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CEE 680: Water Chemistry

Lecture #48
Redox Chemistry:
Log C vs pe Diagrams
(Stumm & Morgan, Chapt.8)
Benjamin; Chapter 9

The Iron Mystery

- If:
  - The Fe^{+2}/Fe^{+3} boundary is at a pe^{o} and pe(w) of 13.03
  - Oxygen saturated water should have a pe(w) of 13.6, but Pankow says the effective pe(w) of surface water is more like 12.6
- Will reduced iron spontaneously oxidize to ferric in surface waters?
  1. Yes
  2. No

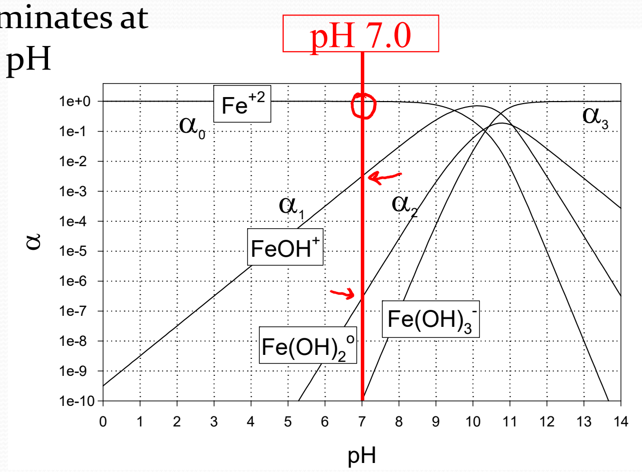
Then why is it so hard to keep reduced iron (ferrous) from oxidizing to the ferric form?

Redox and pH effects

- Often oxidation of metals results in a more hydrolyzed species
  - Acidity of oxidized species is higher, resulting in release of protons
  - Speciation changes and affects the overall reaction
- A good example is the oxidation of ferrous iron to ferric
  - $Fe^{+3} + e^{-} \leftrightarrow Fe^{+2}$
  - $pe^{o} = 13.03$
  - This is very close to the theoretical pe^{o} defined by saturated O_2 in water (13.6), or the effective pe^{o} (e.g., 12.6)
  - But this is deceptive, because Fe^{+3} isn't the dominant species at neutral pH

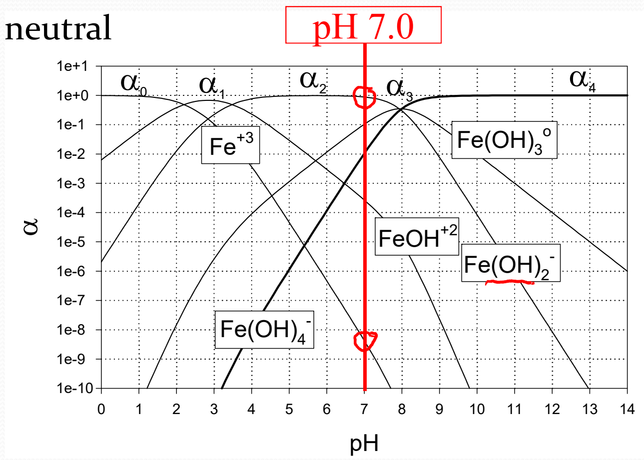
Ferrous Hydroxides: α diagram

- Fe^{+2} dominates at neutral pH



Ferric Hydroxides: α diagram

- Fe^{+3} is a minor species at neutral pH



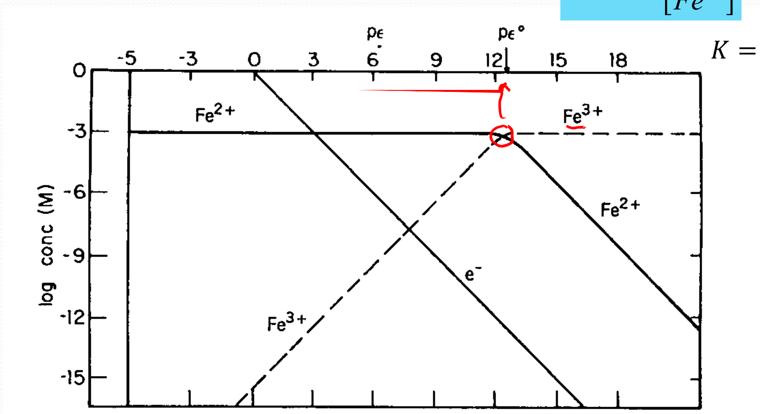
Iron redox diagram

Stumm & Morgan, 1996; Fig. 8.1, pg. 435
Similar to: Benjamin, 2002 Fig 9-3, pg.486

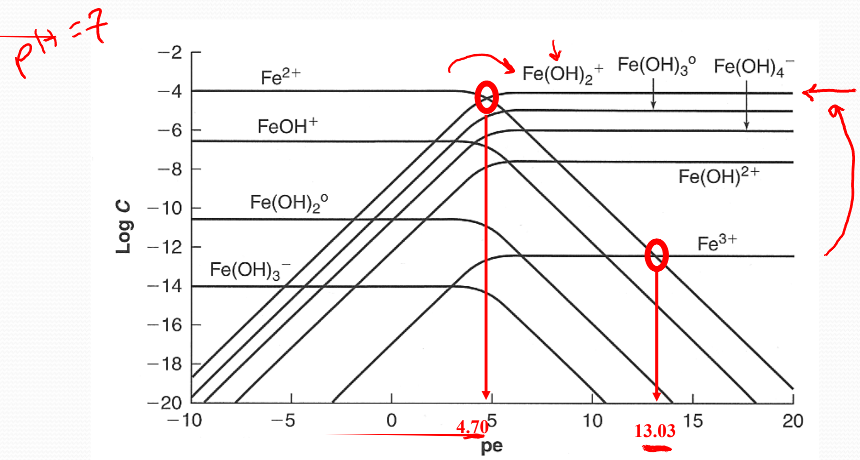
- Analogous to log C vs pH diagram

$$K\{e^-\} = \frac{[Fe^{+2}]}{[Fe^{+3}]}$$

$K = 10^{13.03}$

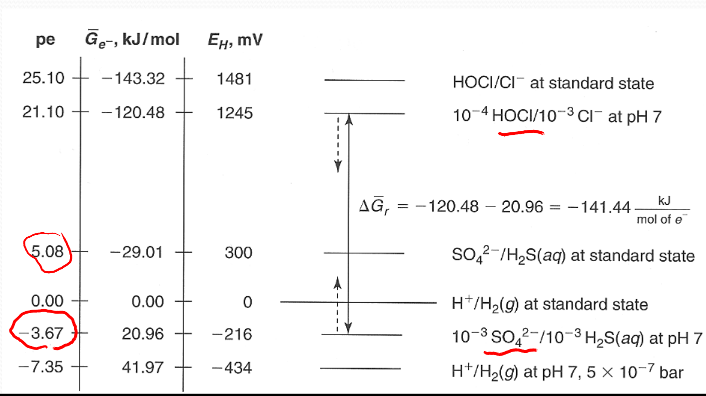


Iron: considering speciation



HOCl and H_2S example

- Neutral pH (~7.0)
  - 0.1 mM HOCl, 1 mM Cl^{-}
  - 1 mM H_2S and SO_4^{-2}



Summary

Table 9.5 Conversion equations among parameters that describe electron energy levels for a half-cell reaction and energy changes accompanying an *n*-electron reduction reaction*

1	Energy of exchangeable electrons in a system	$\bar{G}_{e^-} = \bar{G}_{e^-}^{o} + RT\ln\{e^-\} = -2.303RT\,\mathrm{pe} = -FE_H$
2	Nernst equation: energy of exchangeable electrons associated with a given half-cell reaction	$\mathrm{pe} = \mathrm{pe}^o - \frac{1}{n_e}\log\frac{\{\mathrm{Red}\}}{\{\mathrm{Ox}\}}$ $E_H = E_H^o - \frac{2.303RT}{n_eF}\log\frac{\{\mathrm{Red}\}}{\{\mathrm{Ox}\}}$
3	Gibbs energy of reaction in terms of energy of electrons associated with the two half-cell reactions†	$\Delta\bar{G}_r = n_e\Delta\bar{G}_{e^-}$ $\Delta\bar{G}_r = -2.303RT\,\Delta\mathrm{pe}$ $\Delta\bar{G}_r = -n_eF\,\Delta E_H$
4	Gibbs energy of reaction in terms of extent of disequilibrium	$\Delta\bar{G}_r = \Delta\bar{G}_r^o + 2.303RT\log Q = 2.303RT\log\frac{Q}{K}$
5	Change in electron energy in a reaction in terms of extent of disequilibrium†	$\Delta\bar{G}_r = \Delta\bar{G}_r^o + 2.303RT\log Q$ $\Delta\mathrm{pe} = \Delta\mathrm{pe}^o - \frac{RT}{n_e}\log Q$ $\Delta E_H = \Delta E_H^o - \frac{2.303RT}{n_eF}\log Q$
6	Equilibrium constant in terms of energy change at standard state†	$\log K = \frac{\Delta\bar{G}_r^o}{2.303RT}$ $\log K = n_e\,\Delta\mathrm{pe}^o$ $\log K = \frac{n_eF}{2.303RT}\Delta E_H^o$
7	Conditions for conversion of reactants to products†	$\Delta\bar{G}_r < 0$ $\Delta\mathrm{pe} > 0$ $\Delta E_H > 0$
8	Conditions at equilibrium†	$\Delta\bar{G}_r = \Delta\mathrm{pe} = \Delta E_H = 0$

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$$pe^o = \frac{1}{n}\log K$$

Hypochlorite

- 5×10^{-4}M Cl_T
  - Where:
    $Cl_T = [HOCl] + [OCl^-] + [Cl^-]$

$$\tfrac{1}{2}HOCl + \tfrac{1}{2}H^+ + e^- \leftrightarrow \tfrac{1}{2}Cl^- + \tfrac{1}{2}H_2O$$

$$K = \frac{\{Cl^-\}^{0.5}}{\{HOCl\}^{0.5}\{H^+\}^{0.5}\{e^-\}} = 10^{+25.1}$$

$$p\varepsilon = p\varepsilon^o - \frac{1}{n}\log\left(\frac{[Red]}{[Ox]}\right)$$
$$= 25.1 - \log\left(\frac{\{Cl^-\}^{0.5}}{\{HOCl\}^{0.5}\{H^+\}^{0.5}}\right)$$
$$= 25.1 - \tfrac{1}{2}\log\left(\frac{\{Cl^-\}}{\{HOCl\}}\right) - \tfrac{1}{2}pH$$

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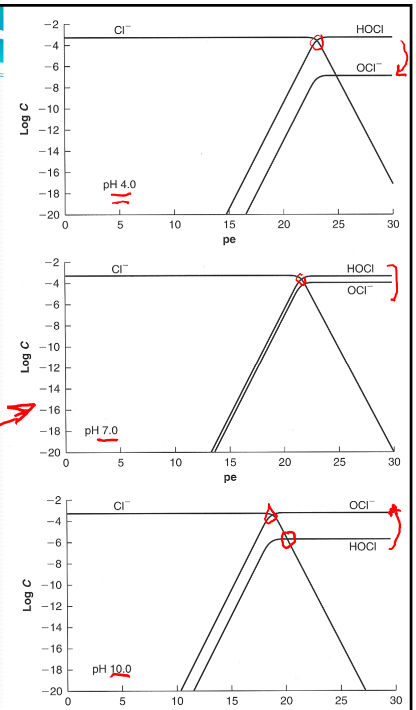


Determining Equilibrium Concentrations

- Graphical solution analogous to acid/base problems
  - Create LogC vs pe diagram
  - Determine location on graph using electron balance
    - Analogous to proton balance in acid/base problems
- Example: HOCl and NaHS
  - Reduced species: Cl^- which is $2e^-$ poor
  - Oxidized species: SO_4^{-2} which is $8e^-$ rich

HOCl & HS^-

- 10^{-4}M S_T
- 5×10^{-4} Cl_T

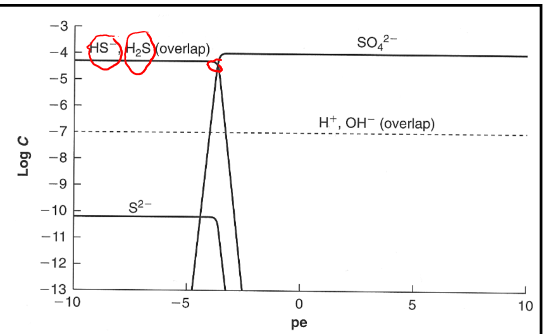
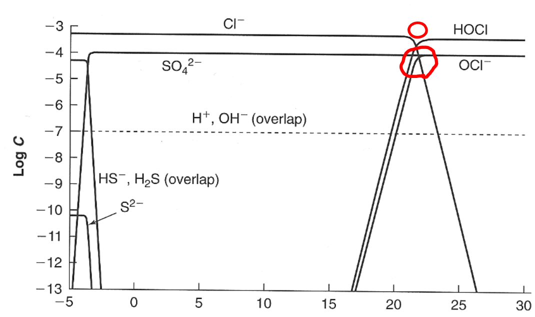


Figure 9.7 Log C–pe diagram for a system containing 10^{-4} *M TOTS* at pH 7.0.



Electron Balance

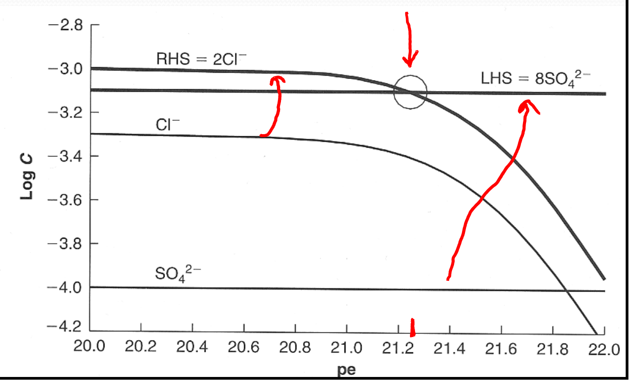
- Oxidation $HOCl + H^+ + 2e^- \leftrightarrow Cl^- + H_2O$
- Reduction $SO_4^{-2} + 9H^+ + 8e^- \leftrightarrow HS^- + 4H_2O$

- e- Balance:

HS-

HOCl

$8[SO_4^{-2}] = 2[Cl^-]$



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Constants

- Reference reaction

$$H^+ + e^- \leftrightarrow \tfrac{1}{2}H_2(g)$$

- Where $\{e^-\}$=1, if all chemical species activities are also unity

$$K = \frac{\{H_2(g)\}^{0.5}}{\{H^+\}\{e^-\}} = 1.0$$

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	1758
$O_3(g) + 2e^- + 2H^+ \leftrightarrow O_2(g) + H_2O$	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

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pE bounds for water I

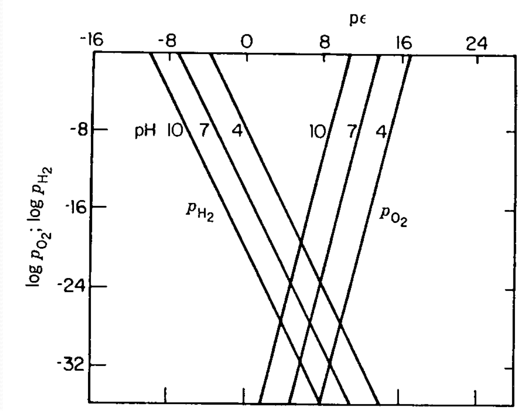
- Oxygen and Hydrogen half cell reactions

$$K = \frac{\{H_{2(g)}\}^{0.5}}{\{H^+\}\{e^-\}} = 1.0$$

$$\{H^+\}\{e^-\} = \{H_{2(g)}\}^{0.5}$$

$$\log\{H^+\} + \log\{e^-\} = 0.5\log\{H_{2(g)}\}$$

$$\log P_{H_2} = -2pH - 2p\varepsilon$$



Stumm & Morgan, 1996; Fig. 8.2, pg. 437

pE bounds for water II

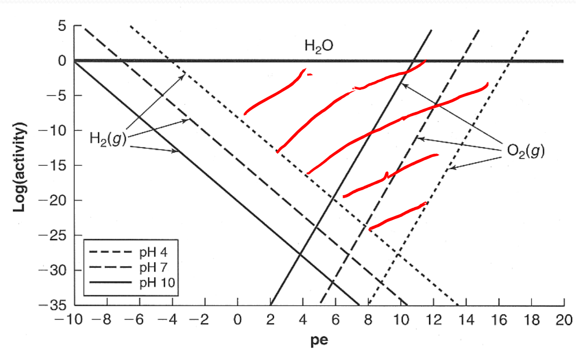


Figure 9.10 Log a–pe diagram for the $H_2(g)/H_2O/O_2(g)$ system at various pH values. Note that the *y* axis is the logarithm of the activity of the species shown, not the logarithm of its concentration. Thus, for the gases, the value on the ordinate is the logarithm of the partial pressure.

Electron Balance for HOCl & HS^-

- Oxidation $HOCl + H^+ + 2e^- \leftrightarrow Cl^- + H_2O$
- Reduction $O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$

$SO_4^{-2} + 9H^+ + 8e^- \leftrightarrow HS^- + 4H_2O$

$4H^+ + 4e^- \leftrightarrow 2H_2$

- e- Balance:

H_2O

HS-

HOCl

$$4[O_2(aq)] + 8[SO_4^{-2}] = 2[Cl^-] + 2[H_2(aq)]$$

HOCl and HS^-

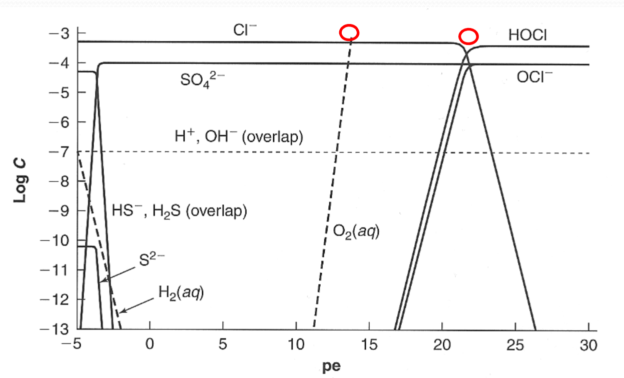


Figure 9.12 Figure 9.8 modified to include equilibria among H_2O, $O_2(aq)$, and $H_2(aq)$.

Close-up of electron balance

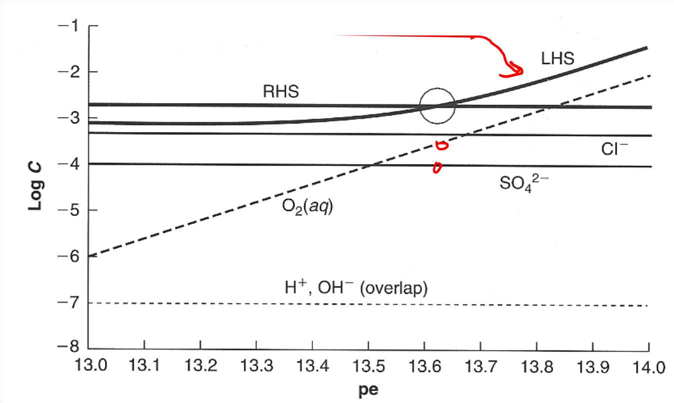
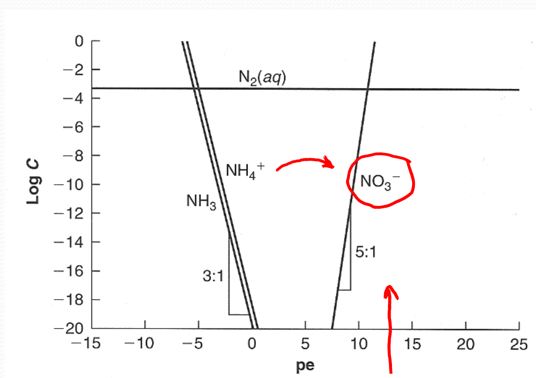


Figure 9.13 Expanded version of a portion of Figure 9.12, also showing the RHS and LHS of the electron condition.

Nitrogen



Nitrogen & Chlorine

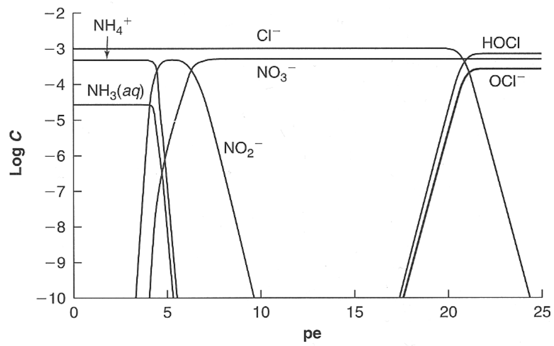


Figure 9.14 Log C–pe diagram for a system containing 10^{-3} *M TOT*Cl and 5×10^{-4} *M TOT*N, assuming that N can exist in the −3, +3, and +5 oxidation states.

Redox Predominance for N

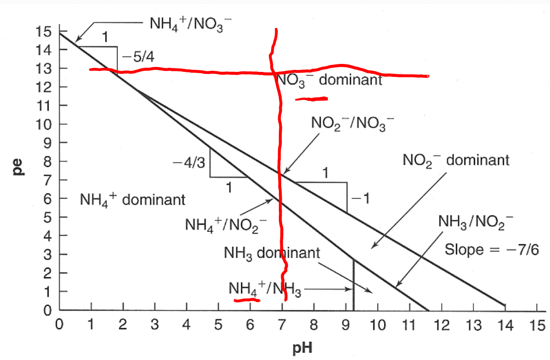


Figure 9.16 Completed pe–pH predominance area diagram considering NH_4^+, NH_3, NO_2^-, and NO_3^-.

- To next lecture

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