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CEE 680: Water Chemistry

Lecture #49

Redox Chemistry: Predominance Diagrams; spanning the range of pe

(Stumm & Morgan, Chapt.8)

Benjamin; Chapter 9

Chlorine Predominance Diagram

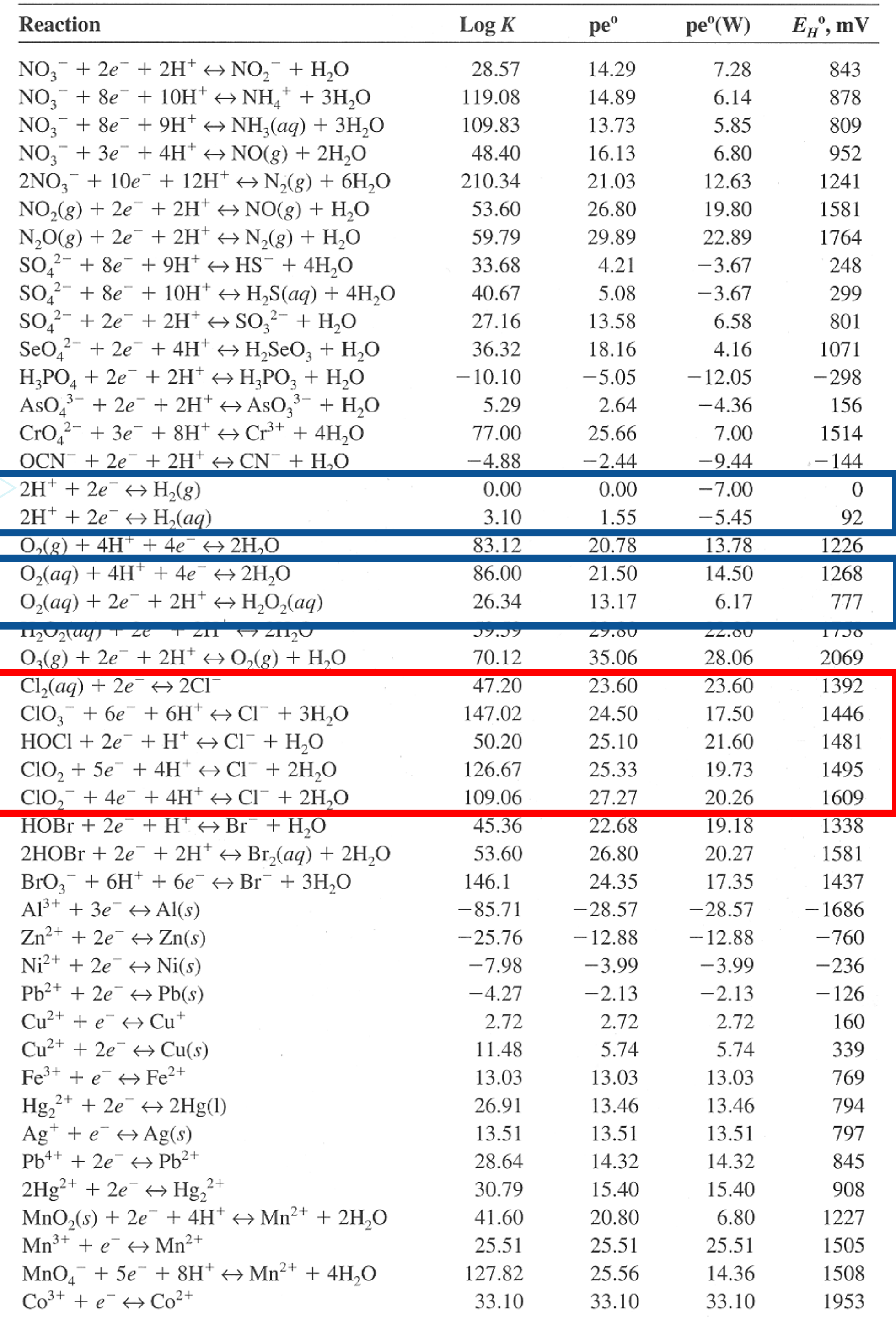
- Features
  - Oxidation state
    - Higher oxidation states (HOCl/OCl-) in upper region
    - Middle oxidation state (Cl_2) in middle at low pH range
    - Chloride in lower region
  - pH divisions
    - Vertical lines at pK_a values

Constants

- Conversions

$$pe^o\left[\equiv p\varepsilon^o\right]=\frac{1}{n}\log K=\frac{1}{0.059}E_H^o\,(volts)$$

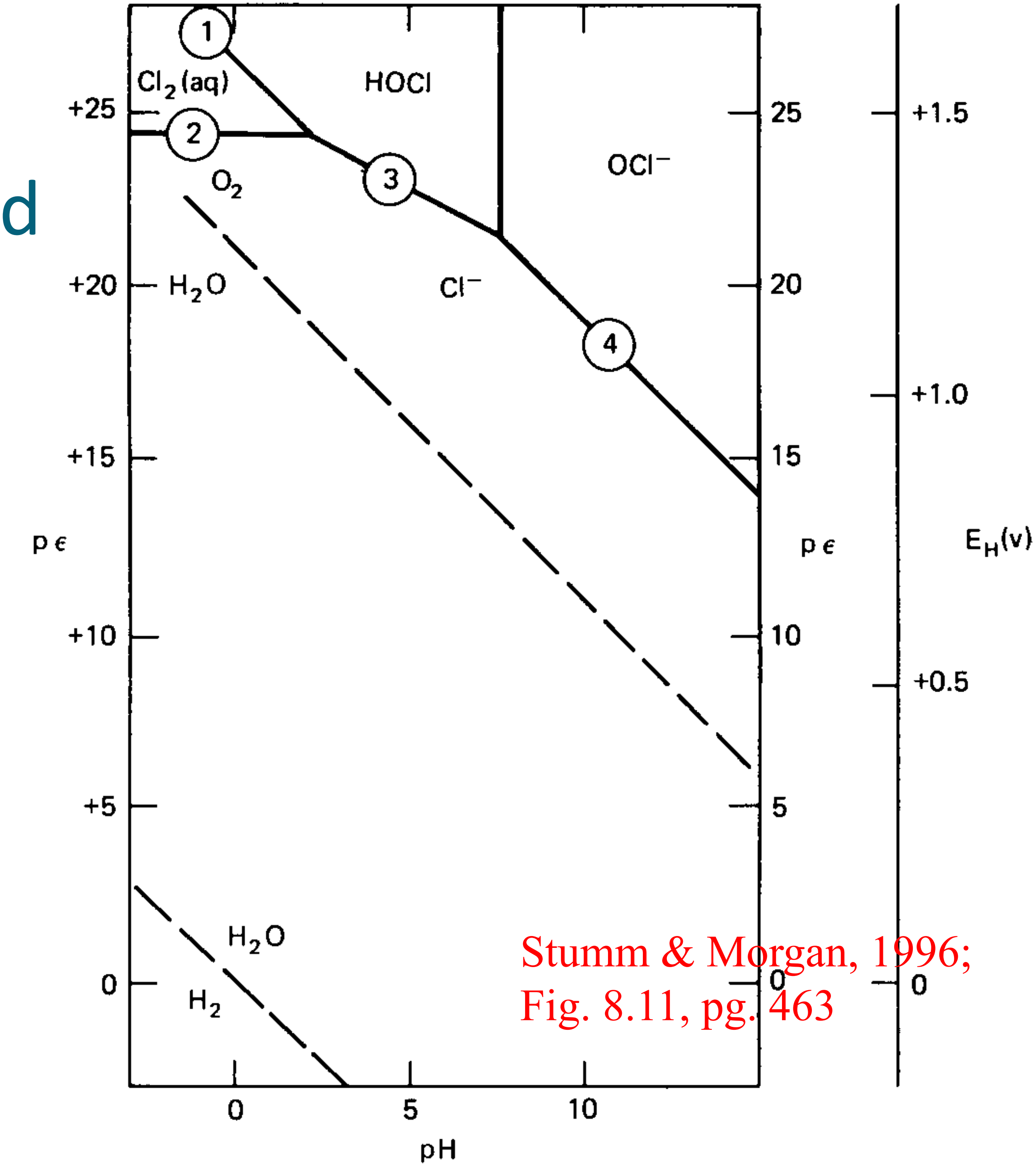
$$0.059=\frac{RT\ln(10)}{F}$$



Reaction	Log K	pe°	pe°(W)	E_H°, mV
$NO_3^- + 2e^- + 2H^+ \leftrightarrow NO_2^- + H_2O$	28.57	14.29	7.28	843
$NO_3^- + 8e^- + 10H^+ \leftrightarrow NH_4^+ + 3H_2O$	119.08	14.89	6.14	878
$NO_3^- + 8e^- + 9H^+ \leftrightarrow NH_3(aq) + 3H_2O$	109.83	13.73	5.85	809
$NO_3^- + 3e^- + 4H^+ \leftrightarrow NO(g) + 2H_2O$	48.40	16.13	6.80	952
$2NO_3^- + 10e^- + 12H^+ \leftrightarrow N_2(g) + 6H_2O$	210.34	21.03	12.63	1241
$NO_2(g) + 2e^- + 2H^+ \leftrightarrow NO(g) + H_2O$	53.60	26.80	19.80	1581
$N_2O(g) + 2e^- + 2H^+ \leftrightarrow N_2(g) + H_2O$	59.79	29.89	22.89	1764
$SO_4^{2-} + 8e^- + 9H^+ \leftrightarrow HS^- + 4H_2O$	33.68	4.21	−3.67	248
$SO_4^{2-} + 8e^- + 10H^+ \leftrightarrow H_2S(aq) + 4H_2O$	40.67	5.08	−3.67	299
$SO_4^{2-} + 2e^- + 2H^+ \leftrightarrow SO_3^{2-} + H_2O$	27.16	13.58	6.58	801
$SeO_4^{2-} + 2e^- + 4H^+ \leftrightarrow H_2SeO_3 + H_2O$	36.32	18.16	4.16	1071
$H_3PO_4 + 2e^- + 2H^+ \leftrightarrow H_3PO_3 + H_2O$	−10.10	−5.05	−12.05	−298
$AsO_4^{3-} + 2e^- + 2H^+ \leftrightarrow AsO_3^{3-} + H_2O$	5.29	2.64	−4.36	156
$CrO_4^{2-} + 3e^- + 8H^+ \leftrightarrow Cr^{3+} + 4H_2O$	77.00	25.66	7.00	1514
$OCN^- + 2e^- + 2H^+ \leftrightarrow CN^- + H_2O$	−4.88	−2.44	−9.44	−144
$2H^+ + 2e^- \leftrightarrow H_2(g)$	0.00	0.00	−7.00	0
$2H^+ + 2e^- \leftrightarrow H_2(aq)$	3.10	1.55	−5.45	92
$O_2(g) + 4H^+ + 4e^- \leftrightarrow 2H_2O$	83.12	20.78	13.78	1226
$O_2(aq) + 4H^+ + 4e^- \leftrightarrow 2H_2O$	86.00	21.50	14.50	1268
$O_2(aq) + 2e^- + 2H^+ \leftrightarrow H_2O_2(aq)$	26.34	13.17	6.17	777
$H_2O_2(aq) + 2e^- + 2H^+ \leftrightarrow 2H_2O$	59.59	29.80	22.80	1763
$O_3(g) + 2e^- + 2H^+ \leftrightarrow O_2(g) + H_2O$	70.12	35.06	28.06	2069
$Cl_2(aq) + 2e^- \leftrightarrow 2Cl^-$	47.20	23.60	23.60	1392
$ClO_3^- + 6e^- + 6H^+ \leftrightarrow Cl^- + 3H_2O$	147.02	24.50	17.50	1446
$HOCl + 2e^- + H^+ \leftrightarrow Cl^- + H_2O$	50.20	25.10	21.60	1481
$ClO_2 + 5e^- + 4H^+ \leftrightarrow Cl^- + 2H_2O$	126.67	25.33	19.73	1495
$ClO_2^- + 4e^- + 4H^+ \leftrightarrow Cl^- + 2H_2O$	109.06	27.27	20.26	1609
$HOBr + 2e^- + H^+ \leftrightarrow Br^- + H_2O$	45.36	22.68	19.18	1338
$2HOBr + 2e^- + 2H^+ \leftrightarrow Br_2(aq) + 2H_2O$	53.60	26.80	20.27	1581
$BrO_3^- + 6H^+ + 6e^- \leftrightarrow Br^- + 3H_2O$	146.1	24.35	17.35	1437
$Al^{3+} + 3e^- \leftrightarrow Al(s)$	−85.71	−28.57	−28.57	−1686
$Zn^{2+} + 2e^- \leftrightarrow Zn(s)$	−25.76	−12.88	−12.88	−760
$Ni^{2+} + 2e^- \leftrightarrow Ni(s)$	−7.98	−3.99	−3.99	−236
$Pb^{2+} + 2e^- \leftrightarrow Pb(s)$	−4.27	−2.13	−2.13	−126
$Cu^{2+} + e^- \leftrightarrow Cu^+$	2.72	2.72	2.72	160
$Cu^{2+} + 2e^- \leftrightarrow Cu(s)$	11.48	5.74	5.74	339
$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	13.03	13.03	13.03	769
$Hg_2^{2+} + 2e^- \leftrightarrow 2Hg(l)$	26.91	13.46	13.46	794
$Ag^+ + e^- \leftrightarrow Ag(s)$	13.51	13.51	13.51	797
$Pb^{4+} + 2e^- \leftrightarrow Pb^{2+}$	28.64	14.32	14.32	845
$2Hg^{2+} + 2e^- \leftrightarrow Hg_2^{2+}$	30.79	15.40	15.40	908
$MnO_2(s) + 2e^- + 4H^+ \leftrightarrow Mn^{2+} + 2H_2O$	41.60	20.80	6.80	1227
$Mn^{3+} + e^- \leftrightarrow Mn^{2+}$	25.51	25.51	25.51	1505
$MnO_4^- + 5e^- + 8H^+ \leftrightarrow Mn^{2+} + 4H_2O$	127.82	25.56	14.36	1508
$Co^{3+} + e^- \leftrightarrow Co^{2+}$	33.10	33.10	33.10	1953

A highly oxidized system

- Chlorine species
  - +I, o and -I oxidation states



Stumm & Morgan, 1996; Fig. 8.11, pg. 463

Chlorine Predominance Diagram

- Features
  - Oxidation state
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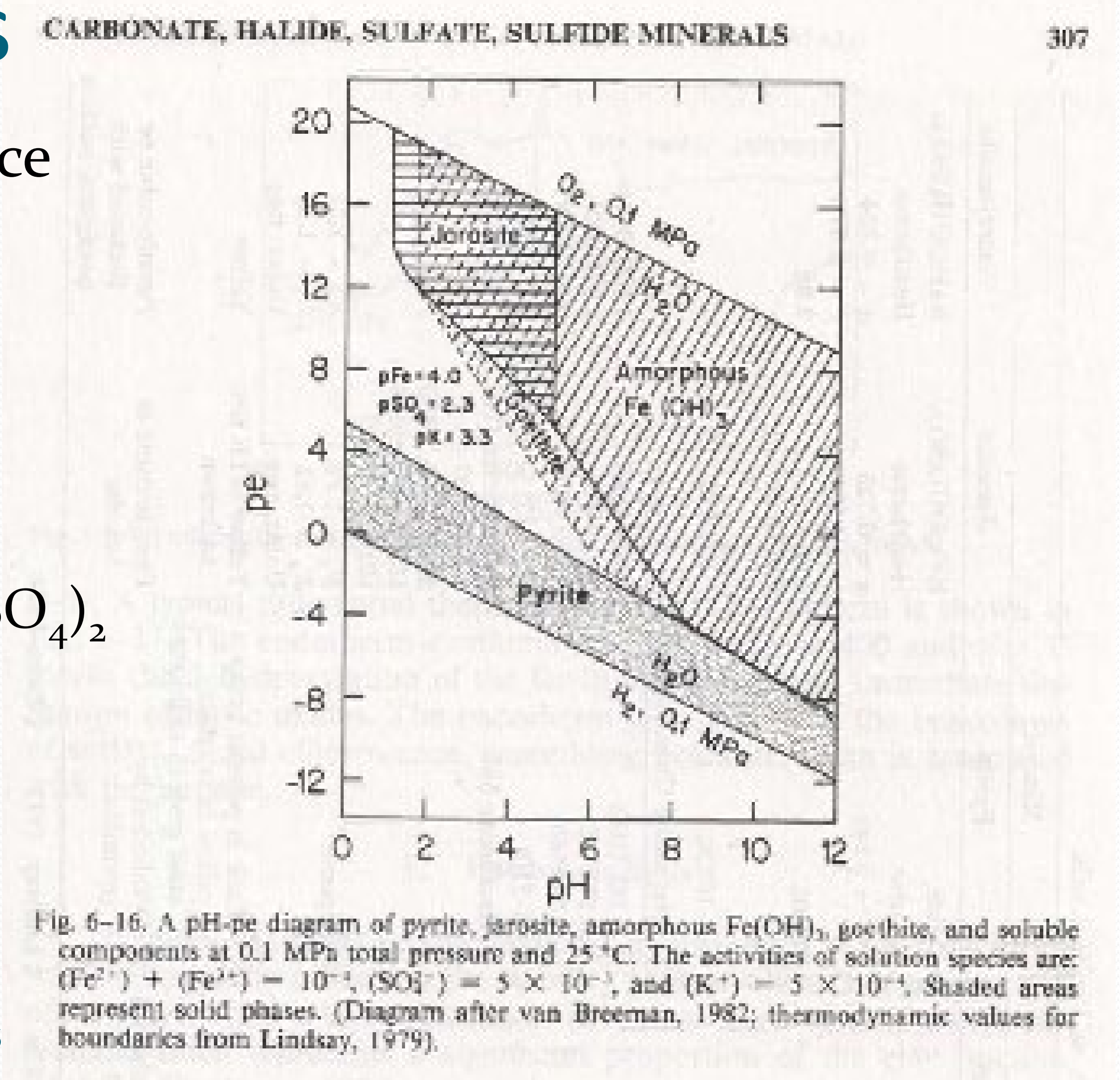
Iron phases

- From Soil Science Literature
  - Pyrite is FeS_2
  - Goethite is $FeO(OH)$
  - Jarosite is $KFe^{3+}_3(OH)_6(SO_4)_2$



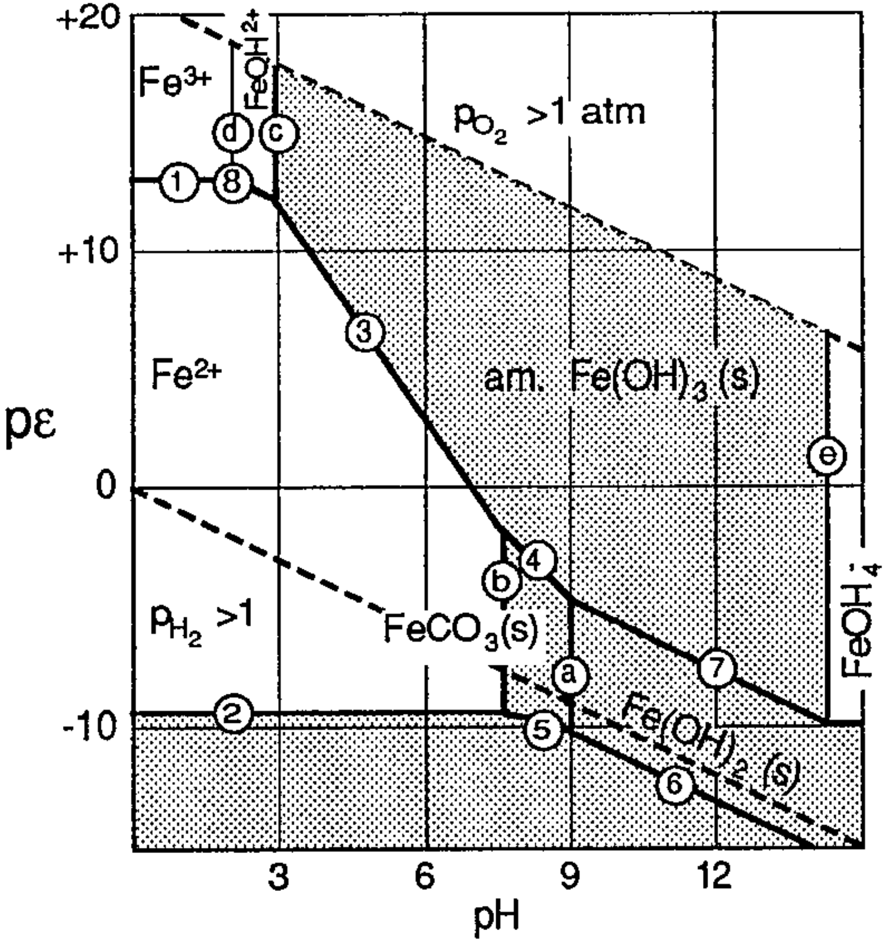
CARBONATE, HALIDE, SULFATE, SULFIDE MINERALS 307

Fig. 6–16. A pH-pe diagram of pyrite, jarosite, amorphous $Fe(OH)_3$, goethite, and soluble components at 0.1 MPa total pressure and 25 °C. The activities of solution species are: $(Fe^{2+}) + (Fe^{3+}) = 10^{-4}$, $(SO_4^{2-}) = 5 \times 10^{-3}$, and $(K^+) = 5 \times 10^{-4}$. Shaded areas represent solid phases. (Diagram after van Breeman, 1982; thermodynamic values for boundaries from Lindsay, 1979).

Iron redox system

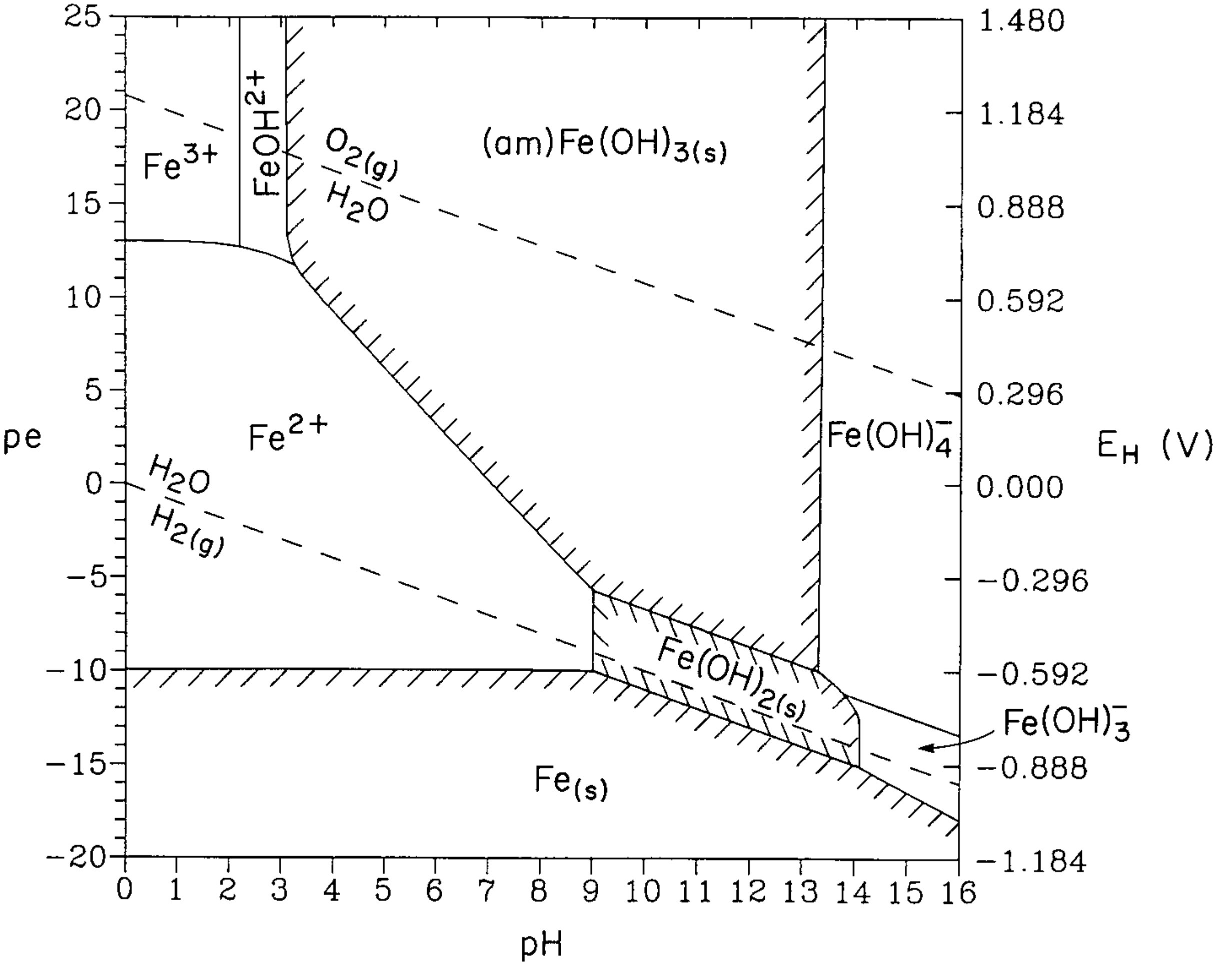
- Ferrous – Ferric
  - hydroxides

Stumm & Morgan, 1996; Fig. 8.8, pg. 461



Iron (cont.)

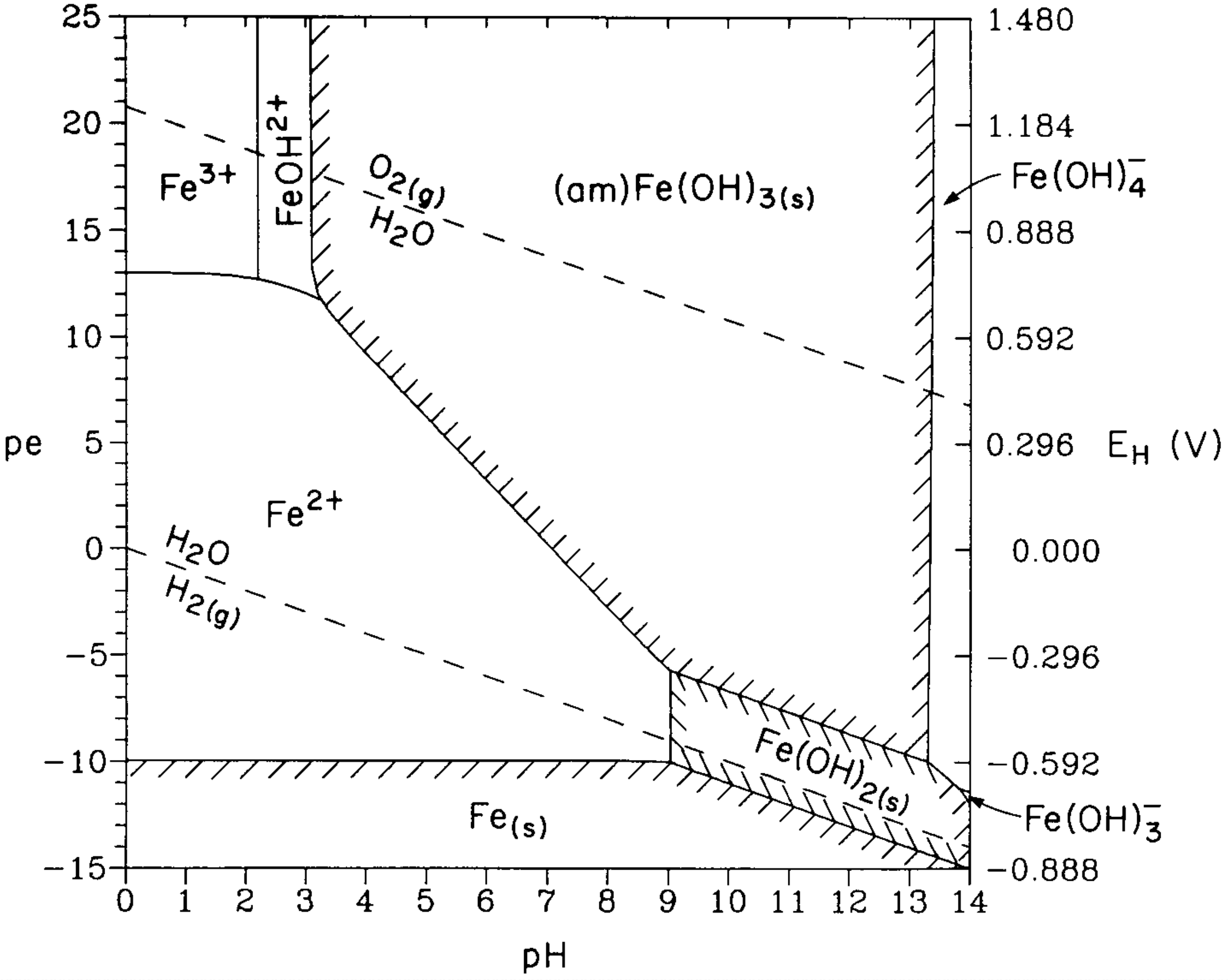
- $Fe_T = 10^{-5}$ M
- No carbonates



From: Aquatic Chemistry Concepts, by Pankow, 1991 (pg 535)

Iron (cont.)

- Same as previous, but pH axis limited to 14



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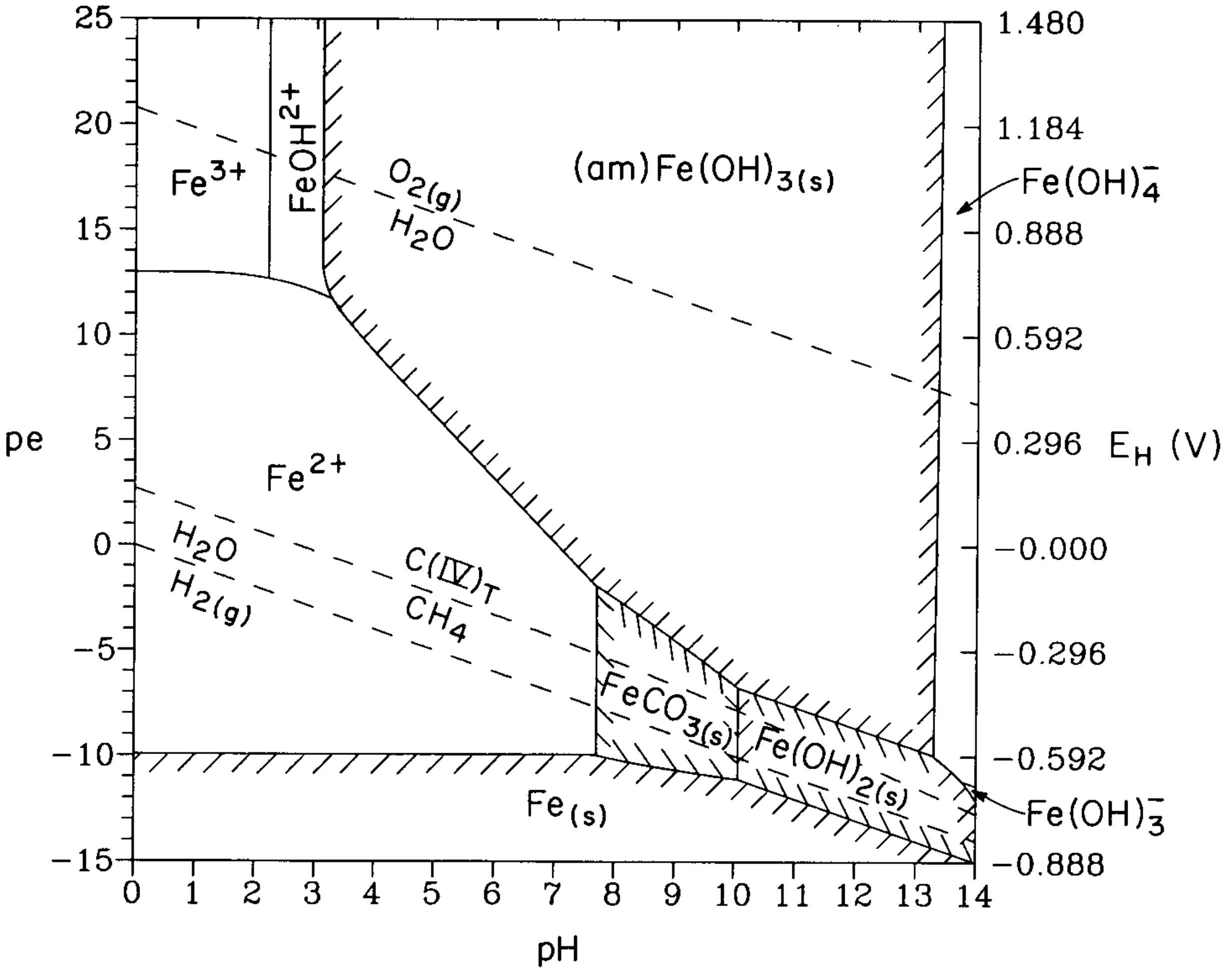
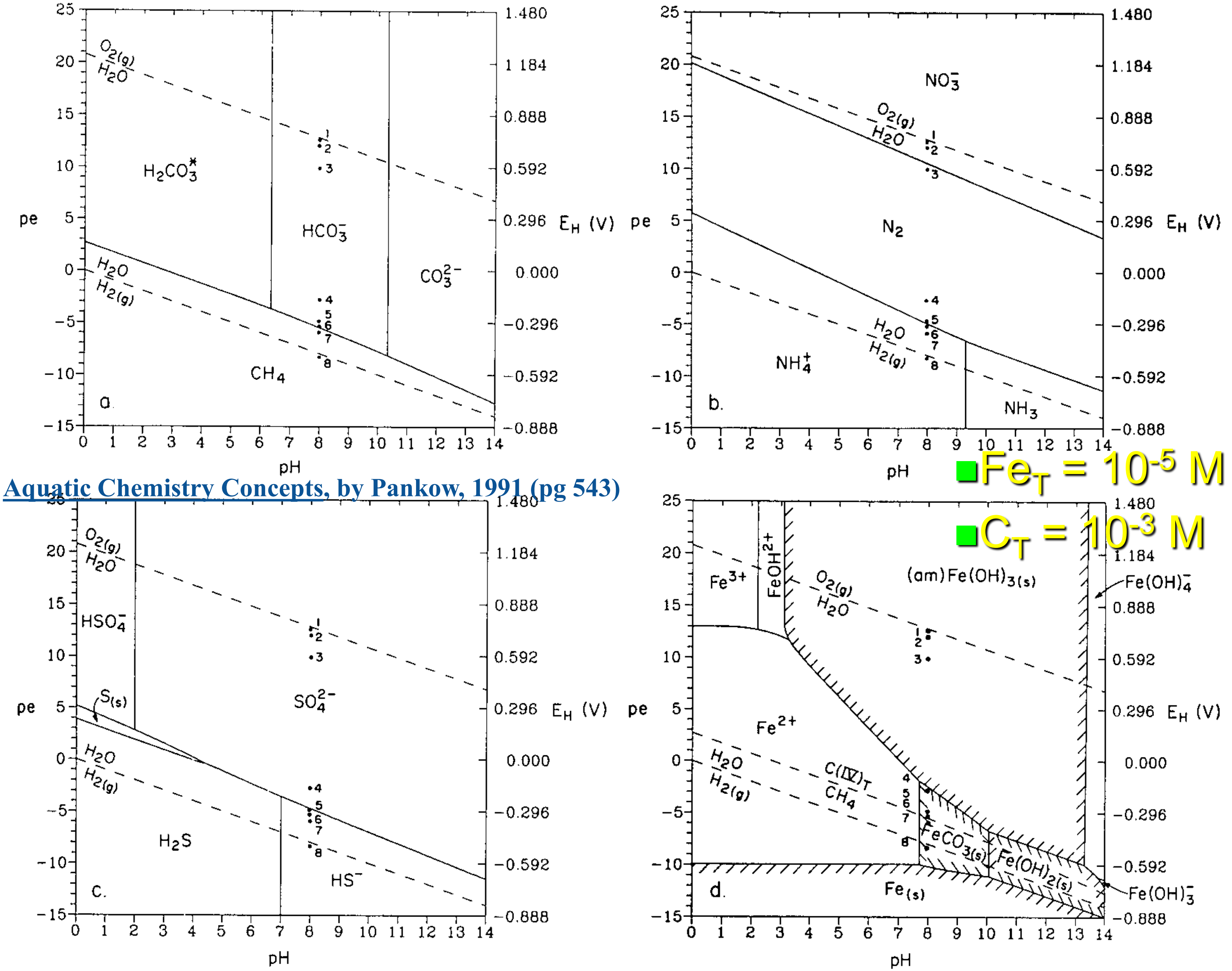
Iron (cont.)

- $Fe_T = 10^{-5}$ M
- 10^{-3} M carbonate



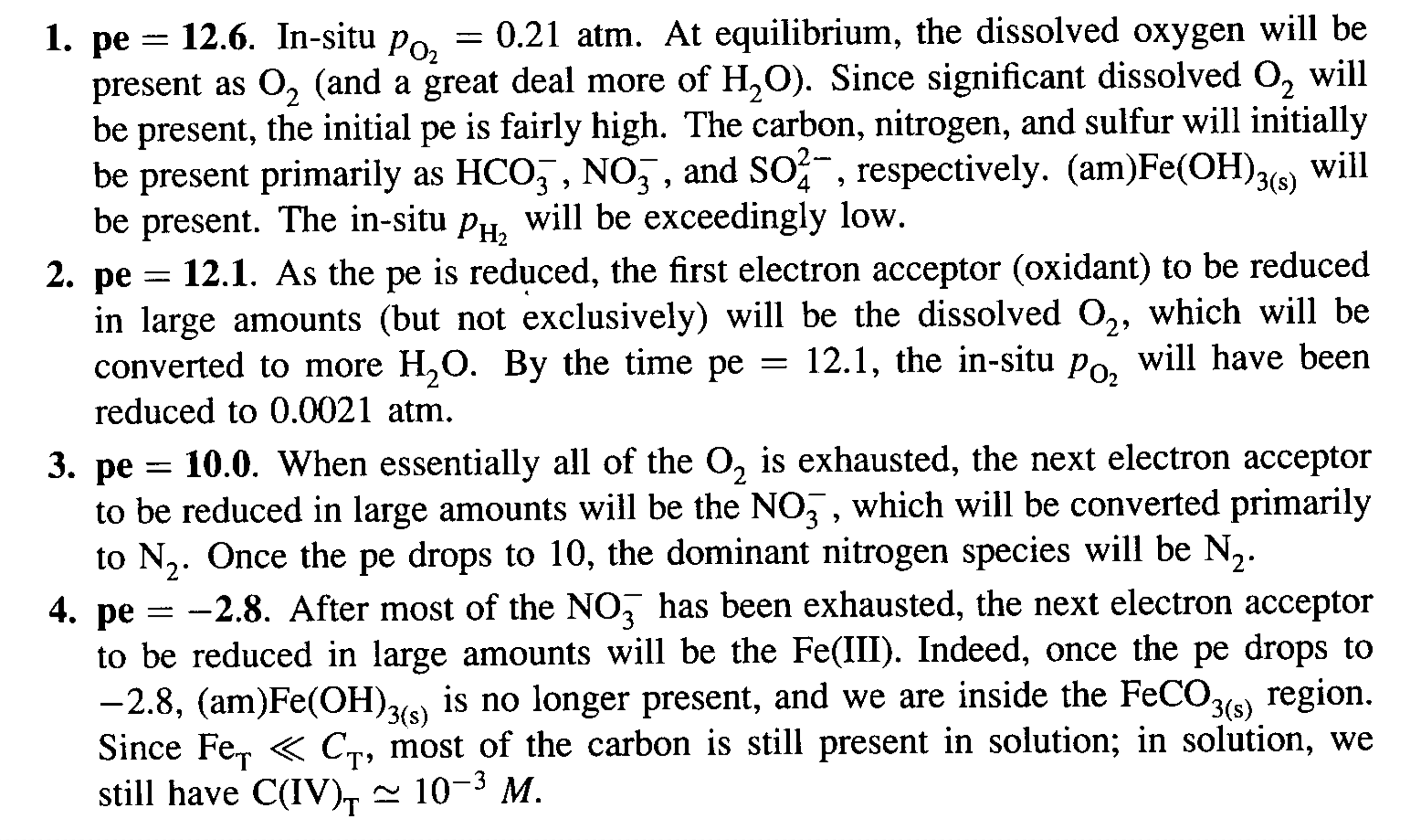
From: <u>Aquatic Chemistry Concepts</u>, by Pankow, 1991



From: Aquatic Chemistry Concepts, by Pankow, 1991 (pg 543)

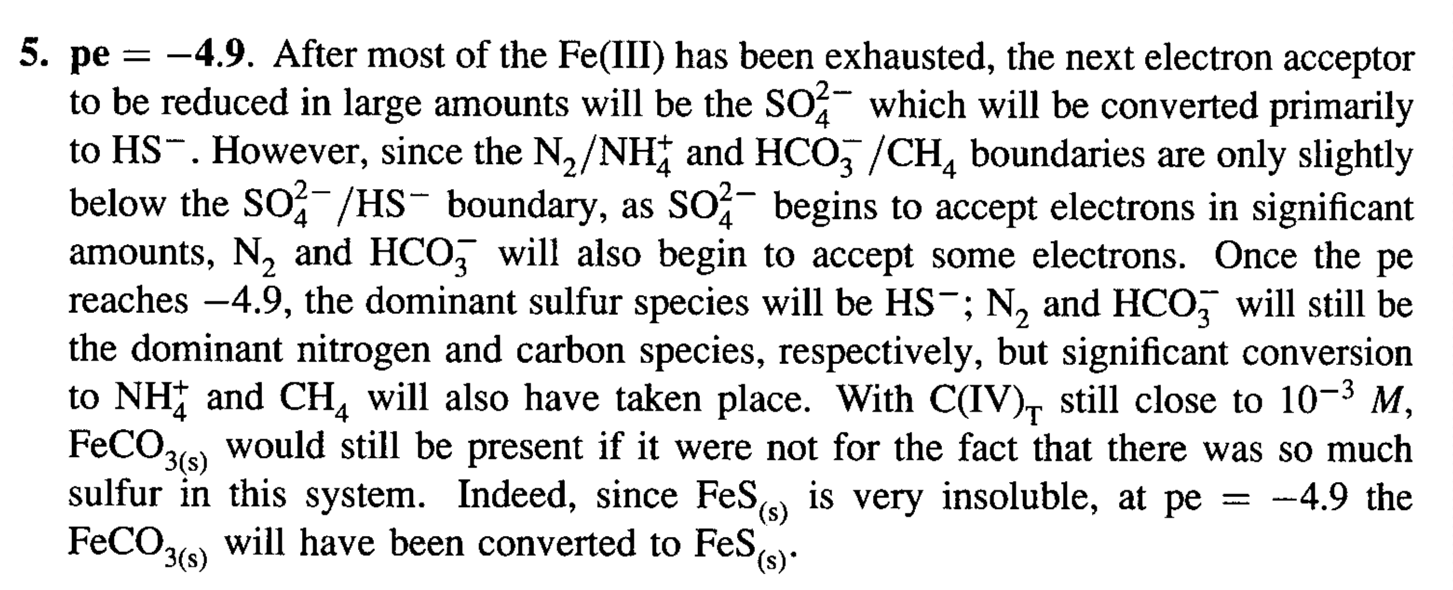
- $Fe_T = 10^{-5}$ M
- $C_T = 10^{-3}$ M

Fully oxygenated to anaerobic

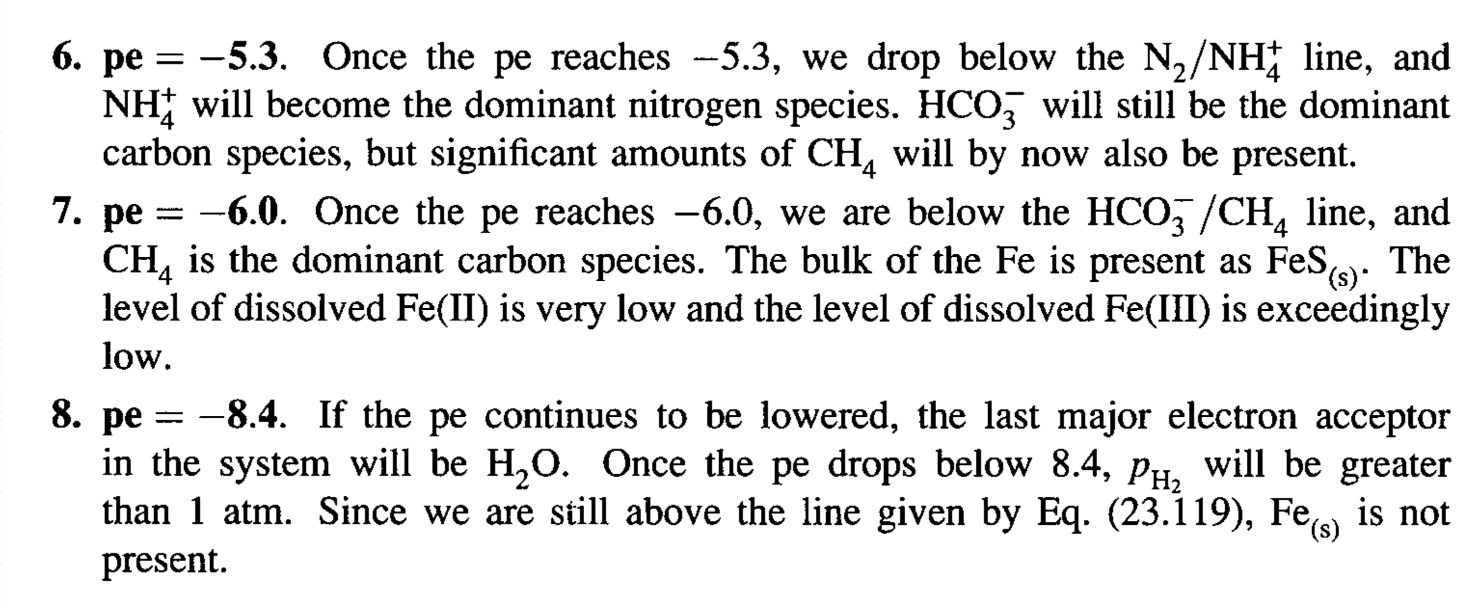


1. **pe = 12.6**. In-situ $p_{O_2} = 0.21$ atm. At equilibrium, the dissolved oxygen will be present as O_2 (and a great deal more of H_2O). Since significant dissolved O_2 will be present, the initial pe is fairly high. The carbon, nitrogen, and sulfur will initially be present primarily as HCO_3^-, NO_3^-, and SO_4^{2-}, respectively. (am)$Fe(OH)_{3(s)}$ will be present. The in-situ p_{H_2} will be exceedingly low.
2. **pe = 12.1**. As the pe is reduced, the first electron acceptor (oxidant) to be reduced in large amounts (but not exclusively) will be the dissolved O_2, which will be converted to more H_2O. By the time pe = 12.1, the in-situ p_{O_2} will have been reduced to 0.0021 atm.
3. **pe = 10.0**. When essentially all of the O_2 is exhausted, the next electron acceptor to be reduced in large amounts will be the NO_3^-, which will be converted primarily to N_2. Once the pe drops to 10, the dominant nitrogen species will be N_2.
4. **pe = −2.8**. After most of the NO_3^- has been exhausted, the next electron acceptor to be reduced in large amounts will be the Fe(III). Indeed, once the pe drops to −2.8, (am)$Fe(OH)_{3(s)}$ is no longer present, and we are inside the $FeCO_{3(s)}$ region. Since $Fe_T \ll C_T$, most of the carbon is still present in solution; in solution, we still have $C(IV)_T \simeq 10^{-3}\ M$.

From: Aquatic Chemistry Concepts, by Pankow, 1991

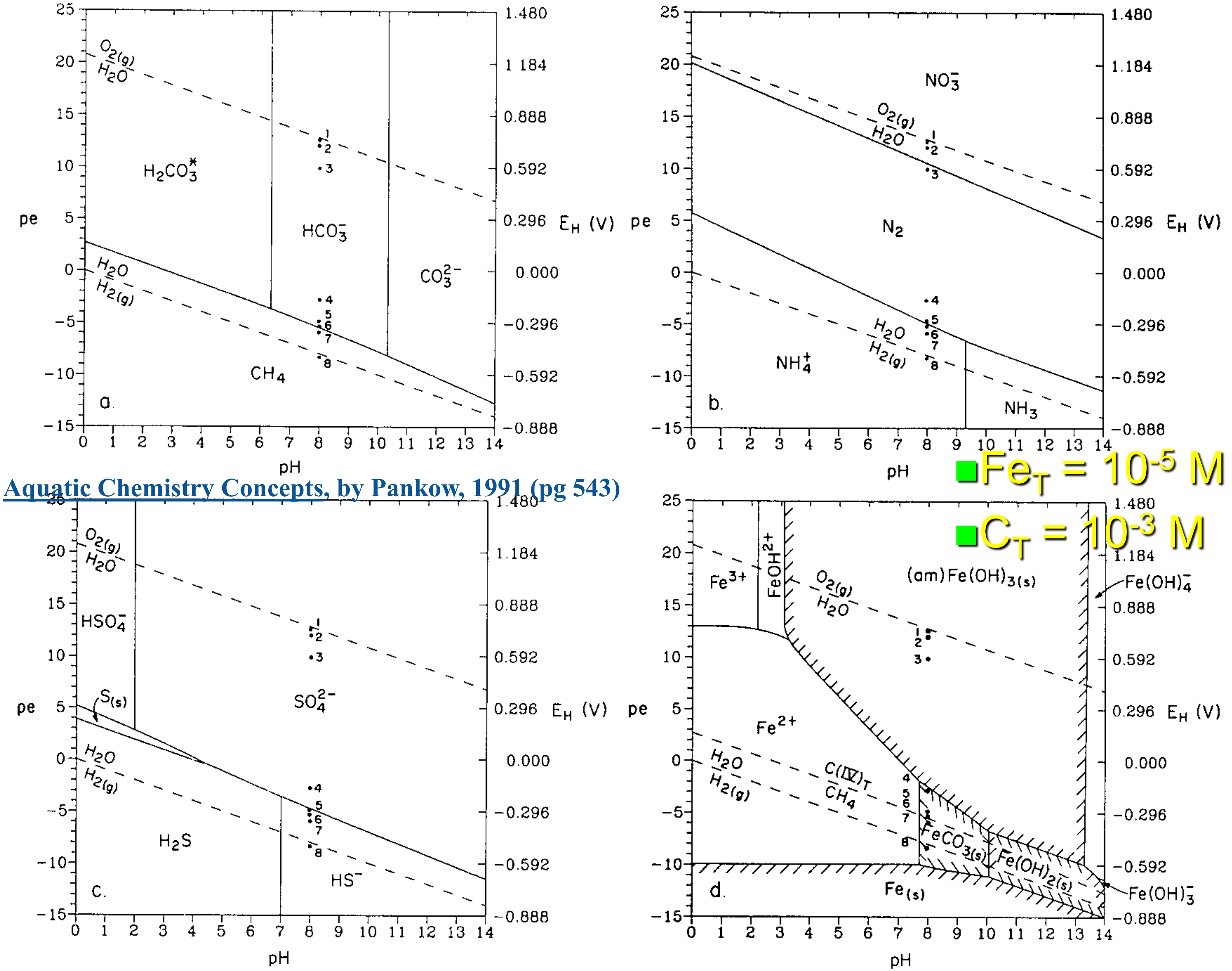


5. **pe = −4.9.** After most of the Fe(III) has been exhausted, the next electron acceptor to be reduced in large amounts will be the SO_4^{2-} which will be converted primarily to HS^-. However, since the N_2/NH_4^+ and HCO_3^-/CH_4 boundaries are only slightly below the SO_4^{2-}/HS^- boundary, as SO_4^{2-} begins to accept electrons in significant amounts, N_2 and HCO_3^- will also begin to accept some electrons. Once the pe reaches −4.9, the dominant sulfur species will be HS^-; N_2 and HCO_3^- will still be the dominant nitrogen and carbon species, respectively, but significant conversion to NH_4^+ and CH_4 will also have taken place. With $C(IV)_T$ still close to 10^{-3} *M*, $FeCO_{3(s)}$ would still be present if it were not for the fact that there was so much sulfur in this system. Indeed, since $FeS_{(s)}$ is very insoluble, at pe = −4.9 the $FeCO_{3(s)}$ will have been converted to $FeS_{(s)}$.



6. **pe = −5.3.** Once the pe reaches −5.3, we drop below the N_2/NH_4^+ line, and NH_4^+ will become the dominant nitrogen species. HCO_3^- will still be the dominant carbon species, but significant amounts of CH_4 will by now also be present.
7. **pe = −6.0.** Once the pe reaches −6.0, we are below the HCO_3^-/CH_4 line, and CH_4 is the dominant carbon species. The bulk of the Fe is present as $FeS_{(s)}$. The level of dissolved Fe(II) is very low and the level of dissolved Fe(III) is exceedingly low.
8. **pe = −8.4.** If the pe continues to be lowered, the last major electron acceptor in the system will be H_2O. Once the pe drops below 8.4, p_{H_2} will be greater than 1 atm. Since we are still above the line given by Eq. (23.119), $Fe_{(s)}$ is not present.

From: Aquatic Chemistry Concepts, by Pankow, 1991



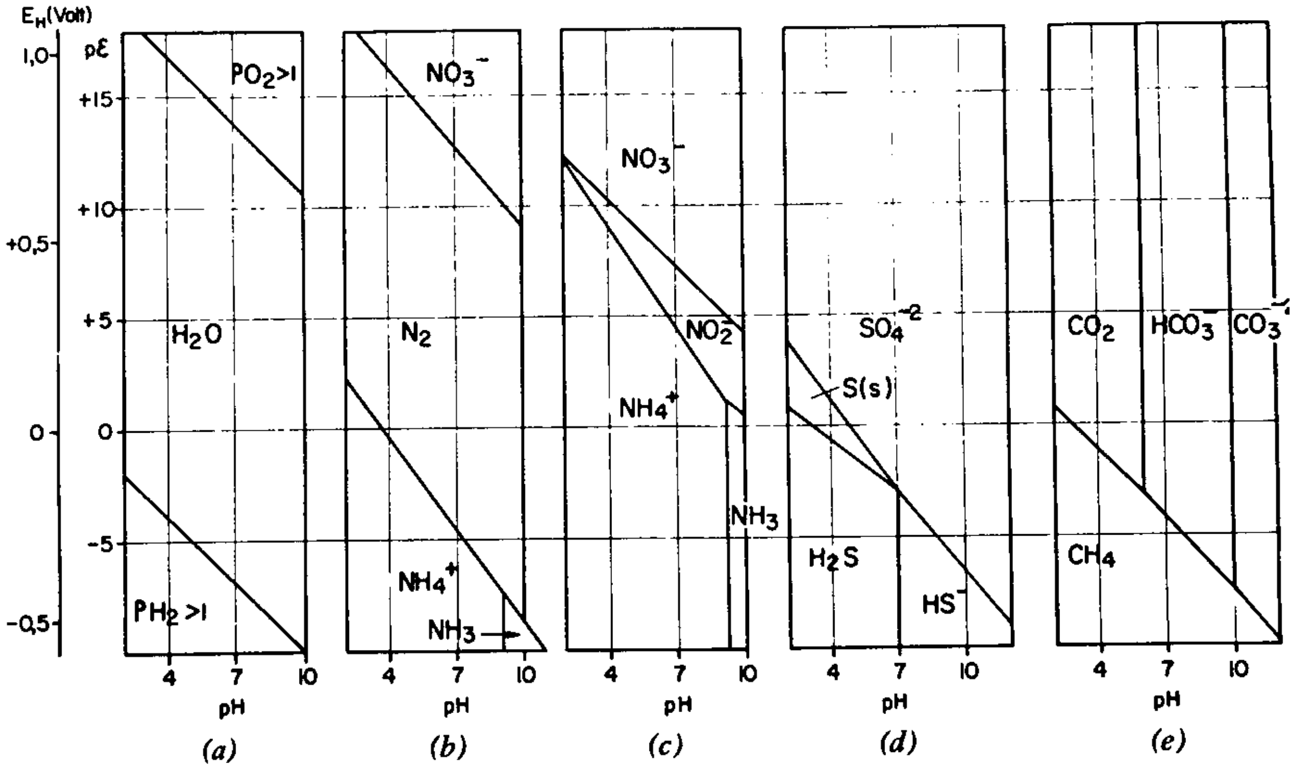
From: Aquatic Chemistry Concepts, by Pankow, 1991 (pg 543)

- $Fe_T = 10^{-5}$ M
- $C_T = 10^{-3}$ M

Other redox systems

- Phosphorus
- Nitrogen
- Sulfur
- carbon

Stumm & Morgan, 1996;
Fig. 8.9, pg. 461



- To next lecture

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