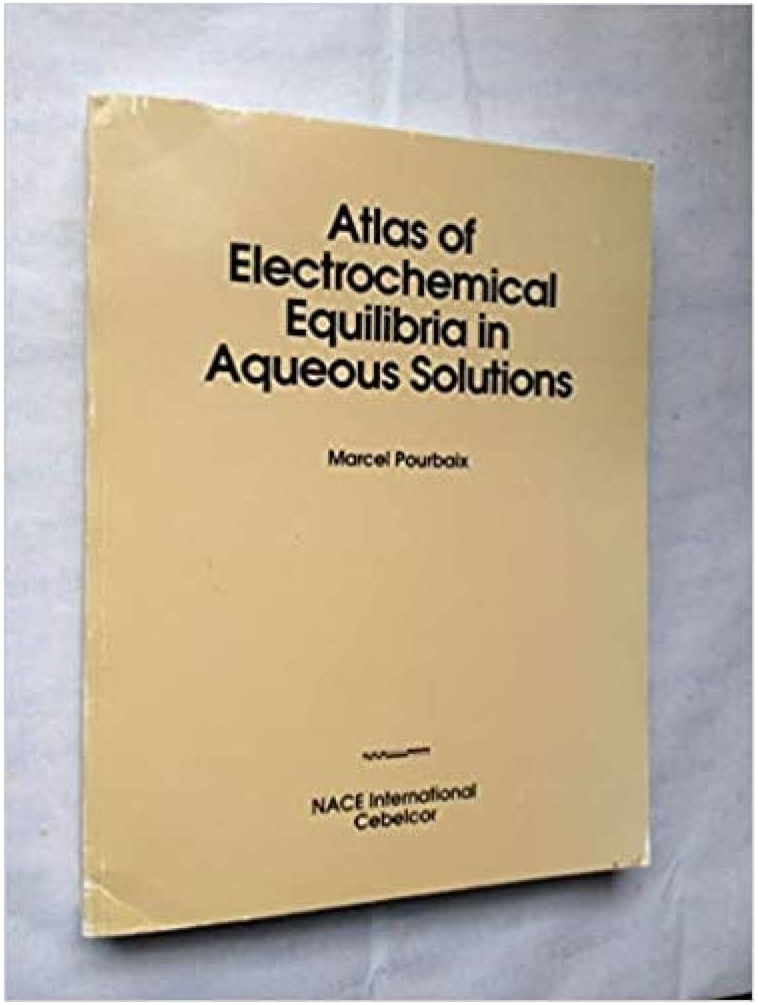
# Corrosion – POURBAIX Diagrams

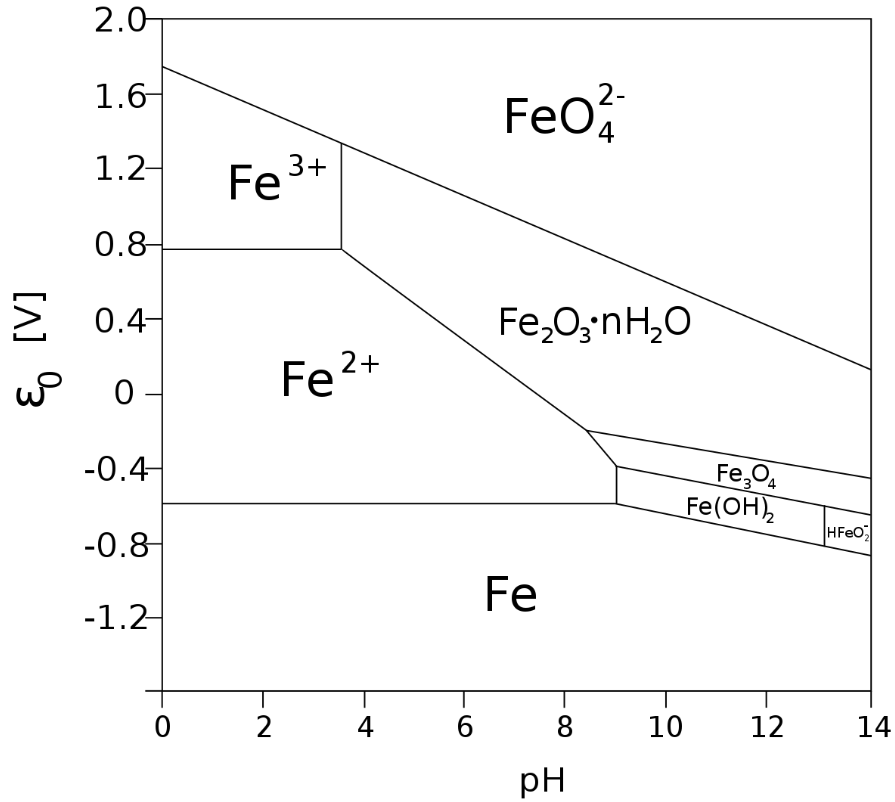
Nicholas Grundy, Huahai Mao

# Marcel POURBAIX




- Russian-born (1904 –1998) Belgian chemist and pianist.
- Studied corrosion @ University of Brussels
- Biggest achievement is the derivation of Eh-pH diagrams –a kind of electrochemical phase diagram.
- 1st Eh-pH diagram presented in 1949
- 1st Edition "Atlas of Electrochemical Equilibria", for all elements known at the time, published in 1963.




Marcel **Pourbaix** (1974): *Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd Ed*, Houston, Tex., National Association of Corrosion Engineers.

# Eh – pH Diagram

pE-pH, E$^{o}$-pH, or potential-pH diagram

**Eh**:

(standard hydrogen) electronic potential, represents the redox state, derived based on Nernst equation.

→ Eh = MUR(ZE)/RNF

where RNF is the Faraday constant (96485.3)

**pH**:

Acidity or concentration of

→ pH = -log10[ACR(H+1,AQUEOUS)*AH2O]]

where AH2O is the molecular weight of the solvent $H_2O$ (55.5)

## The Nernst Equation

For the electrochemical reduction reaction (cathodic reaction)

**Ox + *z* e− → Red**

$\Delta G = \Delta G^0 + RT\ln Q$ Q is the reaction quotient.

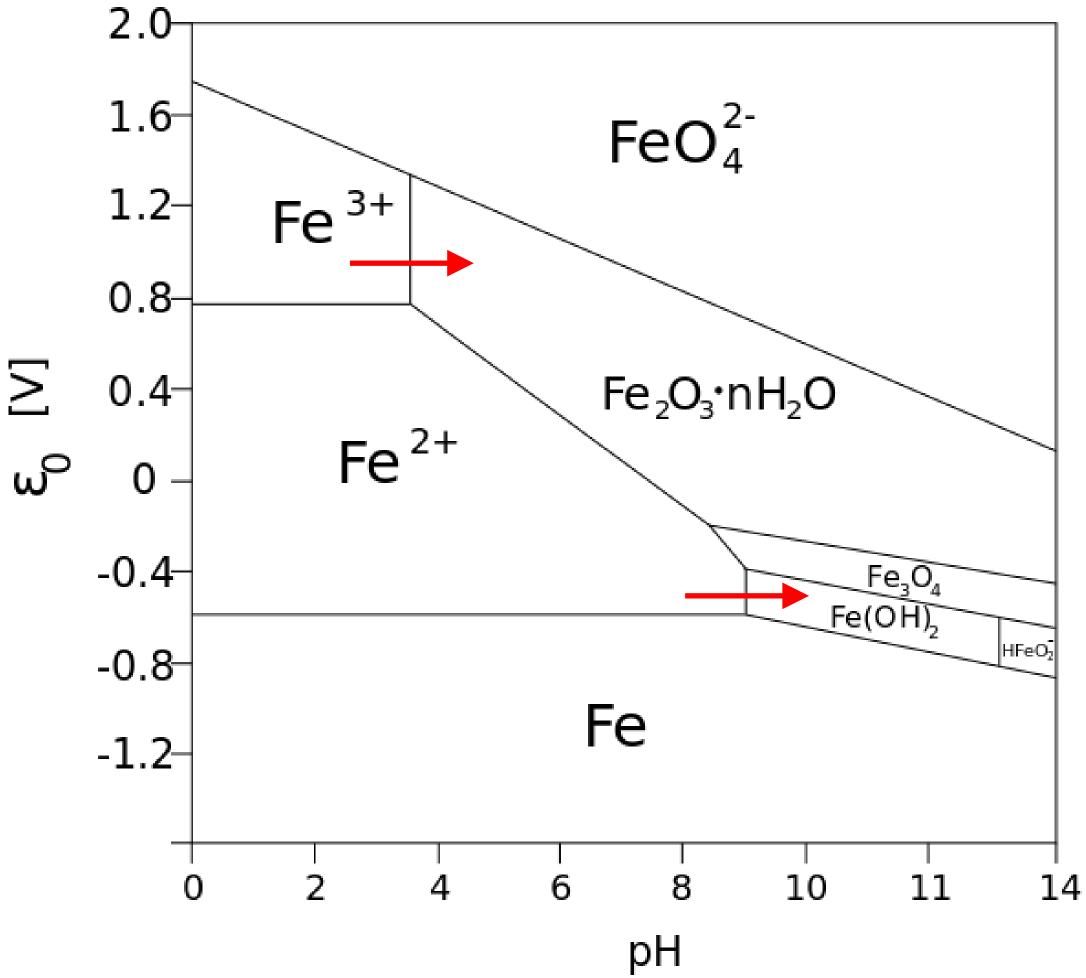
$\Delta G = -zFE$, F is the Faraday constant,

E the electrochemical potential.

The Nernst equation for an electrochemical half-cell is

$$E_{\mathrm{red}} = E^{\ominus}_{\mathrm{red}} - \frac{RT}{zF}\ln Q = E^{\ominus}_{\mathrm{red}} - \frac{RT}{zF}\ln\frac{a_{\mathrm{Red}}}{a_{\mathrm{Ox}}}$$

# POURBAIX Diagrams - Basics




**Vertical lines:**

No e- exchange → indep. of Eh

$Fe^{3+}$ → $Fe_2O_3$ or $Fe^{2+}$ → $Fe(OH)_2$

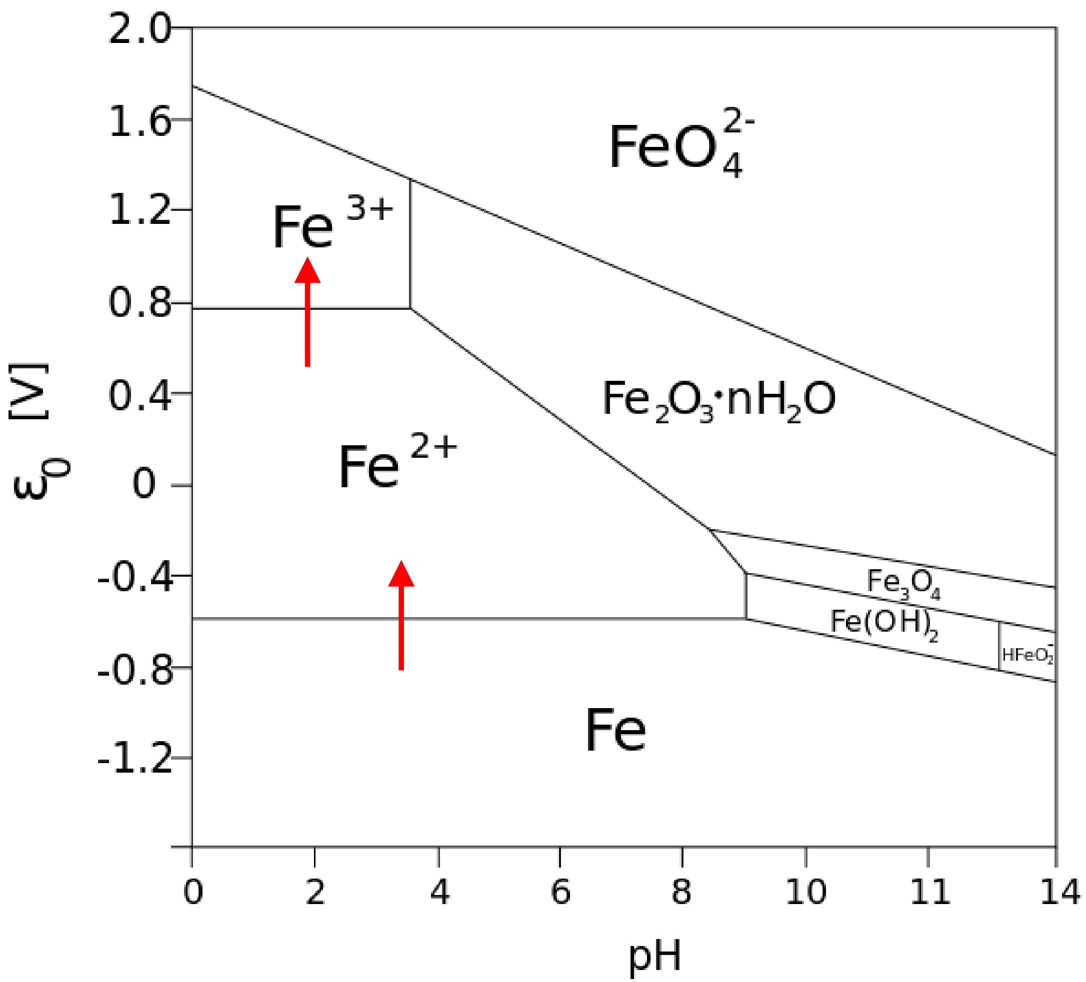
Acid – Base reactions

$$\Delta G^\circ = -8242.5 \mathrm{J/mol}$$

$$2\,\mathrm{Fe}^{3+}(\mathrm{aq}) + 3\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Fe_2O_3(s)} + 6\,\mathrm{H}^{+}(\mathrm{aq})$$

$$\mathrm{pH} = \frac{1}{6}\left(\frac{\Delta G^\circ}{RT\lambda} + \log\left(\frac{[\mathrm{Fe_2O_3}]}{[\mathrm{Fe}^{3+}]^2[\mathrm{H_2O}]^3}\right)\right)$$

# POURBAIX Diagrams - Basics




**Horizontal lines:**

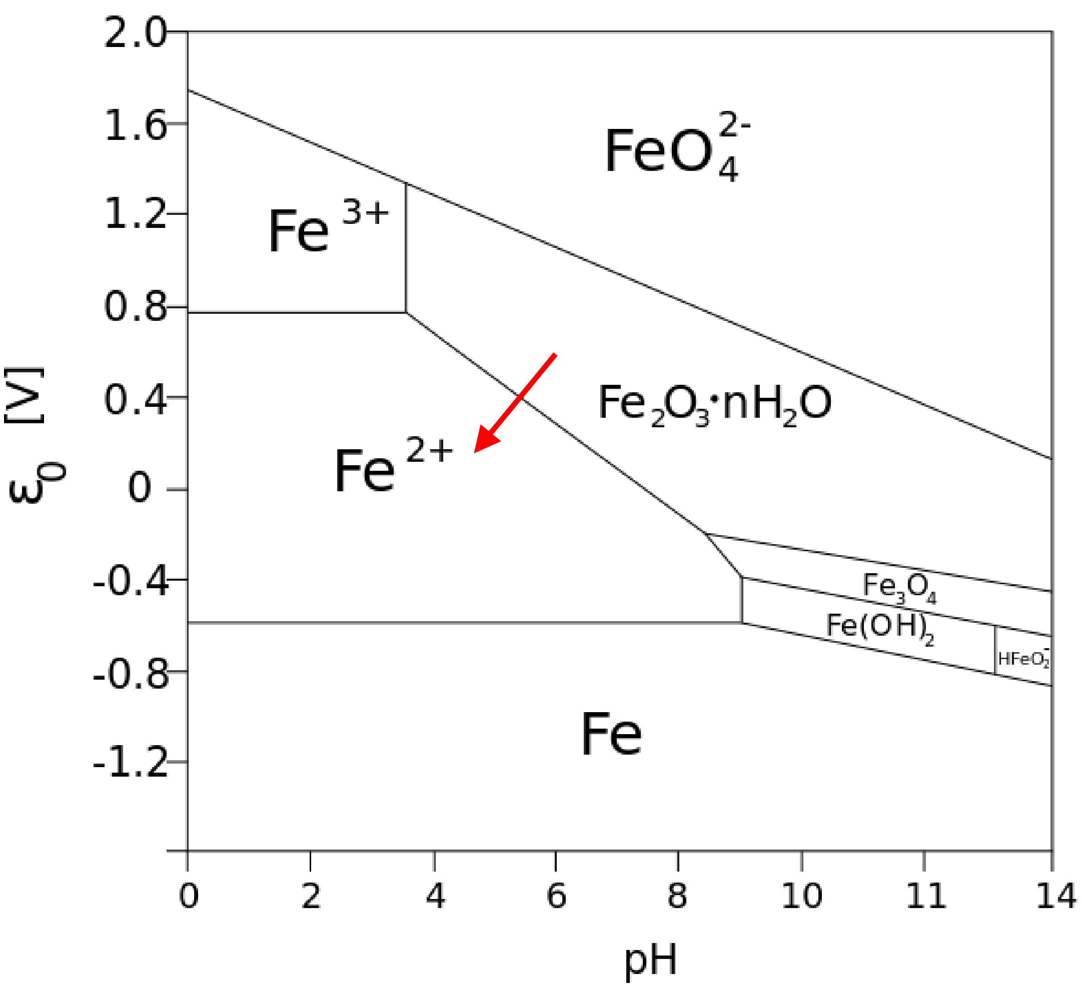
No $H^+$ or $OH^-$ exchange → independent of pH

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

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

Redox reactions

# POURBAIX Diagrams - Basics



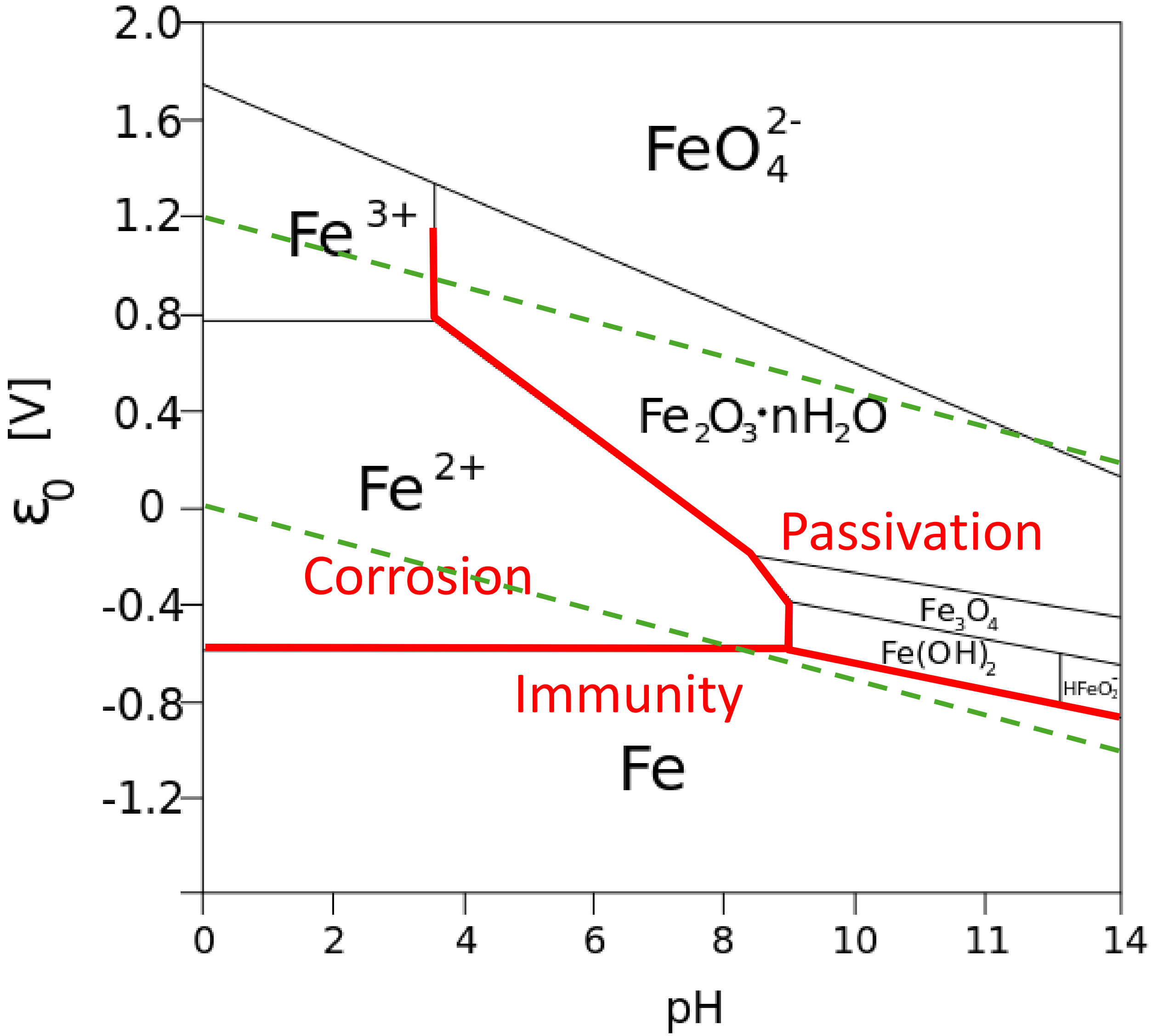

Slopes lines:
$H^+$ or $OH^-$ **and** $e^-$ exchange

$$Fe_2O_3(s) + 6\,H^+(aq) + 2\,e^- \rightleftharpoons 2\,Fe^{2+}(aq) + 3\,H_2O(l)$$

## POURBAIX Diagrams - Basics

Including stability region of water

3 regions can be designated: Corrosion / Passivation / Immunity



## POURBAIX Diagrams - Basics

Including stability region of water

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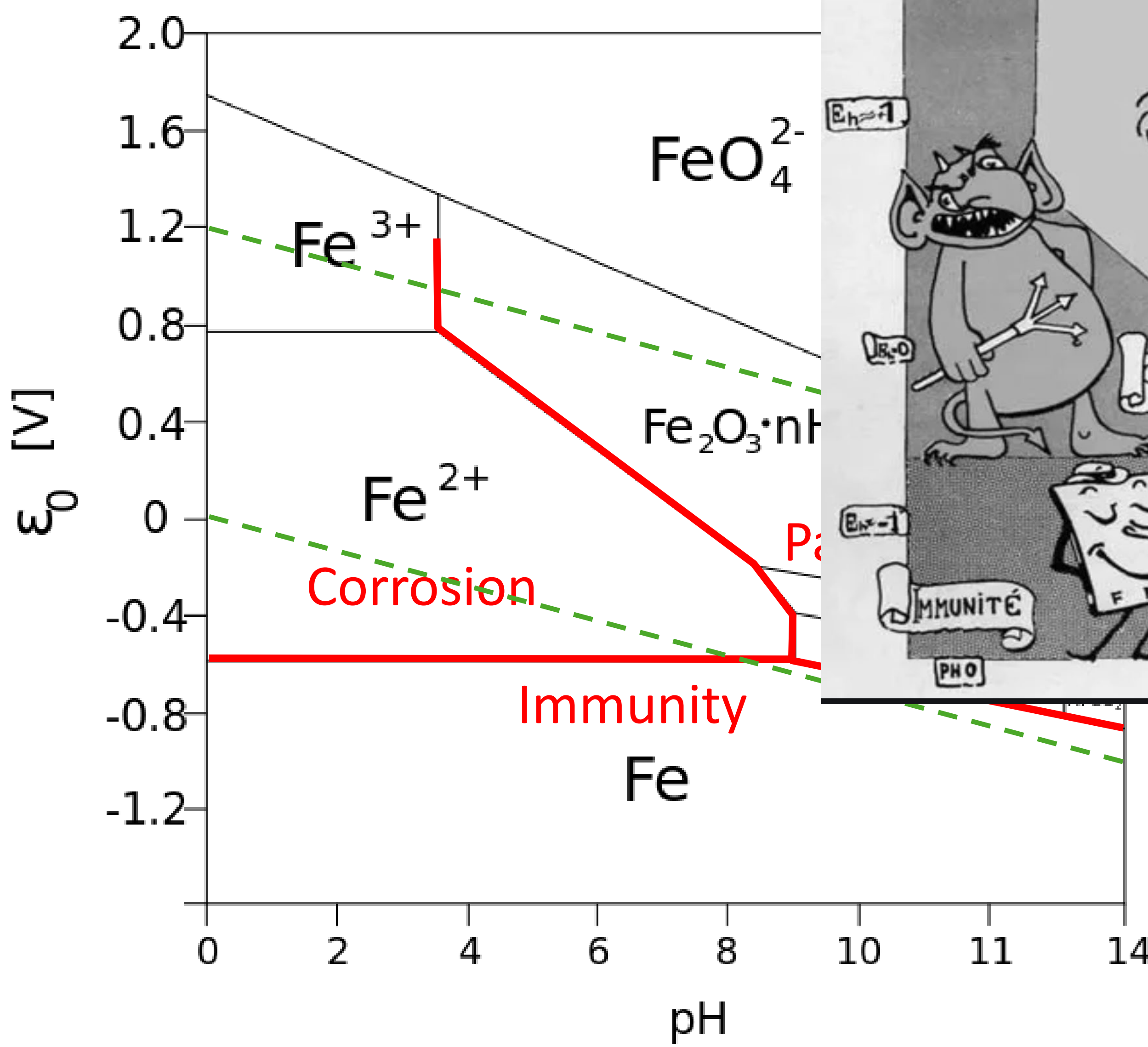
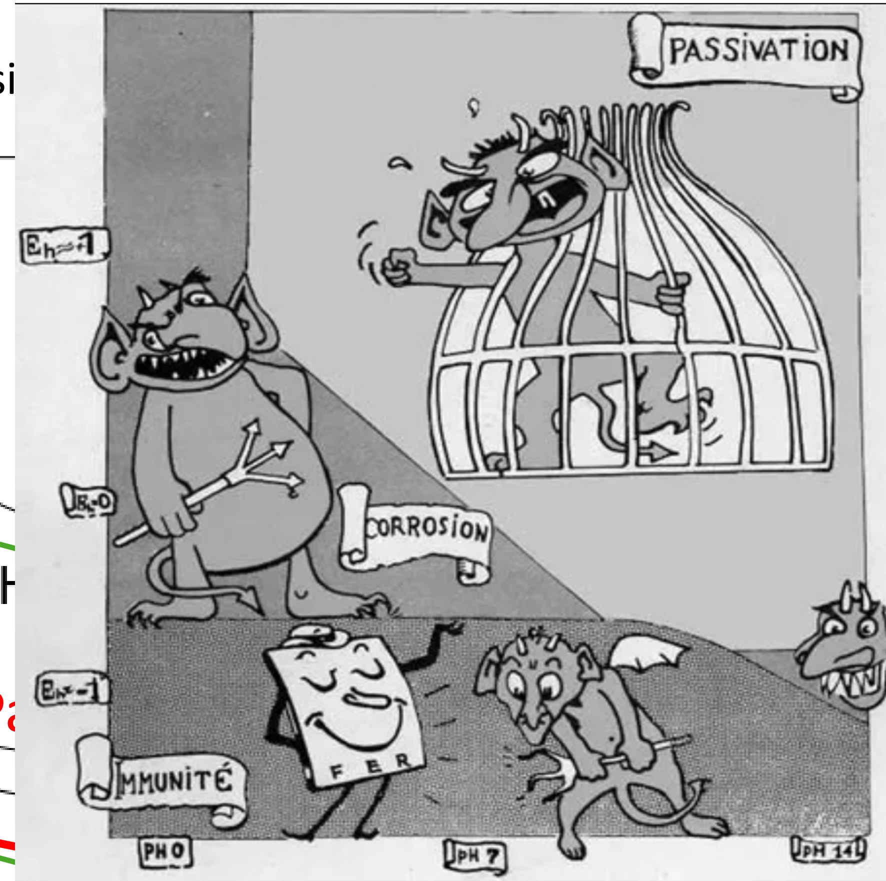
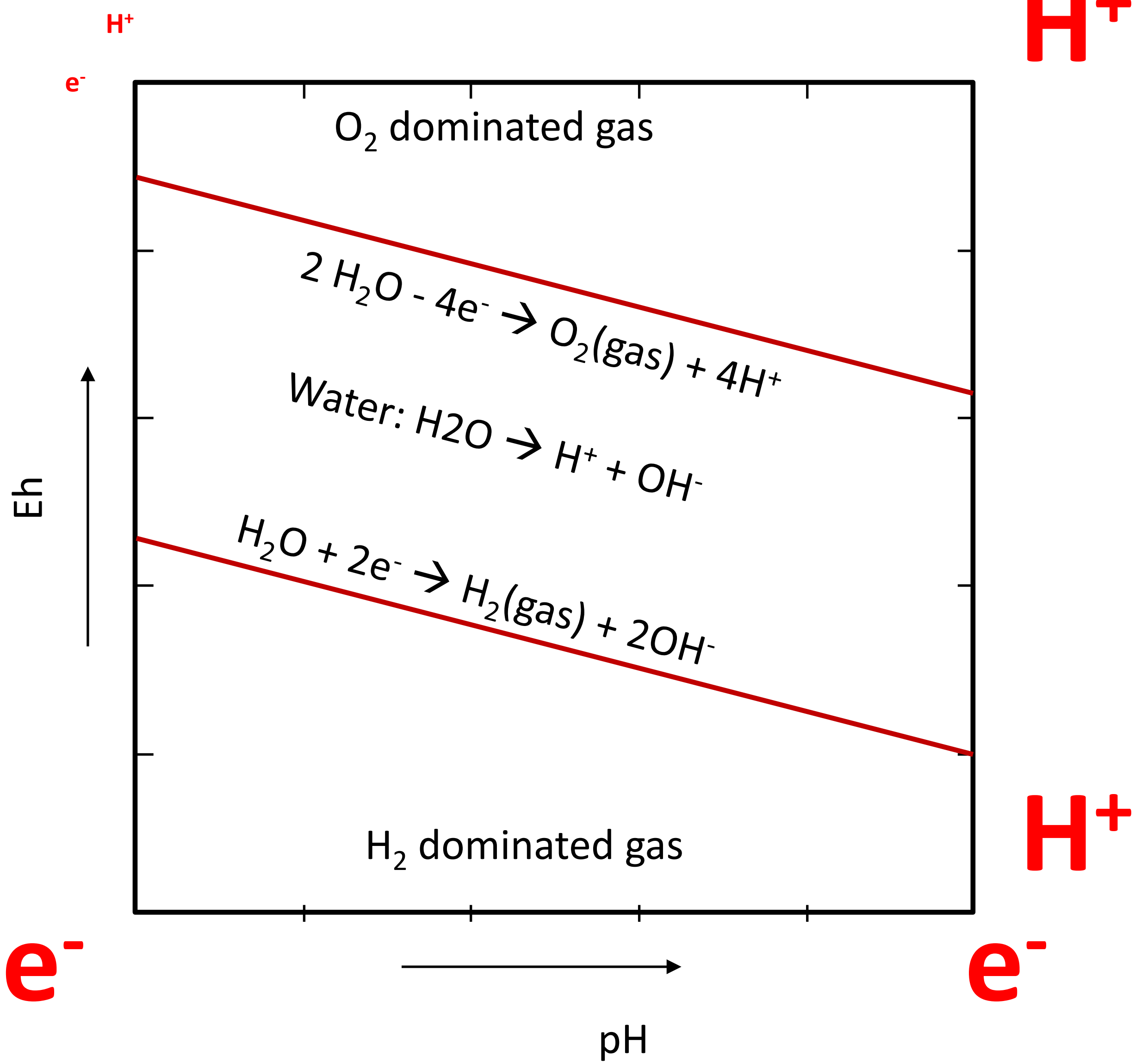


# POURBAIX Diagrams - Basics



# Calculation of POURBAIX Diagrams with Thermo-Calc

Thermo-Calc Software

**Easy set-up in POURBAIX module: Q&A "wizard" SYS:** `GO POURBAIX`

**Required phases and databases**

- AQUEOUS phase, REF_ELEC phase: AQS2, TCAQ3, PAQ2
- Alloy: TCFE9, SSOL6, …
- Phases resulting from chemical or electrochemical reaction (hydroxide, oxide, sulphide, etc…): SSUB6, TCOX8
- Gas phase: SSUB6

**Database descriptions**

AQS2: larges number of elements, originally from TGG (Theoretical Geochemistry Group, Prof. Saxena), applies the generalized HKF (Helgeson-Kirkham-Flowers) model, valid to 1000°C and 5 kbar .

TCAQ3: Applies the SIT (Specific Ion Interaction Theory), valid up to 350°C and 100 bar.

PAQ2: Subset of TCAQ3 includes all phases necessary for calculations.

- For demonstration and simple systems.
- Does not require appending different databases.

# To Calculate in Thermo-Calc

Defining the initial multi-component multi-phase electro-chemical reaction/equilibrium system:

- With 1 kg of water as basis; retrieve AQUEOUS phase, REF_ELEC phase from aqueous solution databases: PAQ2, TCAQ3, AQS2;
- Plus initial concentrated solutes (e.g., composition in sea water);
- Add initial amount of specific alloy or phases (e.g., 0.01 m stainless steel or BCC);
- Inclusion of various secondary phases (e.g. oxides, sulphides, hydroxides, etc.) that would form from interactions;
- Usually include the gas phase

# Two Calculation Strategies in Thermo-Calc

Thermo-Calc Software

**1. Ordinary TDB -> GES -> POLY -> POST Module - Routine**:

- Command-Line-Driven user-interface, or GUI
- Flexible single equilibrium calculation, stepping, mapping
- Special requirements on proper definitions / settings (tips available via the command *database-information*)
- example:TCEX53

## Settings in the TDB – POLY – POST Sequence

Thermo-Calc Software

- Redefine the **components**as follows:
  DEF-COMP H2O H+1 ZeFe Ni NaClCl-1 S <& other components> ;
- appropriately define the **equilibriumconditions**, e.g.,
  SET-COND P=1e5 T=300 B=1000 N(H+1)=0 N(Ze)=0 N(Fe)=1e-6 N(NaCl)=3...;
- set the necessary **reference states**for some components, e.g.,
  SET-REFERENCE-STATE H2O AQUEOUS * 1E5 ;
  SET-REFERENCE-STATE ZE REF_ELEC * 1E5 ;
  SET-REFERENCE-STATE NaCl HALITE * 1E5 ;
  SET-REFERENCE-STATE Fe BCC * 1E5 ;
- The **pH** and **Eh** are thus defined by entering the following functions:
  ENT-SYM FUNC pH = -log10(ACR(H+1), AQUEOUS) ;
  ENT-SYM FUNC Eh=MUR(ZE)/RNF ;
- The **REF_ELECTRODE** phase is the reference electrode which should ALWAYS be included in a defined system involving aqueous solution for the purpose of calculating electron potential [MUR(ZE)], while this phase must ALWAYS be SUSPENDED in all the POLY calculations.

# Two Calculation Strategies in Thermo-Calc

**2. Advanced POURBAIX Module**

- Question-Answer-Driven user-interface
- Easy set-up
- Multiple options for various mapping/stepping calculations
- Multiple choices for different post-processing purposes
- Automatic and straightforward definitions/settings
- example: TCEX40

# POURBAIX Module

```
SYS: go POURBAIX_DIAGRAM
WELCOME TO THE POURBAIX MODULE
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
for Quick Calculations of Pourbaix Diagrams
==========================================
Pingfang Shi and Bo Sundman
Thermo-Calc Software AB
NorraStationsgatan93
SE-113 47 Stockholm, Sweden
(Version 7.0, Mar. 2014)
Need any instruction on the POURBAIX module? /N/:
Enforce a PAUSE after plotting when running a MACRO? /N/:
------------------------------------------------------------
|                                                           |
| 1. Start a completely new POURBAIX diagram calculation    |
| 2. Open an old file & plot other property diagrams        |
| 3. Open an old file & make another POURBAIX calculation   |
| 4. Open an old file & make another STEPPING calculation   |
|                                                           |
------------------------------------------------------------
Select option /1/:
```

## POURBAIX Module

*Possible quantities for plotting property diagrams:*

| | |
|---|---|
| ✓ T | Temperature (°C or K) |
| ✓ P | Pressure (Pa) |
| ✓ NP | Stable Phase (mole/kg of water) |
| ✓ BP | Stable Phase (gram/kg of water) |
| ✓ pH | Acidity |
| ✓ Eh | Electronic Potential (V) |
| ✓ Ah | Electronic Affinity (kJ) |
| ✓ pe | Electronic Activity (log10ACRe) |
| ✓ IS | Ionic Strength |
| ✓ TM | Total Concentration (in molality) |
| ✓ Aw | Activity of Water |
| ✓ Oc | Osmotic Coefficient |
| ✓ MF(AQsp) | Mole Fractions of Aqueous Species |
| ✓ ML(AQsp) | Molalities of Aqueous Species |
| ✓ AI(AQsp) | Activities of Aqueous Species |
| ✓ RC(AQsp) | Activity Coefficients of Aqueous Species |

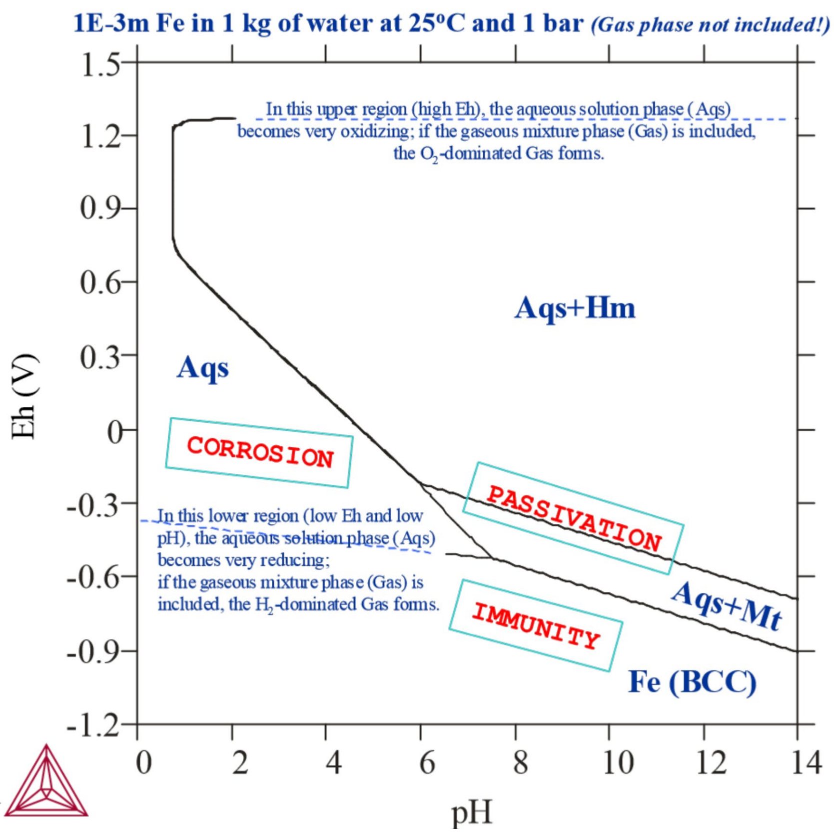
# Factors Affecting the Stability Region

The shape of a Pourbaix diagram of a complex multi-component alloy and the stability relations of various secondary phases (oxides, hydroxides, sulfides, sulfates, carbonates, nitrates, silicates, halides, or other forms) depend upon the following important factors:

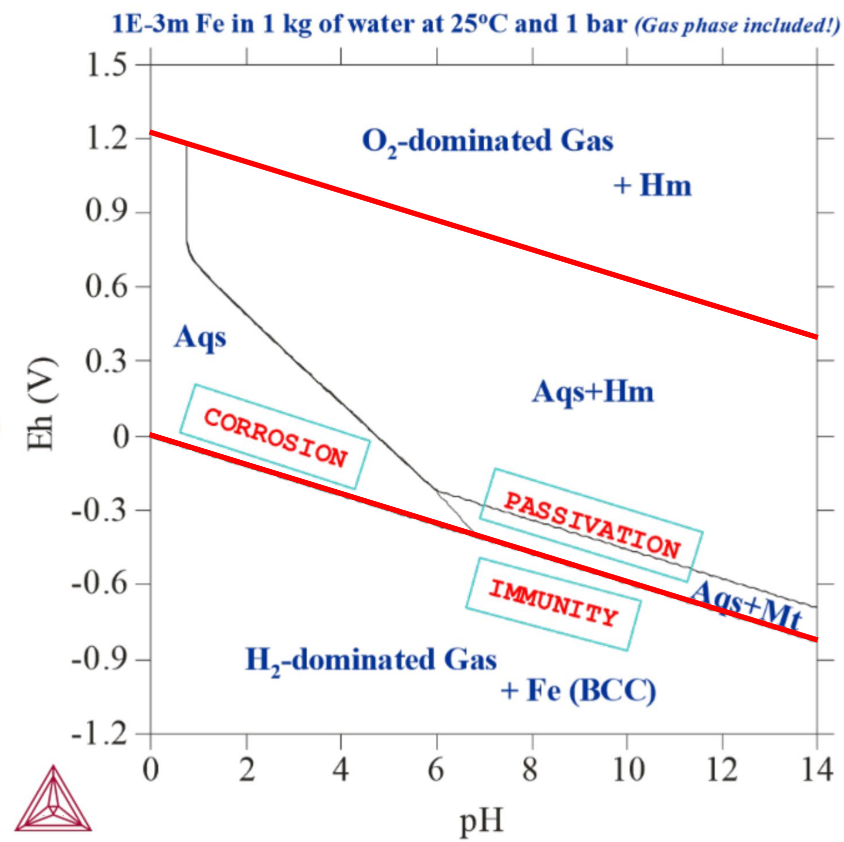
- ✓ Initial amount and composition of the alloy
- ✓ Initial amount and composition of the aqueous solution
- ✓ Model treatments on various phases
- ✓ Temperature and pressure conditions

# Examples of POURBAIX Calculations in Thermo-Calc

Excluding GAS phase

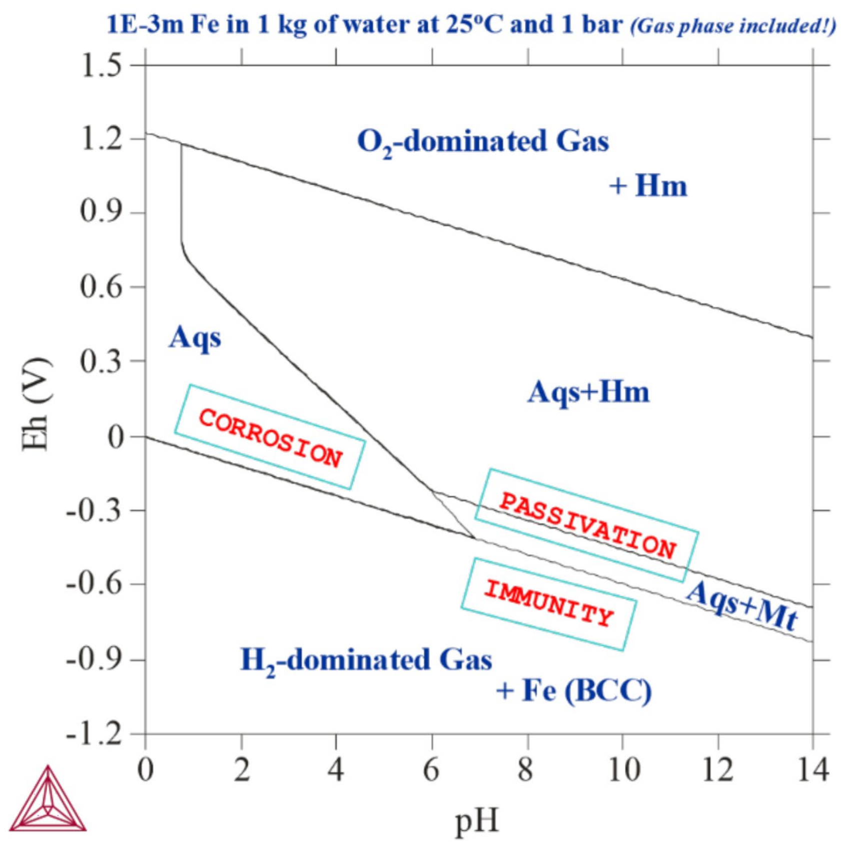


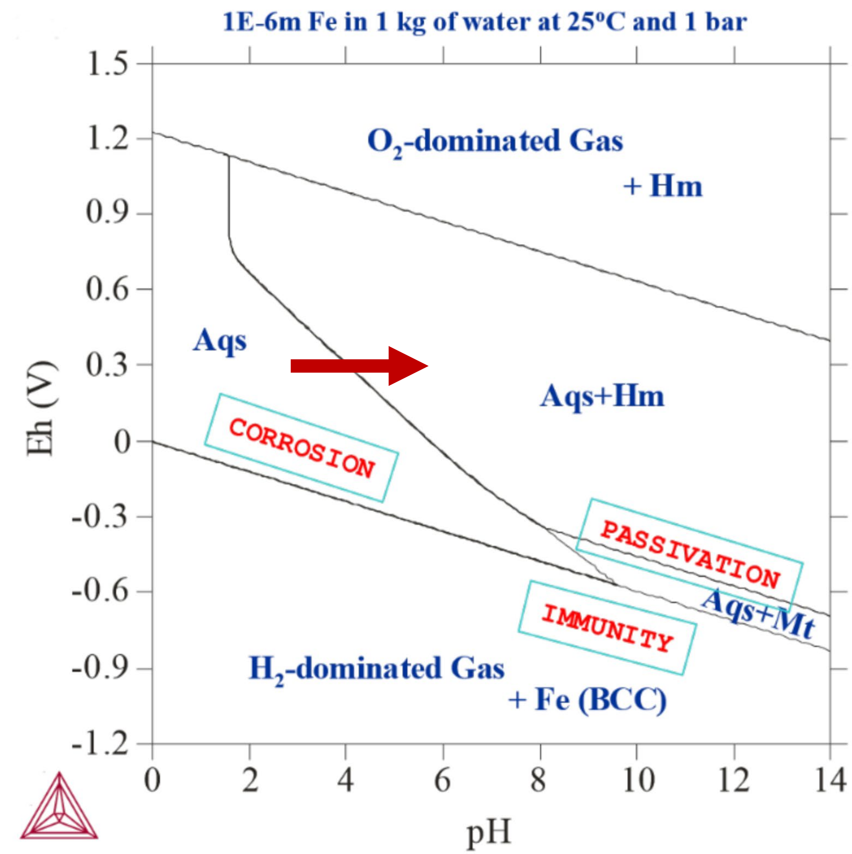

Including GAS phase



# Examples of POURBAIX Calculations in Thermo-Calc

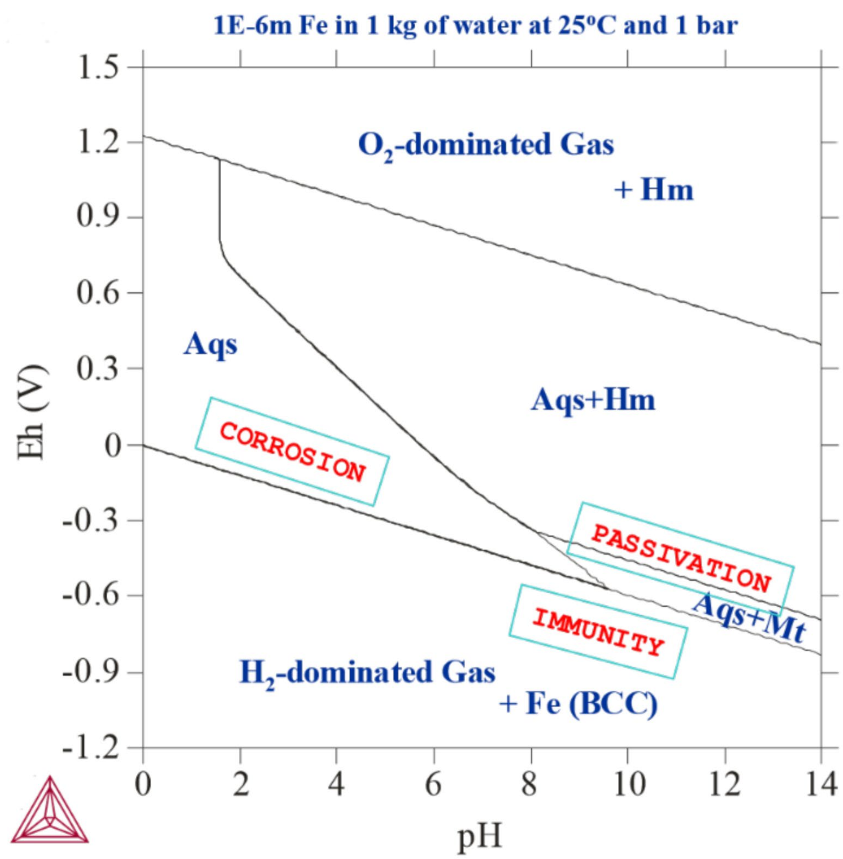
Lowering Fe content in aqueous phase

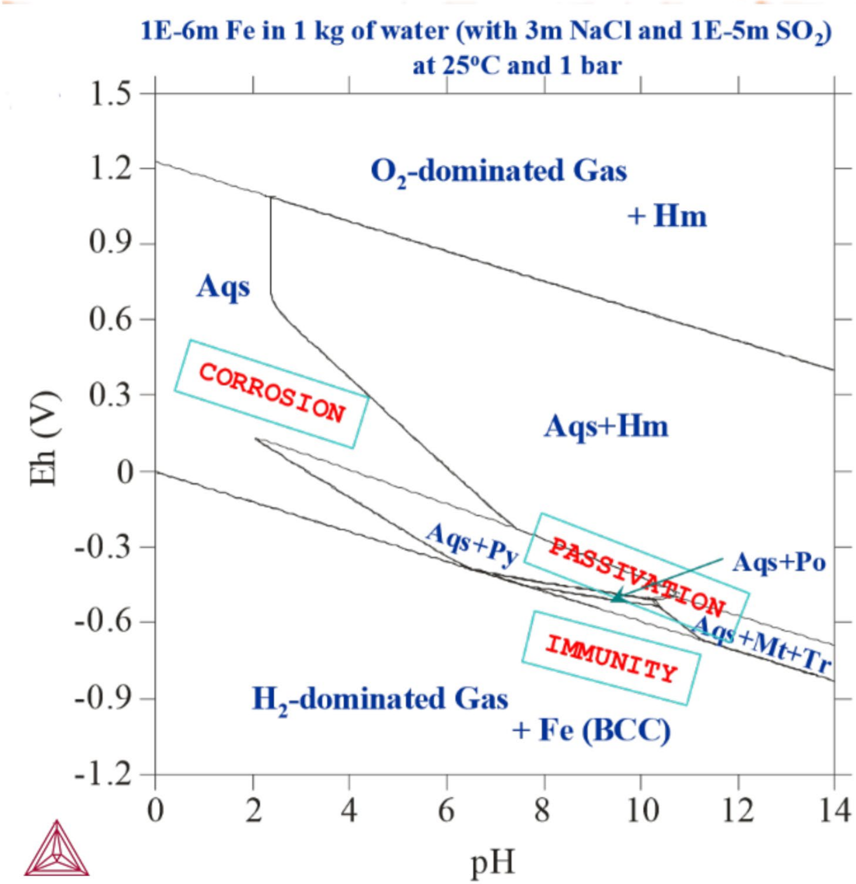


# Examples of POURBAIX Calculations in Thermo-Calc

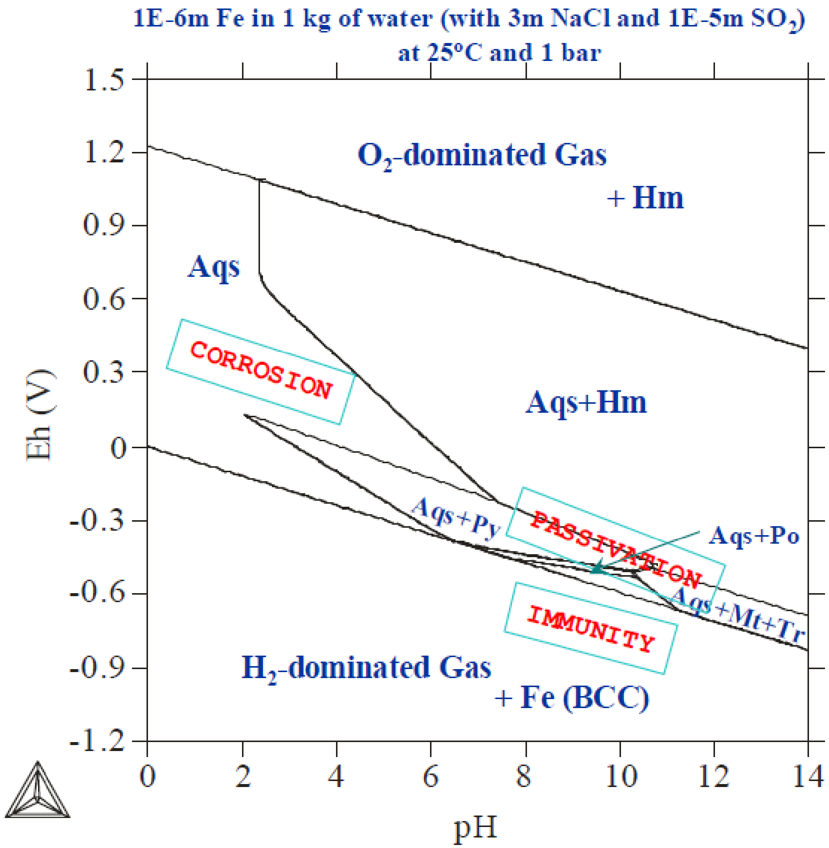
Adding $SO_2$ ($H_2S$ has the same effect)



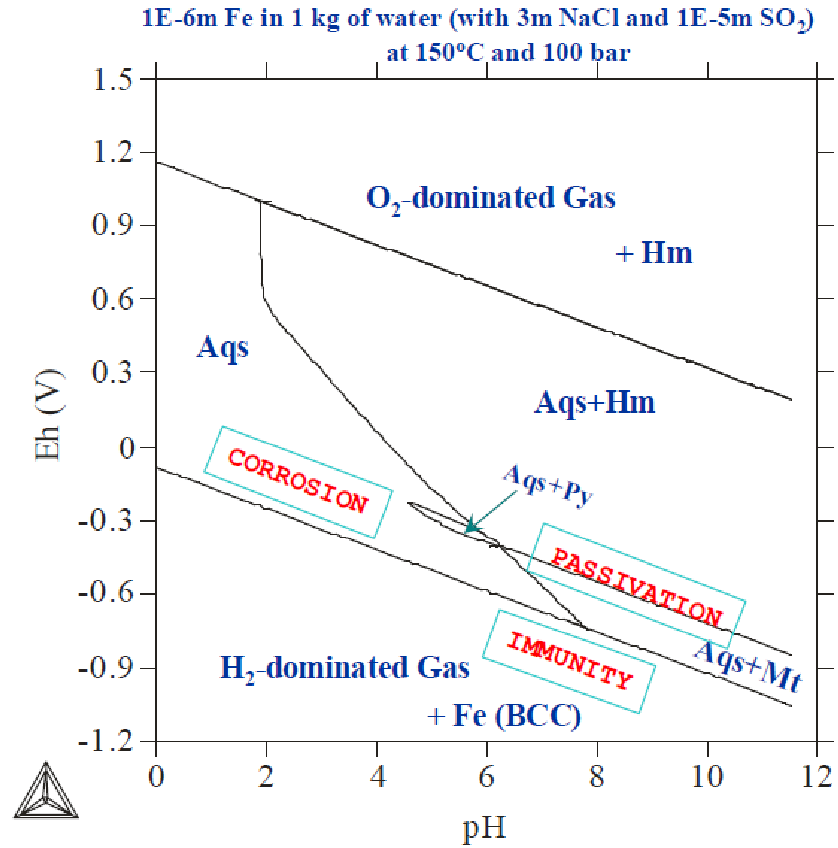



# Examples of POURBAIX Calculations in Thermo-Calc

Different P-T conditions

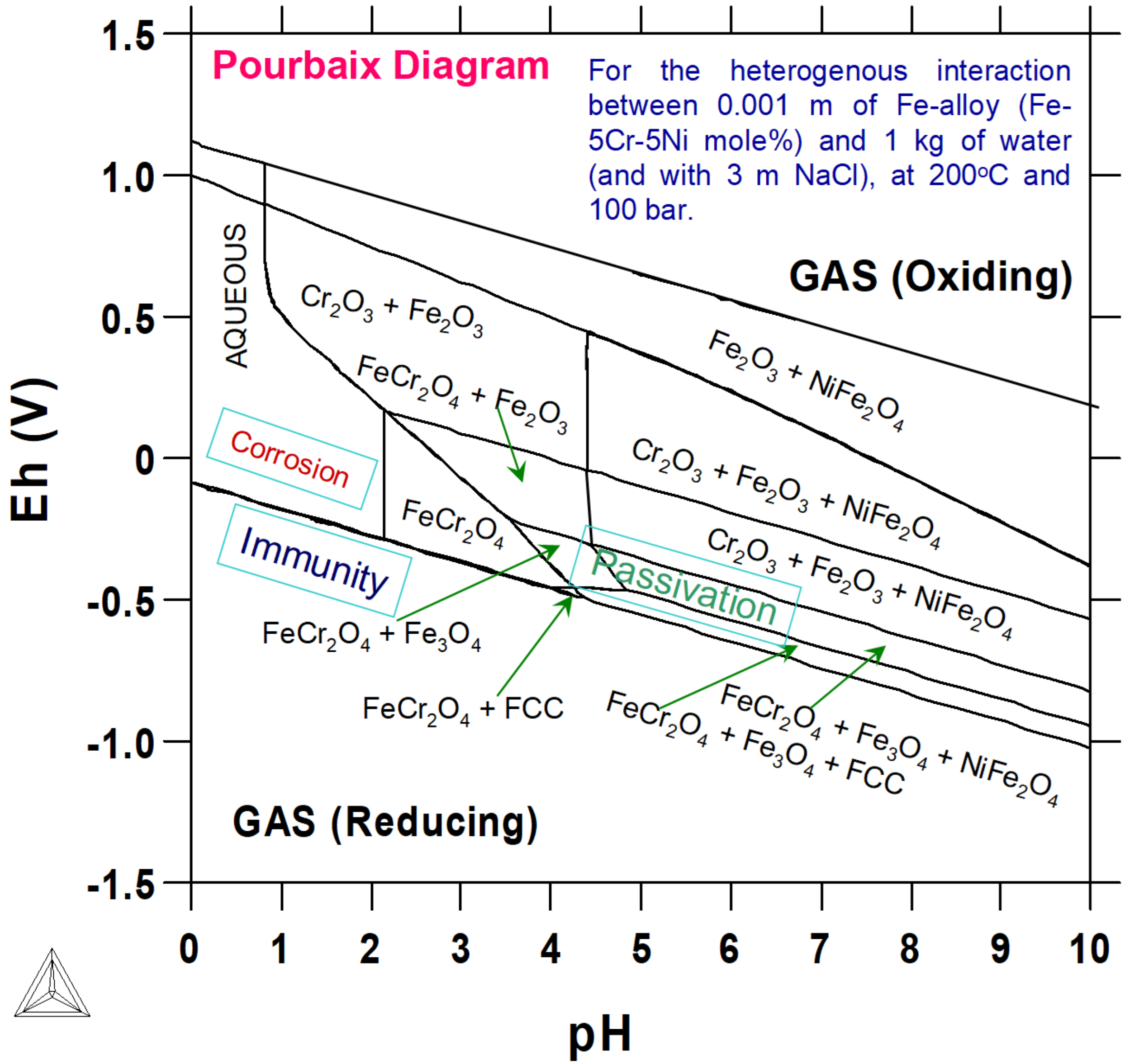



25 °C, 1 bar



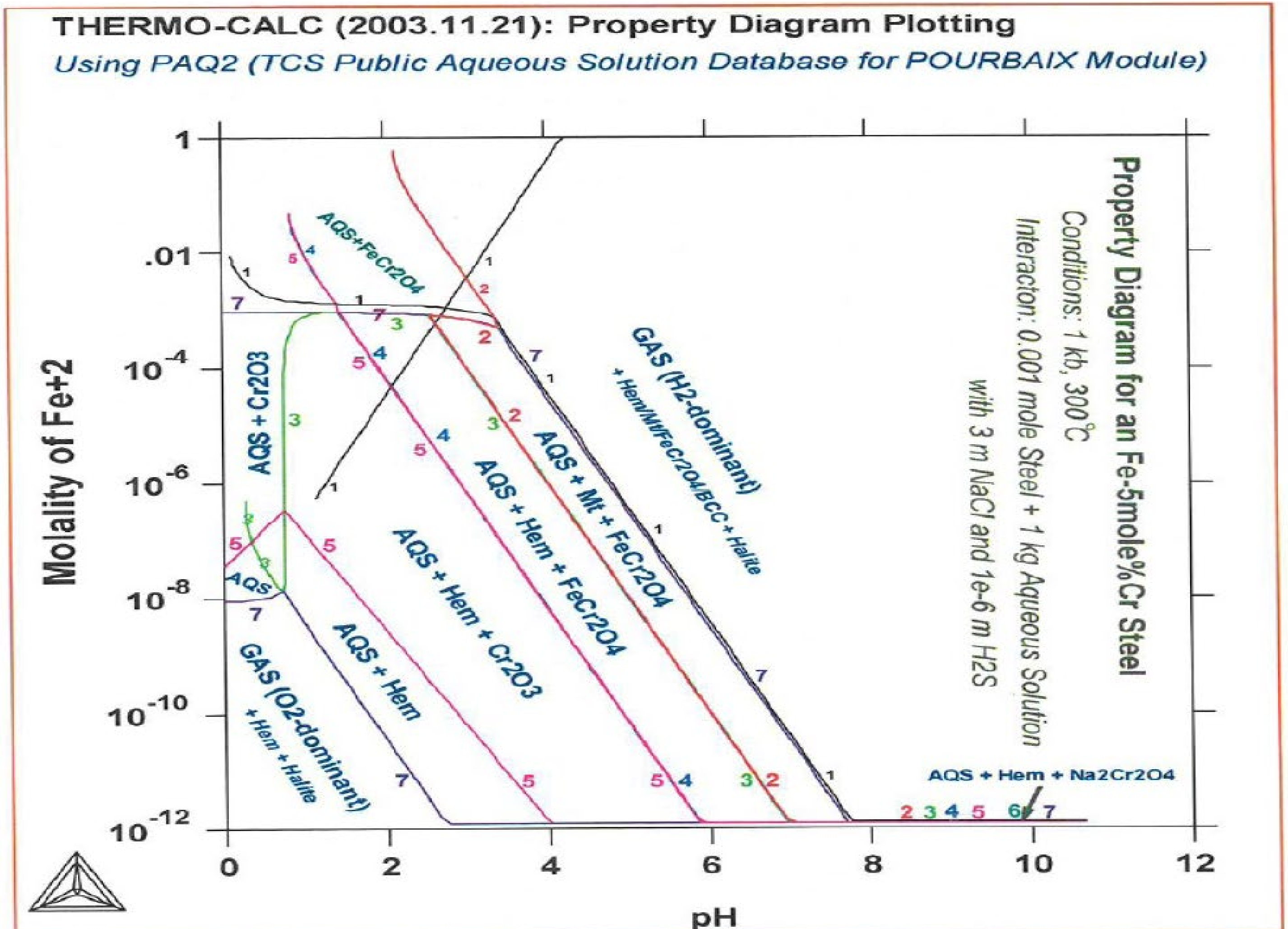

150 °C, 100 bar

# Example of More Complex System



# Example of More Complex System

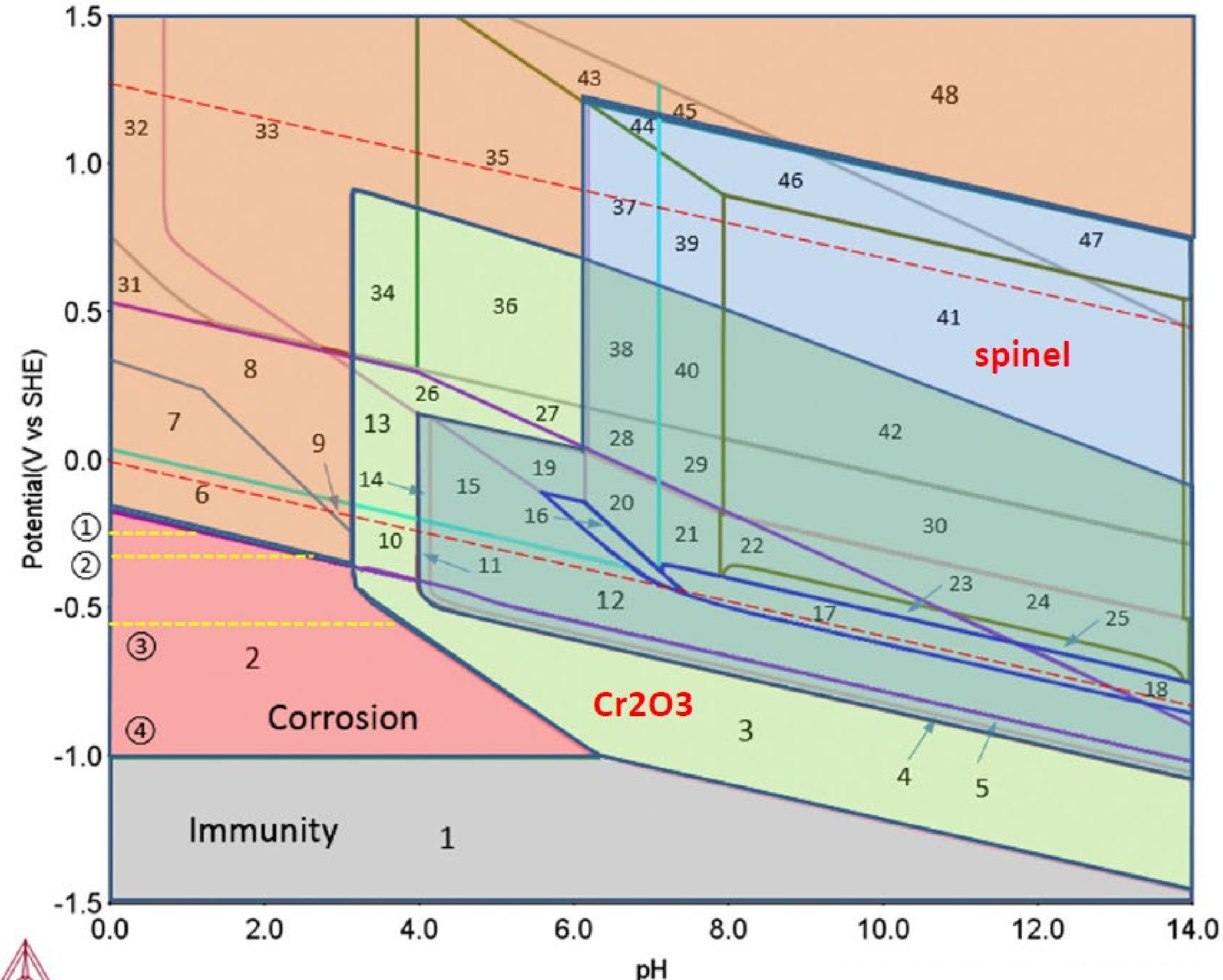
## Fe-5at% Cr steel, 1kbar, 300°C in 1 kg water with NaCl and $H_2S$




**Property Diagrams:** Many types of relevant property diagrams, using various X-/Y-axis variables, can be generated from a single POURBAIX-module calculation.

# Example of More Complex System

## $Ni_{38}Cr_{21}Fe_{20}Ru_{13}Mo_{6}W_{2}$ HEA water at 25°C and 1 atm




1. HEA alloy
2. Aqueous (predominantly $Cr^{2+}$)
3. $Cr_2O_3$
4. $FeCr_2O_4 + Cr_2O_3$
5. $FeCr_2O_4$
6. $WO_2$
7. $WO_3$
8. $MoO_2 + WO_3$
9. $MoO_2 + WO_2$
10. $MoO_2 + WO_2 + Cr_2O_3$
11. $FeCr_2O_4 + MoO_2 + WO_2 + Cr_2O_3$
12. $FeCr_2O_4 + MoO_2 + WO_2$
13. $MoO_2 + WO_3 + Cr_2O_3$
14. $FeCr_2O_4 + MoO_2 + WO_3 + Cr_2O_3$
15. $FeCr_2O_4 + MoO_2 + WO_3$
16. $FeCr_2O_4 + Fe_3O_4 + MoO_2 + WO_3$
17. $FeCr_2O_4 + Fe_3O_4 + MoO_2$
18. $FeCr_2O_4 + Fe_3O_4$
19. $FeCr_2O_4 + MoO_2 + WO_3 + Fe_2O_3$
20. $FeCr_2O_4 + NiFe_2O_4 + MoO_2 + WO_3$
21. $FeCr_2O_4 + NiFe_2O_4 + MoO_2$
22. $FeCr_2O_4 + NiFe_2O_4 + MoO_2 + NiO$
23. $FeCr_2O_4 + NiFe_2O_4 + MoO_2$
24. $FeCr_2O_4 + NiFe_2O_4 + NiO$
25. $FeCr_2O_4 + NiFe_2O_4$
26. $MoO_2 + WO_3 + Cr_2O_3 + Fe_2O_3$
27. $WO_3 + Cr_2O_3 + Fe_2O_3$
28. $WO_3 + Cr_2O_3 + NiFe_2O_4$
29. $Cr_2O_3 + NiFe_2O_4$
30. $Cr_2O_3 + NiFe_2O_4 + NiO$
31. $MoO_3 + WO_3$
32. $MoO_3 + WO_3 + RuO_2$
33. $MoO_3 + WO_3 + RuO_2 + Fe_2O_3$
34. $Cr_2O_3 + MoO_3 + WO_3 + RuO_2 + Fe_2O$
35. $WO_3 + RuO_2 + Fe_2O_3$
36. $Cr_2O_3 + WO_3 + RuO_2 + Fe_2O_3$
37. $WO_3 + RuO_2 + NiFe_2O_4$
38. $Cr_2O_3 + WO_3 + RuO_2 + NiFe_2O_4$
39. $RuO_2 + NiFe_2O_4$
40. $Cr_2O_3 + RuO_2 + NiFe_2O_4$
41. $NiO + RuO_2 + NiFe_2O_4$
42. $Cr_2O_3 + NiO + RuO_2 + NiFe_2O_4$
43. $WO_3 + RuO_2 + Fe_2O_3 + NiOOH$
44. $WO_3 + RuO_2 + NiFe_2O_4 + NiOOH$
45. $RuO_2 + Fe_2O_3 + NiOOH$
46. $RuO_2 + NiFe_2O_4 + NiOOH$
47. $NiFe_2O_4 + NiOOH$
48. $Fe_2O_3 + NiOOH$

① $Mo/Mo^{3+}$
② $Ni/Ni^{2+}$
③ $Fe/Fe^{2+}$


Lu et al., Scripta Materialia **152** (2018) 19-22

# Limitations of Experimental Pourbaix Diagrams

- Pourbaix diagrams are **fully-equilibrium** phase diagrams. No information on corrosion kinetics is provided by such thermodynamically-derived diagrams
- Pourbaix diagrams are derived for some **selected T and P** conditions (normally 1 atm and 25°C.
- Pourbaix diagrams are derived for **selected concentrations** of ionic species (*e.g.* $10^{-6}$ M of metal in 1kg of water).
- Most Pourbaix diagrams consider **pure substances** only (*e.g.* pure iron in pure water only). Additional computations must be made separately if other species are involved.

# Advantages of CALPHAD-based Calculations

Thermo-Calc Software

**Complex Phases:**

- ✓ Alloy compound / solid solution phases
- ✓ Oxide / Sulfide / Silicate / … solution phases
- ✓ Aqueous solution phases
- ✓ Gaseous mixture phases.

**Complex Environments:**

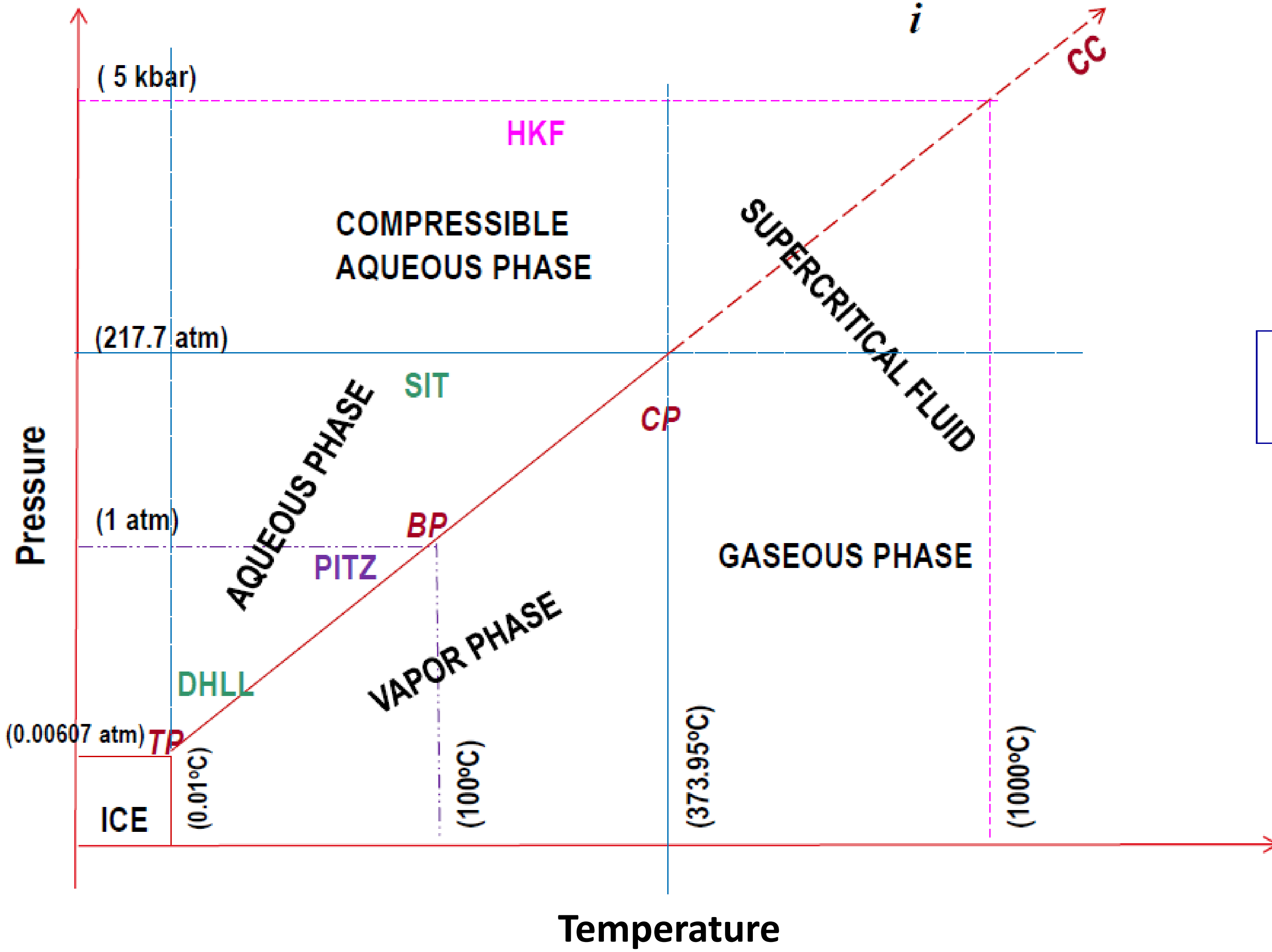
- ✓ Very wide P-T ranges
- ✓ Concentrated aqueous solutions

**Multiple Functionality:**

- ✓ Many types of phase diagrams & property diagrams

# Modelling G of Aqueous Solutions

$$G_m = G_{water(P,T,X)} + \sum_i G_{solute(P,T,X)}$$




PVT-EOS
of H2O

# Aqueous Models & Databases in Thermo-Calc

Thermo-Calc Software

**Thermodynamic models**

- ✓ **DHLL** - Debye-Hückel Limiting Law Term
- ✓ **SIT** - Specific Interaction Theory Model
- ✓ **HKF** - Complete Revised HKF Model (Helgeson-Kirkham-Flowers)
- ✓ **PITZ** - Generalized Pitzer's Formalism

**Thermodynamic databases**

- ✓ **AQS2** - HKF model, valid to 1000°C, 5kbar and 6 molality
  - includes 82 elements.
- ✓ **TCAQ3** - developed in TCSAB, SIT model, valid to 350°C, 100bar & 3 mol
  - includes 75 elements.
- ✓ **PAQ2** - TCSAB demo database, subsets of TCAQ2 + SSUB4 + SSOL4.
  - includes 11 elements (Fe-Co-Cr-Na-Ni-C-H-O-N-S-Cl)

# Applications in Material Science and Engineering and Others…

- ✓ Hydro-Metallurgical Processes
- ✓ Hydrothermal Formation and Separation Processes
- ✓ High- / Low Temperature Corrosion Processes
- ✓ Recycling Processes
- ✓ Aqueous Chemistry
- ✓ Chemical Engineering
- ✓ Food, Medicine & Energy Production
- ✓ Geochemical Systems (Natural Resources)
- ✓ Environmental Protections of Water Resources
- ✓ Environmental Impact of Nuclear Fuel Waste
- ✓ Environmental Assessment of Industrial Pollution

--- *and many more*