Redox Equilibrium

- *Redox = Reduction/Oxidation; characterized by transfer of electrons (e^-)*

- *Gain or loss of e^- changes the charge on an atom, conventionally called its oxidation number or oxidation state and often designated in parentheses:* Fe(II) *or* Fe(III)

- *Electron transfer occurs between species that form conjugate redox pairs. The species that has the transferable e^- is reduced, and the one lacking the transferable e^- is oxidized; (analogous to base and acid for species having or lacking transferable H^+). Reduction can be described as "electronation" and oxidation as "de-electronation."*

Redox Equilibrium

- *The same element often has vastly different properties in different redox states (valences, oxidation states, oxidation numbers); e.g.,* Cr(III) *vs.* Cr(VI)*;* S(–II) *vs.* S(0) *vs.* S(VI)*;* O(0) *vs.* O(–II)*; many other examples*

- *Bonds are formed by electron sharing and are preferentially closer to the more* electronegative *atom; for simplicity, electrons are usually assigned entirely to a single atom, according to well established conventions*

Redox Equilibrium

- *Rules and conventions for charge assignment*

  - ❖ *Charge must be conserved; i.e., the sum of the charges on all atoms in a molecule must equal the charge on the whole molecule*

  - ❖ H *is assigned a charge of +1*

  - ❖ O *is assigned a charge of* -2

  - ❖ N *is assigned a charge of* -3 *when bonded only to C and H*

  - ❖ S *is assigned a charge of* -2 *when bonded only to C and H*

  - ❖ *Above guidelines followed in order; i.e., conventions higher on the list "trump" those lower on the list*

- *Examples:* H_2O, $H_2(aq)$, H_2O_2, NH_3, NH_4^+, HCO_3^-, CO_3^{2-}, CH_3COOH, CH_3CH_2COOH

Oxidation Number Calculations

- Oxidation number of C in H_2CO_3:
 $2(+1) + C + 3(-2) = 0$; $C = +4$

    Oxidation number of C in HCO_3^-:
    $1(+1) + C + 3(-2) = -1$; $C = +4$
    Same result for CO_2, CO_3^{2-}

- Oxidation number of C in glucose ($C_6H_{12}O_6$):
    $6*C + 12(+1) + 6(-2) = 0$; $C = 0$

- Oxidation number of S in SO_4^{2-}, H_2S:
    In SO_4^{2-}: $S + 4(-2) = 0$; $S = +6$
    In H_2S: $2(+1) + S = 0$; $S = -2$

- Oxidation number of Fe in Fe(*s*), Fe(OH)$_3$(*s*):
    In Fe(*s*): Fe = 0
    In Fe(OH)$_3$(*s*): $Fe + 3(-2) + 3(+1) = 0$; $Fe = +3$

- *Most redox reactions involved transfer of one or more <u>pairs</u> of electrons, so charge on oxidized and reduced atoms differs by 2, 4, 6, or 8; transfer of 1, 3, or 5 e^- occurs but is less common*

- *Many redox reactions can be written as transfers of only e^- and water:*

  ❖ $Fe^{2+} \leftrightarrow Fe^{3+} + e^-$

  ❖ $H_2(g) \leftrightarrow 2H^+ + 2e^-$

  ❖ $AsO_3^{3-} + H_2O \leftrightarrow H_2AsO_4^- + 2e^-$

- *When written using dominant species, redox reactions often involve transfer of H+; in almost all cases, the more oxidized species is more acidic, so H+ and e^- are both released in an oxidation reaction:*

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

  ❖ $Fe^{2+} + 2H_2O \leftrightarrow Fe(OH)_2^+ + 2H^+ + e^-$

Redox Equilibrium

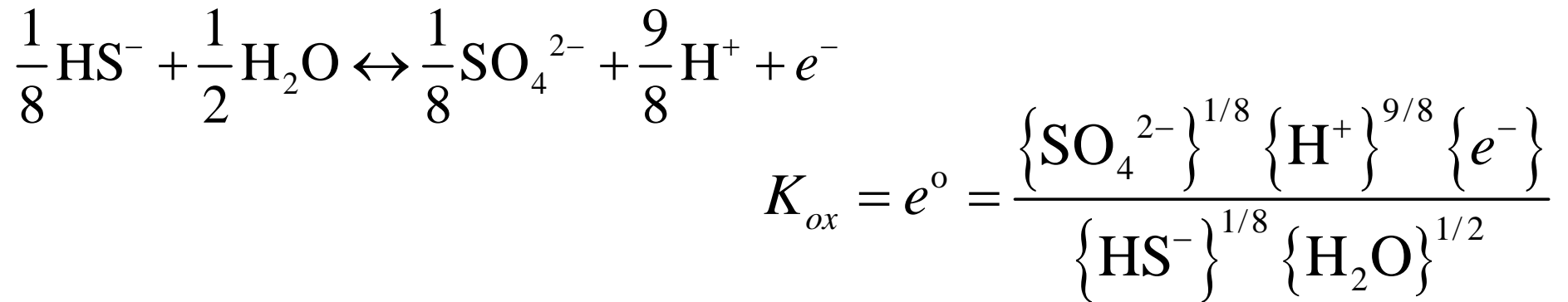*Equilibrium constant expressions for redox reactions are written exactly as for other reactions, e.g.:*

$$HS^- + 4H_2O \leftrightarrow SO_4^{2-} + 9H^+ + 8e^- \qquad K_{ox} = \frac{\{SO_4{}^{2-}\}\{H^+\}^9\{e^-\}^8}{\{HS^-\}\{H_2O\}^4}$$
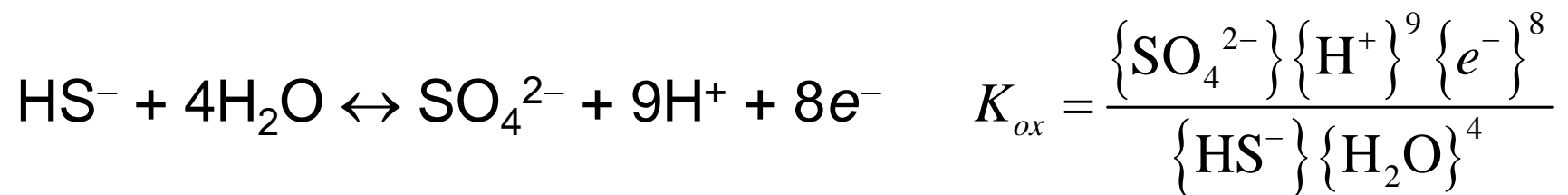
Or in general:

Reduced species $\leftrightarrow$ Oxidized species + n_HH$^+$ + n_ee$^-$
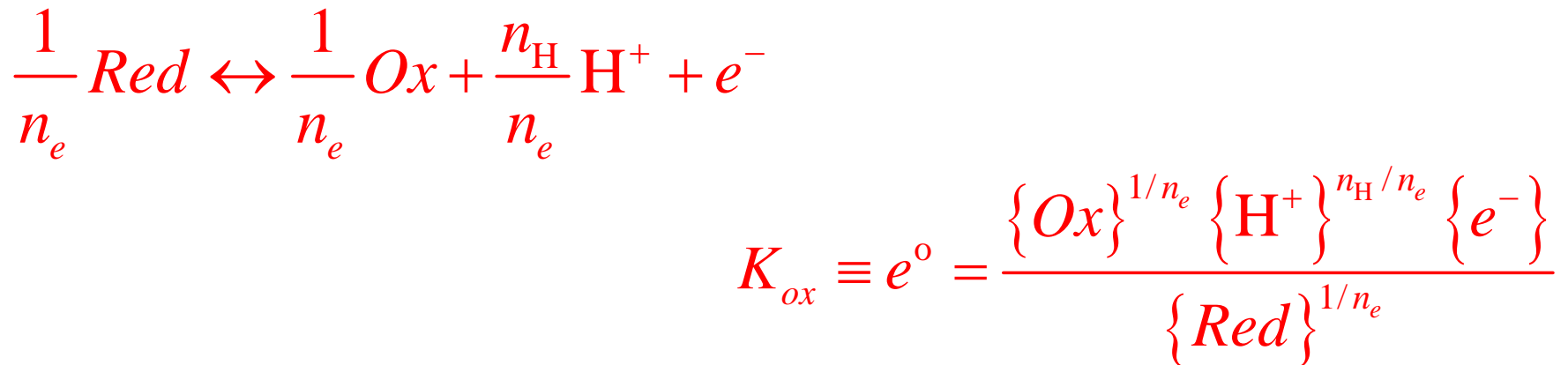
$$K_{ox} = \frac{\{Ox\}\{H^+\}^{n_H}\{e^-\}^{n_e}}{\{Red\}}$$

Redox Equilibrium

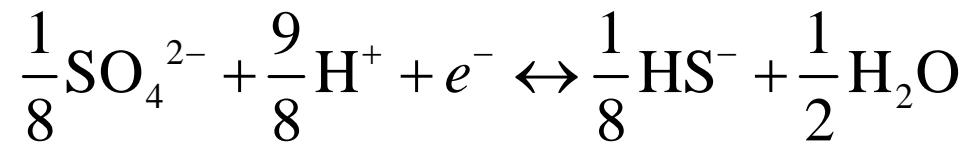*Equilibrium constant written for release of one electron (analogous to K_a) is designated e^o:*

$$\frac{1}{8}HS^- + \frac{1}{2}H_2O \leftrightarrow \frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e^-$$

$$K_{ox} = e^o = \frac{\{SO_4^{2-}\}^{1/8}\{H^+\}^{9/8}\{e^-\}}{\{HS^-\}^{1/8}\{H_2O\}^{1/2}}$$

Or, in general:

$$\frac{1}{n_e}Red \leftrightarrow \frac{1}{n_e}Ox + \frac{n_H}{n_e}H^+ + e^-$$

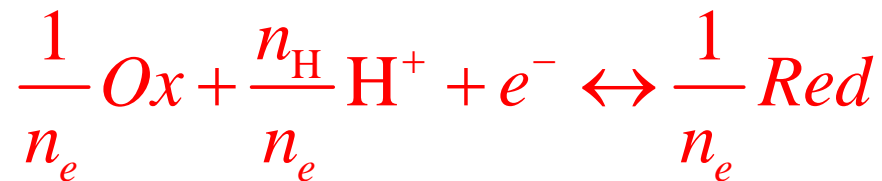$$K_{ox} \equiv e^o = \frac{\{Ox\}^{1/n_e}\{H^+\}^{n_H/n_e}\{e^-\}}{\{Red\}^{1/n_e}}$$

Redox Equilibrium

Redox reactions are conventionally written as one-electron reductions, in which case K=1/e^o, and logK=log(1/e^o)=pe^o:

$$\frac{1}{8}SO_4{}^{2-} + \frac{9}{8}H^+ + e^- \leftrightarrow \frac{1}{8}HS^- + \frac{1}{2}H_2O$$

$$K_{red} = \frac{1}{e^o} = \frac{\{HS^-\}^{1/8}\{H_2O\}^{1/2}}{\{SO_4{}^{2-}\}^{1/8}\{H^+\}^{9/8}\{e^-\}}$$

$$\frac{1}{n_e}Ox + \frac{n_H}{n_e}H^+ + e^- \leftrightarrow \frac{1}{n_e}Red$$

$$K_{red} = \frac{1}{e^o} = \frac{\{Red\}^{1/n_e}}{\{Ox\}^{1/n_e}\{H^+\}^{n_H/n_e}\{e^-\}}$$

$$\log K_{red} = \log\frac{1}{e^o} = pe^o$$
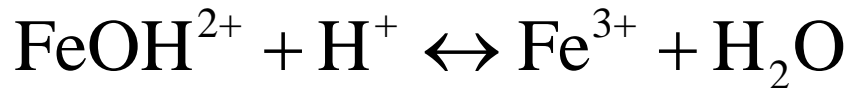
Redox Equilibrium

Note that redox reactions relate particular species, not oxidation states

Therefore, for example, K_{ox}, K_{red}, e^o, and pe^o for Fe^{3+}/Fe^{2+} are different from the corresponding values for $FeOH^{2+}/Fe^{2+}$
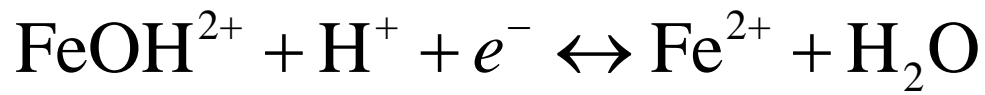
$$\underline{\log K}$$

$$Fe^{3+} + e^- \leftrightarrow Fe^{2+} \qquad pe^o_{Fe^{3+}/Fe^{2+}} = 13.03$$

$$\underline{FeOH^{2+} + H^+ \leftrightarrow Fe^{3+} + H_2O} \qquad \underline{-\log(K_{a1}) = 2.19}$$
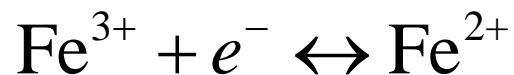
$$FeOH^{2+} + H^+ + e^- \leftrightarrow Fe^{2+} + H_2O \qquad pe^o_{FeOH^{2+}/Fe^{2+}} = 15.22$$

Redox Equilibrium

In general, for a 1-e⁻ reduction reaction:

$$\log K_{red} = pe^{\circ} = \frac{1}{n_e}\log\frac{\{Red\}}{\{Ox\}} + \frac{n_H}{n_e}\mathrm{pH} + pe$$

$$pe = pe^{\circ} - \frac{1}{n_e}\log\frac{\{Red\}}{\{Ox\}} - \frac{n_H}{n_e}\mathrm{pH} \qquad \textbf{\textit{Nernst Equation}}$$

*The Nernst equation yields the pe that **would apply if the given couple were in equilibrium** in the given solution. Note that, since redox systems are often not at equilibrium, we might compute different values of pe for different redox couples*

Nernst Equation

$$pe = pe^{\circ} - \frac{n_{\mathrm{H}}}{n_e}\mathrm{pH} - \frac{1}{n_e}\log\frac{\{Red\}}{\{Ox\}}$$
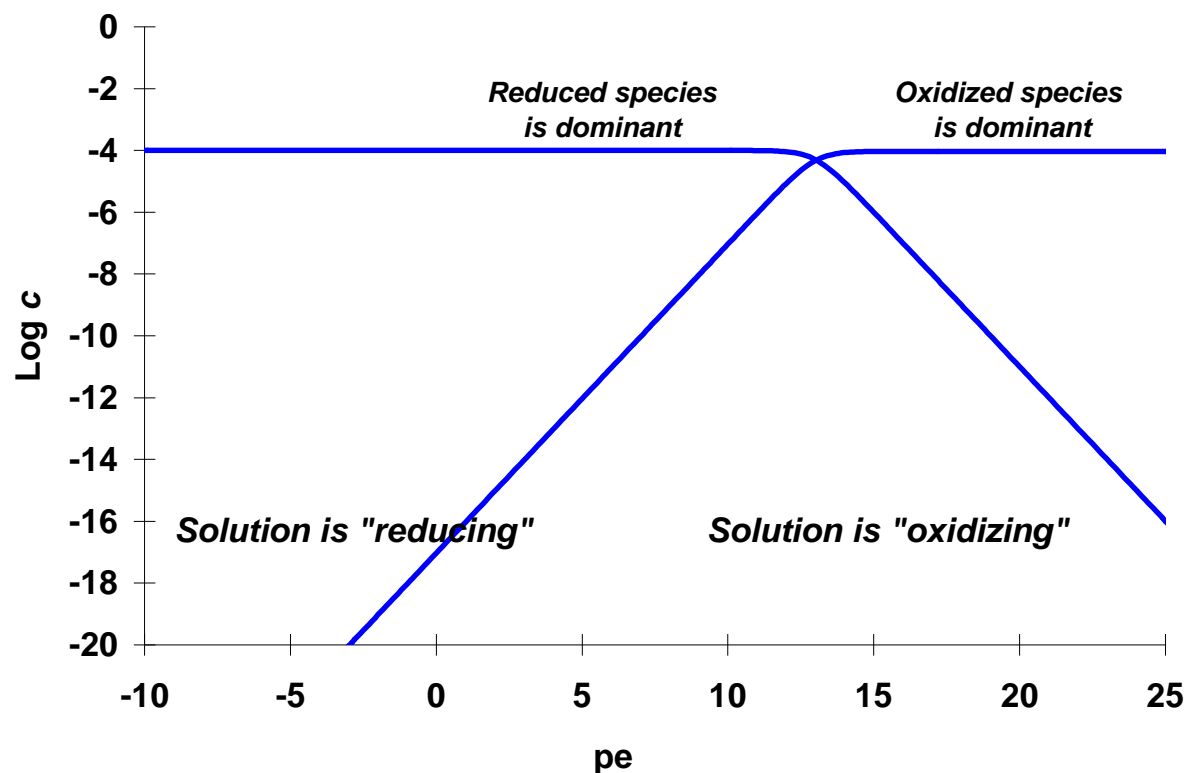
Analogous calculation for pH:

$$\log K_{protonation} = pK_a = \log\frac{\{Acid\}}{\{Base\}\{\mathrm{H^+}\}} = \log\frac{\{Acid\}}{\{Base\}} + \mathrm{pH}$$
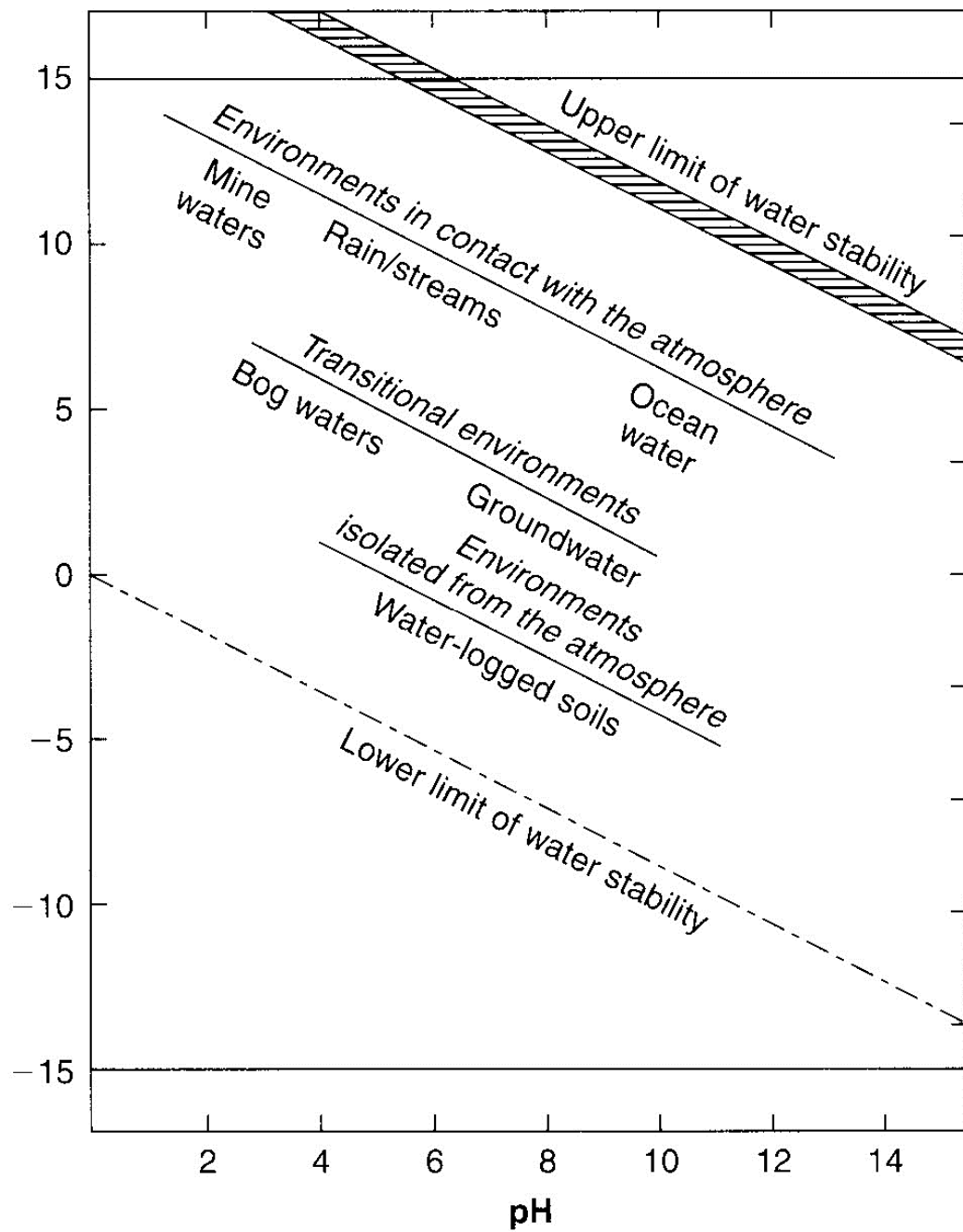
$$\mathrm{pH} = pK_a - \log\frac{\{Acid\}}{\{Base\}}$$

pH is easy to measure directly, so we don't normally utilize this expression. By contrast, pe is difficult to measure, so the Nernst equation is commonly used to calculate it

- *Just like each solution has an equilibrium pH, it has an equilibrium pe. The speciation of a given acid/base couple depends on its chemistry (as embedded in the K_a value) and on the acid/base status of the solution (pH). Similarly, the speciation of a given redox couple depends on its chemistry (as embedded in e^o or pe^o) and on the redox status of the solution (pe).*

For a system that has only one oxidized and one reduced species:

Reduced species is dominant

Oxidized species is dominant

Solution is "reducing"

Solution is "oxidizing"

Log c

pe

Redox Equilibrium

- *To evaluate e^o and to draw log c − pe diagrams, we need to quantify the activity of e^-*

- *Like the free proton (H^+), the free electron (e^-) is extremely unstable in water; however, the <u>hydrated</u> electron (H_2O^-) is also extremely unstable, so we consider all electrons in solution to be associated with species other than H_2O.*

- *Nevertheless, it is conventional to assign a finite value to the activity of free electrons, by choosing a standard state concentration that is exceedingly small. This has no substantial effect on calculations for equilibrium of redox reactions, except that even in an ideal solution, $[e^-] << \{e^-\}$*

Redox Equilibrium

- *Standard state for e^- (activity of $e^- \equiv 1.0$) is a solution in equilibrium with H^+ and $H_2(g)$, both in their standard states. Consequently, K=1.0 for:*

$$2\ H^+ + 2e^- \leftrightarrow H_2(g) \qquad K=1.0$$
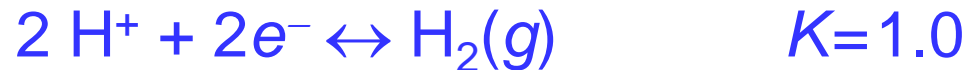
   Note that, in an ideal system (all γ's = 1.0) with all species in their standard states: $\{H^+\}=\{H_2(g)\}=\{e^-\}=1.0$, and $[H^+]=1.0$ mol/L, $P_{H2(g)}=1.0$ atm, but $[e^-]$ is negligible

- *Preceding definition of standard state of e^- allows K for any other redox reaction to be determined experimentally. For example, by determining $\{Fe^{2+}\}$ and $\{Fe^{3+}\}$ in a solution with $\{e^-\}$ computed as above:*
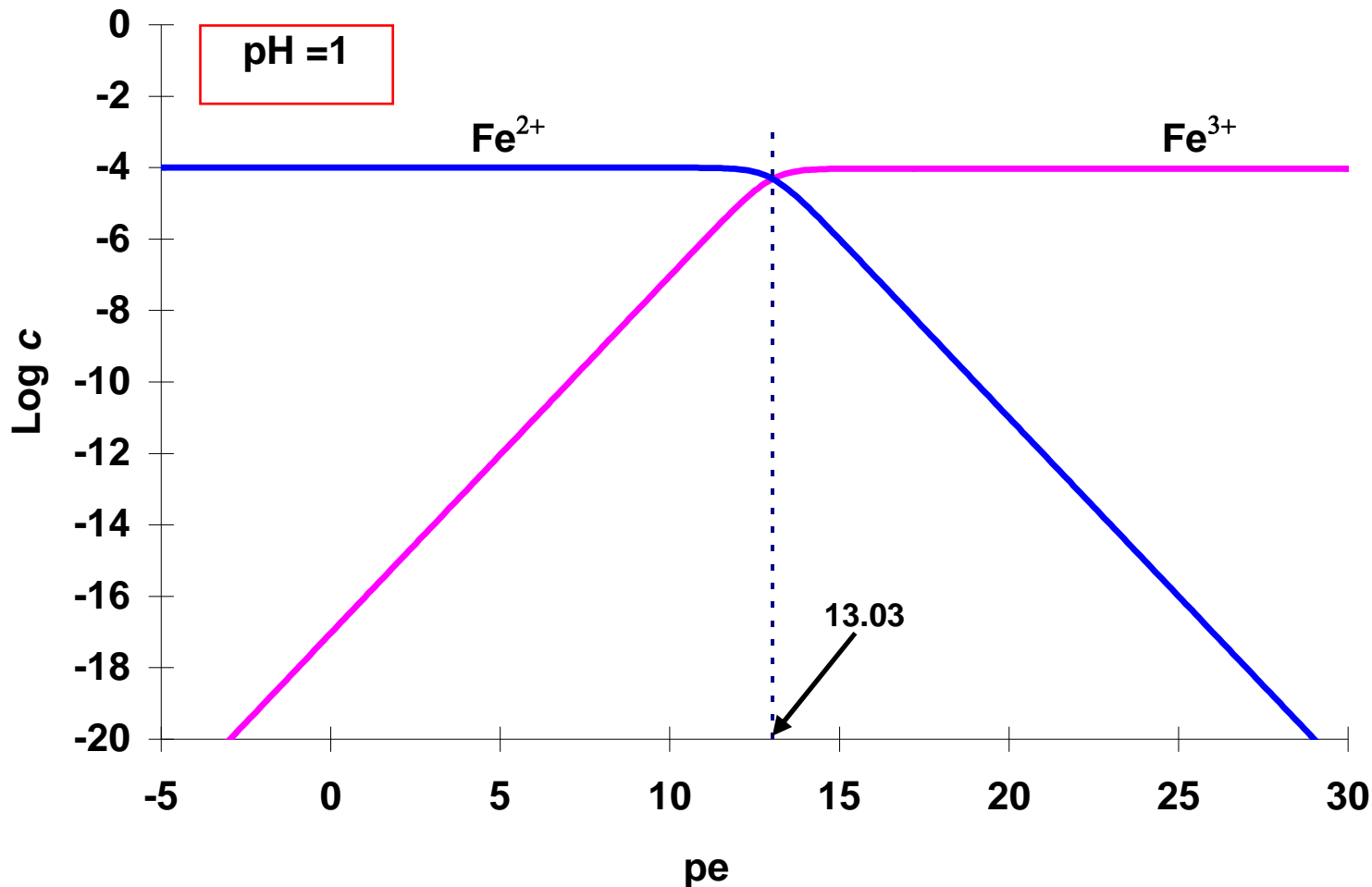
$$Fe^{3+} + e^- \leftrightarrow Fe^{2+} \qquad K=10^{13.03}$$

Redox Equilibrium

$$Fe^{3+} + 1e^- \leftrightarrow Fe^{2+}$$

$$\log K = pe^o = 13.03 = \log \frac{\left\{ Fe^{2+} \right\}}{\left\{ Fe^{3+} \right\}\left\{ e^- \right\}}$$

$$13.03 = \log \frac{\left\{ Fe^{2+} \right\}}{\left\{ Fe^{3+} \right\}} - \log \left\{ e^- \right\} = \log \frac{\left\{ Fe^{2+} \right\}}{\left\{ Fe^{3+} \right\}} + pe$$

If $\{Fe^{3+}\} = \{Fe^{2+}\}$: $\qquad pe = 13.03 = pe^o$

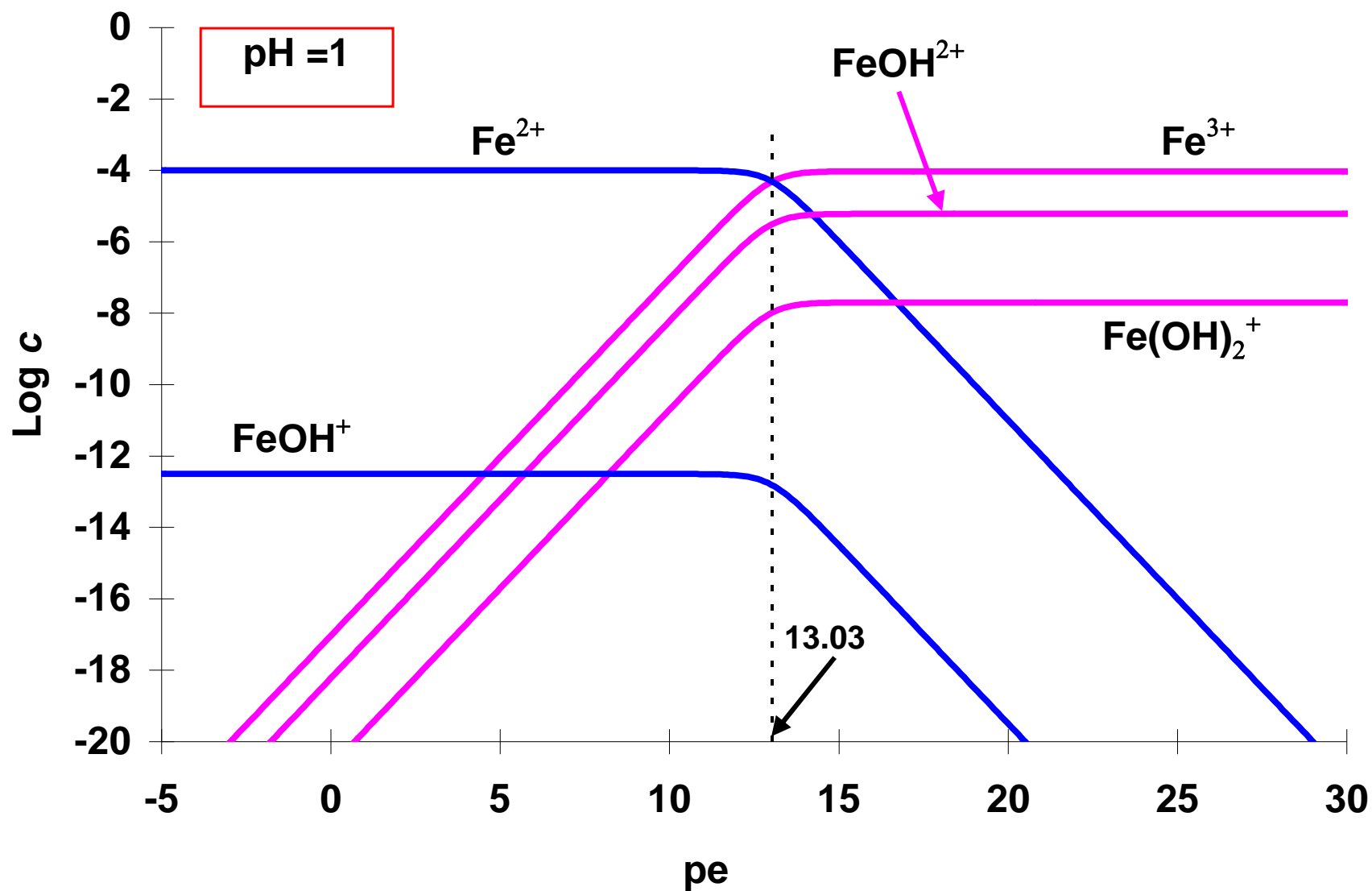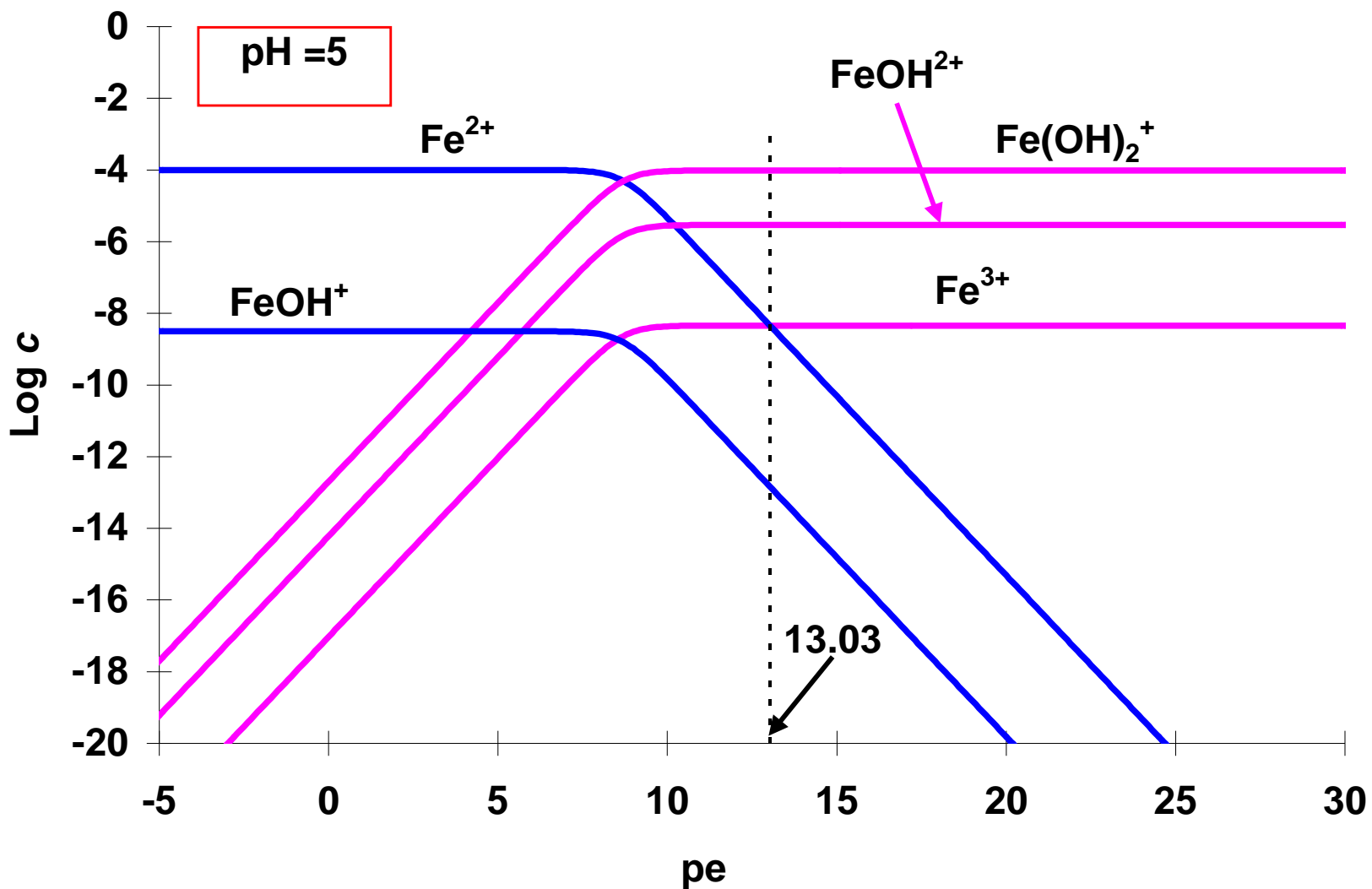If pe increases by 1, log $\{Fe^{3+}\}/\{Fe^{2+}\}$ decreases by 1

- *Slopes are +/− 1; intersection is at pe=pe⁰*

- *Range of reasonable pe's bigger than range of reasonable pH's*

- *Why is pH specified? Where would lines for $Fe(OH)_x$ species be?*
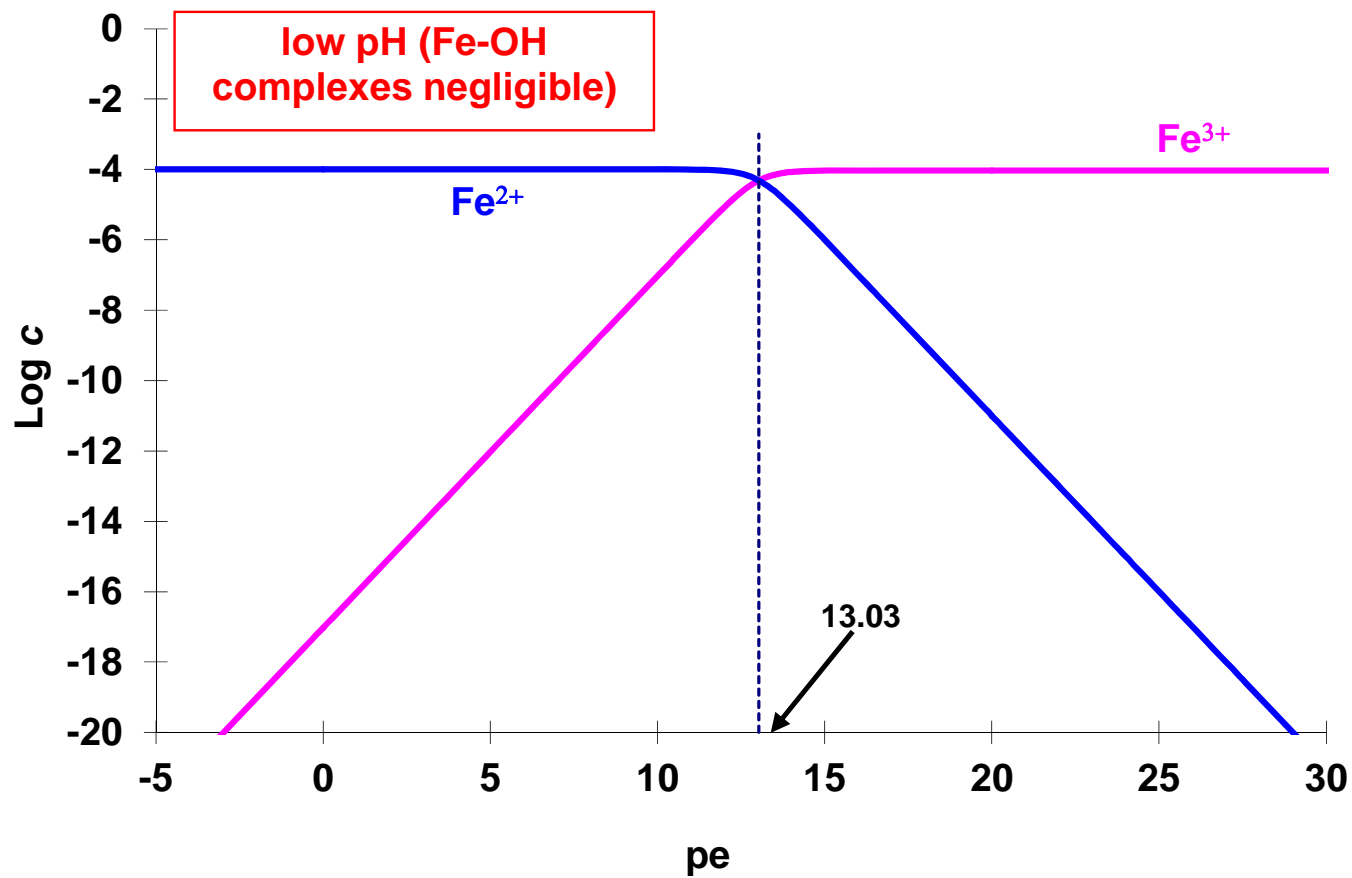
- *For* Fe(II)*: $pK_{a1}=9.50$*

- *For* Fe(III)*: $pK_{a1}=2.19, pK_{a2}=3.48$*

- *TOTFe = 10^{-4} everywhere on graph*
- *All K's satisfied (complexation and redox) everywhere on graph*

pH =5

FeOH^{2+}

Fe^{2+}
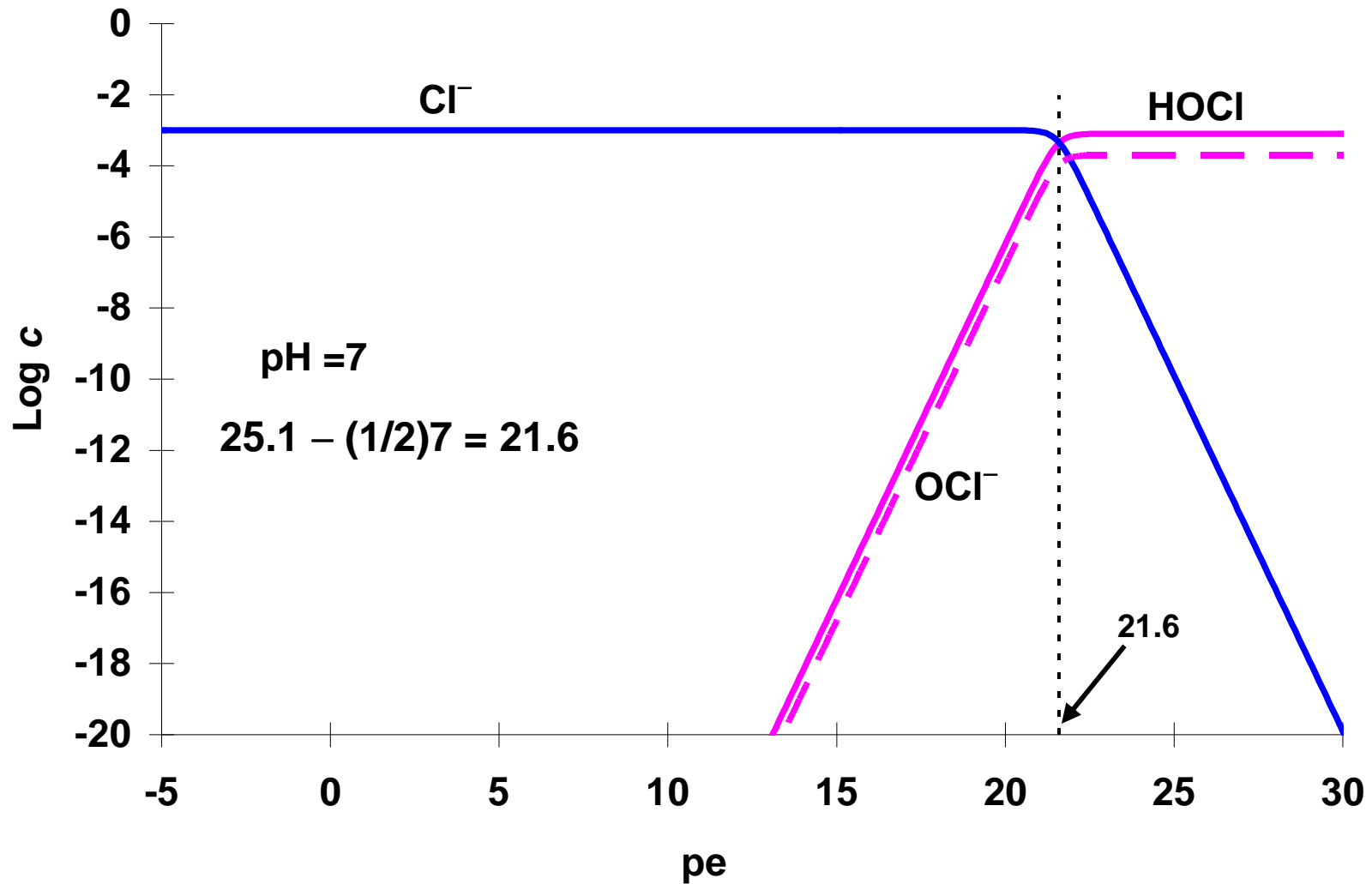
Fe(OH)$_2$$^+$

FeOH$^+$

Fe^{3+}

13.03

• Fe^{2+}/Fe^{3+} intersection still at pe=pe^o because no H$^+$ in reaction:

Fe^{3+} + 1e$^-$ ↔ Fe^{2+}

Redox Equilibrium

- *If the redox reaction involves transfer of both H⁺ and e⁻, the crossover pe will depend on pH.*

$$pe = pe^{\circ} - \frac{1}{n_e}\log\frac{\{Red\}}{\{Ox\}} - \frac{n_H}{n_e}pH$$

If {Red}={Ox}:

$$pe = pe^{\circ} - \frac{1}{n_e}\log(1) - \frac{n_H}{n_e}pH = pe^{\circ} - \frac{n_H}{n_e}pH$$

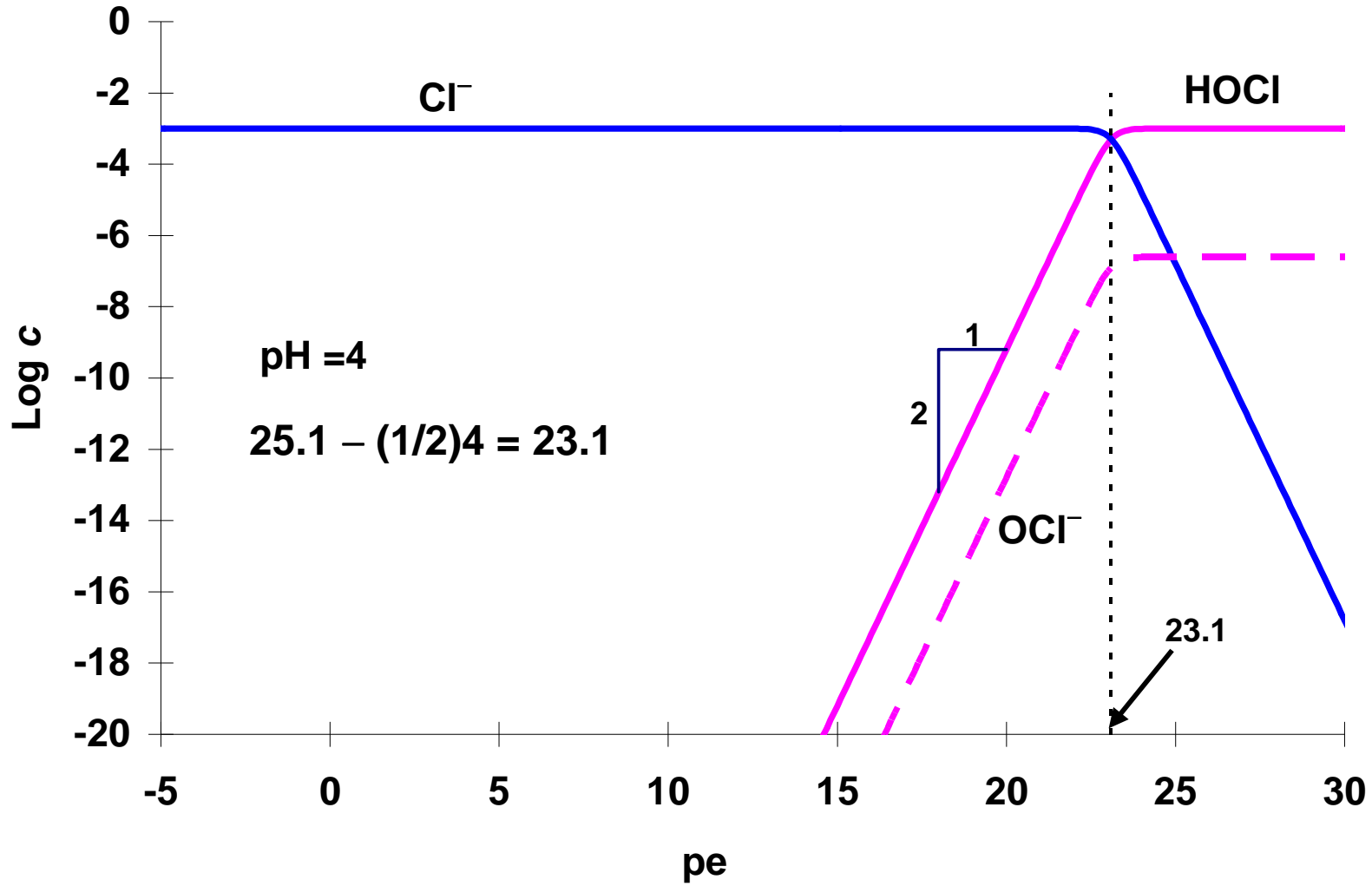# Redox Equilibrium

- $HOCl + H^+ + 2\ e^- \leftrightarrow Cl^- + H_2O$ $pe^o = 25.1,\ n_H = 1,\ n_e = 2$

$$pe = 25.1 - \frac{1}{2}\log\frac{\{Cl^-\}}{\{HOCl\}} - \frac{1}{2}pH$$

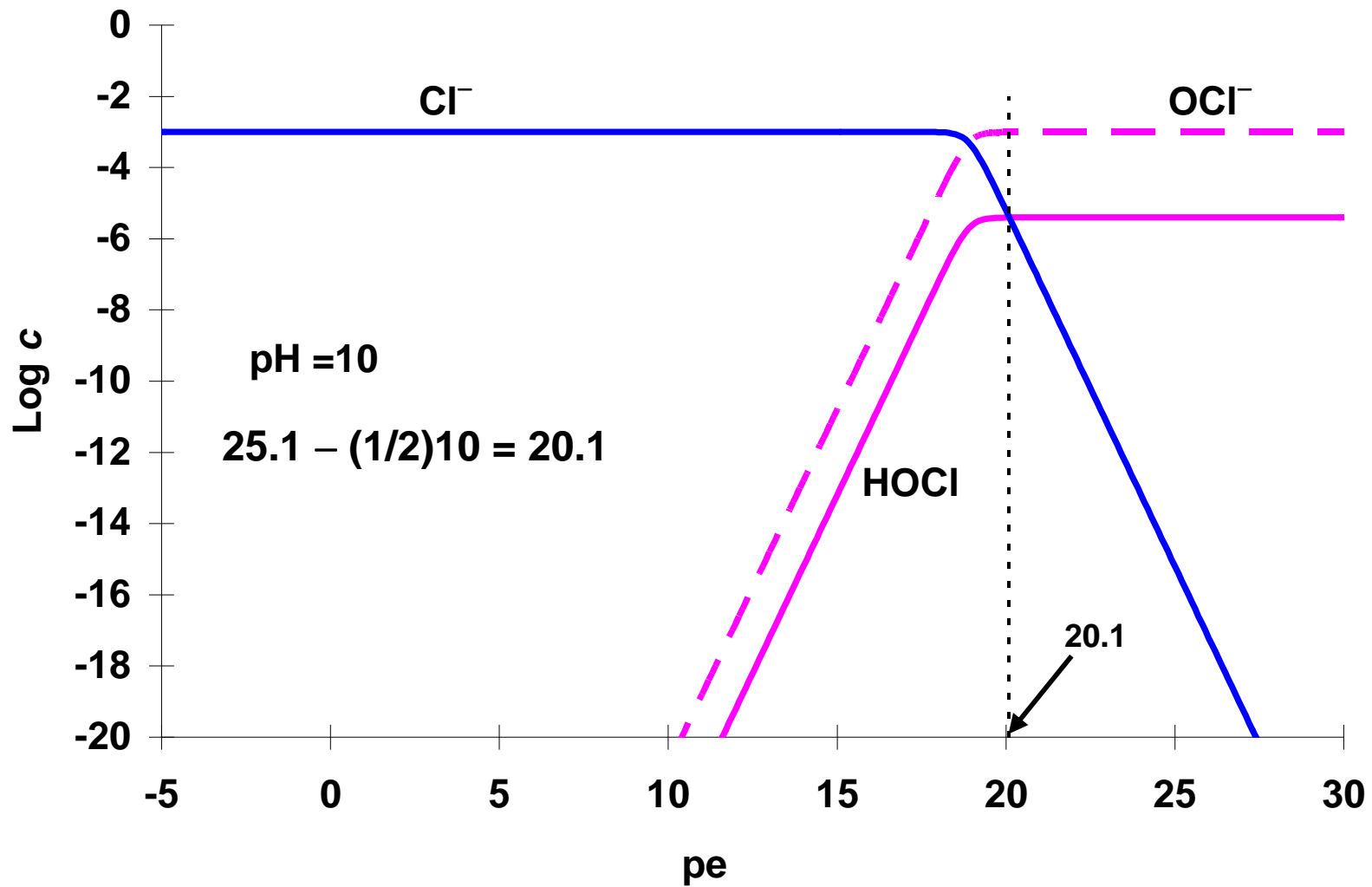If {Red}={Ox}: $pe = 25.1 - \frac{1}{2}pH$

- *Because $n_e=2$, slopes of HOCl and Cl^- curves will always differ by 2 on a log c – pe diagram*

- *Because H^+ appears in reaction, pe at crossover depends on pH*

- *TOTCl = 10^{-3} everywhere*
- *All K's satisfied (acid-base and redox) everywhere*

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- *All K's satisfied (acid-base and redox) everywhere*

Redox Equilibrium

Frequently, rather than knowing the pe and wanting to determine the speciation, it is necessary to use analytical data for speciation to infer the pe. In that case, if we want to use, for example, the Fe^{3+}/Fe^{2+} couple to <u>determine</u> pe:
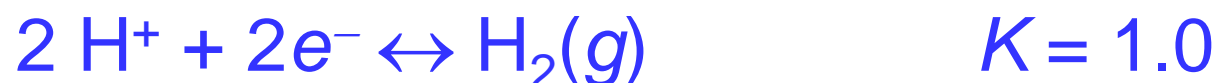
$$13.03 = \log \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}} + pe$$

$$pe = 13.03 - \log \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}}$$

Reminder: since redox systems are often not at equilibrium, we might compute different values of pe for different redox couples

Redox Equilibrium

- *The Standard Gibbs (Free) Energy of the Electron*

$$2\,H^+ + 2e^- \leftrightarrow H_2(g) \qquad K = 1.0$$

$$\Delta \bar{G}^o_r = -RT \ln K = -RT \ln(1) = 0 \text{ kJ/mol}$$

$$\bar{G}^o_{H_2(g)} - 2\bar{G}^o_{H^+} - 2\bar{G}^o_{e^-} = 0 \text{ kJ/mol}$$

$$0 - 2\bar{G}^o_{e^-} - 2(0) = 0 \text{ kJ/mol}$$

$$\bar{G}^o_{e^-} = 0 \text{ kJ/mol}$$

Redox Equilibrium

- *The Gibbs (Free) Energy of the Electron in Non-Standard-State Conditions*

$$\bar{G}_{e^-} = \bar{G}_{e^-}^{o} + RT \ln\left(e^-\right)$$

$$= 2.303 RT \log\left(e^-\right)$$

$$= -\left(5.71 \frac{\text{kJ}}{\text{mol}}\right) pe \qquad (25^oC)$$

The pe is a direct indicator of the electron energy level: high pe → low energy

Redox Equilibrium

- *If redox equilibrium applies, a single pe characterizes all redox couples in the system; transferable electrons on different couples all have equal available energy*

- *If a solution is not at redox equilibrium, transferable electrons associated with different redox conjugate pairs have different available energies, as indicated by the pe value computed using their activities in the Nernst equation*

- *In a disequilibrated redox system, it is thermodynamically favorable for transferable electrons with higher available energy (lower "local pe") to shift to the lower energy (higher local pe) environments*

- *Redox couples can be grossly out of equilibrium, so that the change in available energy accompanying a small amount of reaction is huge*

Redox Equilibrium

- *Example: A groundwater at pH 7.5 contains 4 mg/L TOTFe(II) and 0.01 mg/L TOTFe(III). It is bubbled with air until the dissolved oxygen concentration is 2 mg/L.*

(a) *Compute the pe that characterizes each redox couple in the solution and the molar Gibbs energy of the electrons associated with each couple. What redox reaction is favored?*

(b) *Immediately after the oxygen dissolves, how much energy would be released per mole of Fe(II) reacting?*

(c) *Draw a log c – pe diagram showing species in the Fe(III)/Fe(II) and O(0)/O(–II) couples. Treat H_2O and OH^- as possible O(–II) species*

(d) *What is the predicted, ultimate equilibrium condition?*

(a) Compute the pe that characterizes each redox couple in the initial solution.
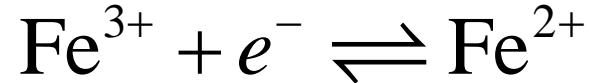
$$pe = pe^o - \frac{1}{n_e}\log\frac{\{Red\}}{\{Ox\}} - \frac{n_H}{n_e}\text{pH}$$ **Nernst Equation**

- *For* Fe(III): $pK_{a1}=2.19$, $pK_{a2}=3.48$, $pK_{a3}=7.93$, $pK_{a4}=8.00$; $\alpha_0 = 3.14 \times 10^{-10}$; TOTFe(III)=0.01 mg/L $= 1.79 \times 10^{-7}$ M $= 10^{-6.75}$ M; $\{Fe^{3+}\} = 5.62 \times 10^{-17}$

- *For* Fe(II): $pK_{a1}=9.50$, $pK_{a2}=11.07$, $pK_{a3}=10.03$; $\alpha_0 = 0.99$; TOTFe(II) $= 4.0$ mg/L $= 7.18 \times 10^{-5}$ M $= 10^{-4.14}$ M; $\{Fe^{2+}\} = 7.09 \times 10^{-5}$

Compute the pe that characterizes each redox couple in the initial solution.

$$pe = pe^o - \frac{1}{n_e}\log\frac{\{Red\}}{\{Ox\}} - \frac{n_H}{n_e}pH$$ **Nernst Equation**

For the Fe^{3+}/Fe^{2+} couple:

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

$$pe_{Fe^{3+}/Fe^{2+}} = pe^o - \frac{1}{1}\log\frac{\{Fe^{2+}\}}{\{Fe^{3+}\}} - \frac{0}{1}pH = pe^o - \log\frac{\{Fe^{2+}\}}{\{Fe^{3+}\}}$$

$$= 13.03 - \log\frac{7.11\times10^{-5}}{5.62\times10^{-17}} = 0.929$$

$$pe = pe^{\circ} - \frac{1}{n_e} \log \frac{\{Red\}}{\{Ox\}} - \frac{n_{\mathrm{H}}}{n_e} \mathrm{pH}$$ **Nernst Equation**

For the $O_2(aq)/H_2O$ couple:

$$O_2(aq) + 4e^- + 4H^+ \rightleftharpoons 2H_2O$$

$$pe_{O_2(aq)/H_2O} = pe^{\circ} - \frac{1}{4} \log \frac{\{H_2O\}^2}{\{O_2(aq)\}} - \frac{4}{4} \mathrm{pH}$$

$$= 21.50 - \frac{1}{4} \log \frac{(1.0)^2}{6.25 \mathrm{x} 10^{-5}} - (1)(7.5) = 12.95$$

Compute the molar Gibbs energy of the electrons associated with each couple.

For $O_2(aq)/H_2O$: $\quad \bar{G}_{e^-} = -\left(5.71\dfrac{kJ}{mol}\right) pe_{O_2(aq)/H_2O}$

$$= -\left(5.71\dfrac{kJ}{mol}\right)(12.95) = -73.94\dfrac{kJ}{mol}$$

For Fe^{3+}/Fe^{2+}: $\quad \bar{G}_{e^-} = -\left(5.71\dfrac{kJ}{mol}\right) pe_{Fe^{3+}/Fe^{2+}}$

$$= -\left(5.71\dfrac{kJ}{mol}\right)(0.929) = -5.30\dfrac{kJ}{mol}$$

What redox reaction is favored?

The electrons associated with the $Fe(II)/Fe(III)$ couple are at higher energy than those associated with the $O(-II)/O(0)$ couple, so the driving force favors movement of electrons from $Fe(II)$ to $O(0)$; i.e., oxidation of $Fe(II)$ by $O(0)$

(b) Immediately after the oxygen has dissolved, how much energy would be released per mole of $Fe(II)$ reacting?

The energy released per mole of electrons transferred is simply the difference in the electron energy levels. In this case, the change is:

$$\Delta \overline{G}_{e^-} = \left(-73.59 - \left(-5.30 \right) \right) \frac{kJ}{mol} = -68.64 \frac{kJ}{mol}$$

Since one mole of electrons oxidizes one mole of $Fe(II)$, the energy released per mole of $Fe(II)$ oxidized is 68.64 kJ
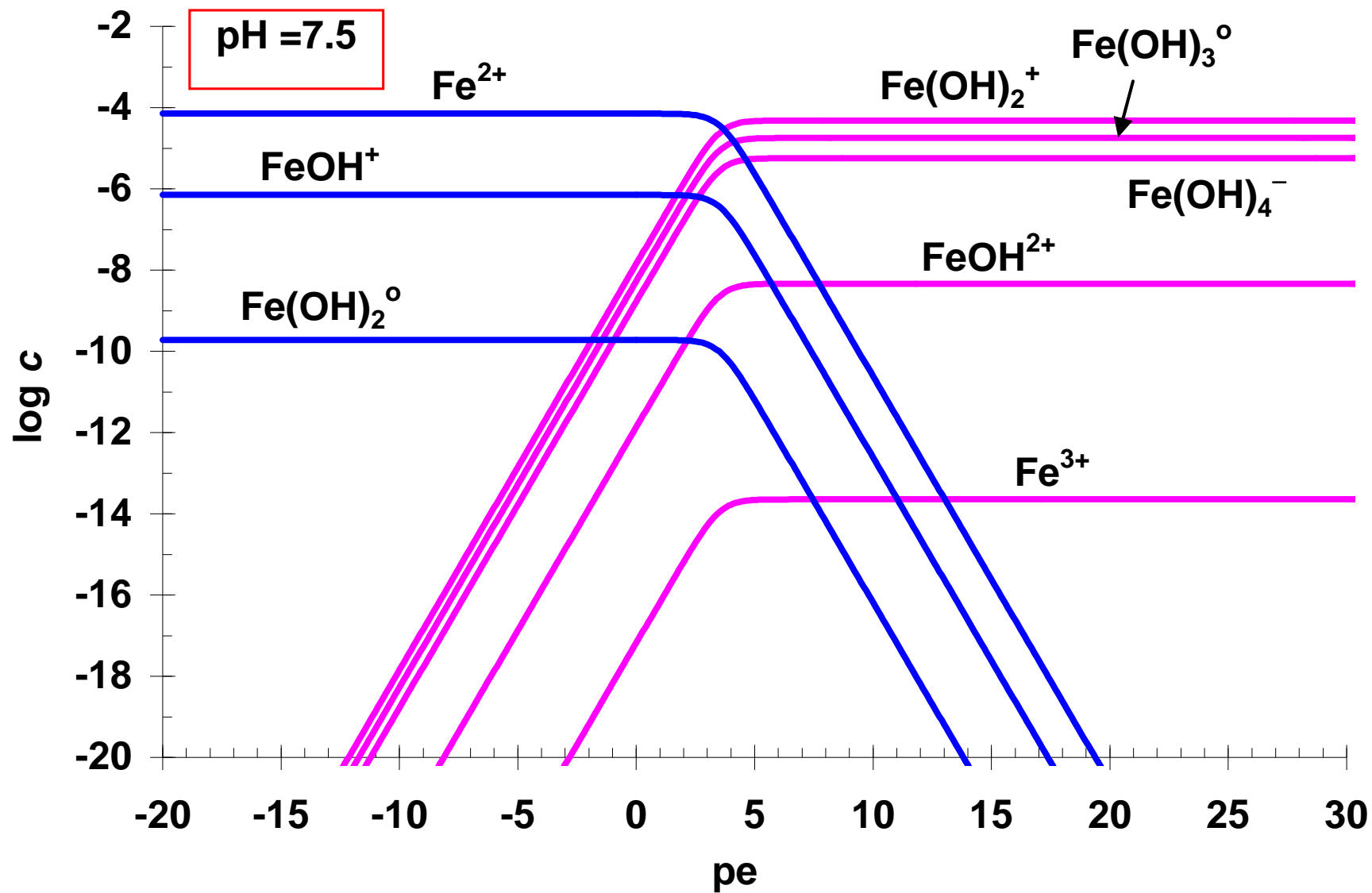
(c) Draw a log c − pe diagram showing species in the Fe(III)/Fe(II) and O(0)/O(−II) couples. Treat H_2O and OH^- as possible O(−II) species

Relevant issues for Fe(III)/Fe(II) *speciation:*

- *TOTFe=4.01 mg/L = 7.18×10^{-5} = $10^{-4.14}$*

- *For* Fe(III): $pK_{a1}=2.19$, $pK_{a2}=3.48$, $pK_{a3}=7.93$, $pK_{a4}=8.00$*

- *For* Fe(II): $pK_{a1}=9.50$, $pK_{a2}=11.07$, $pK_{a3}=10.03$*

- *For* Fe^{3+}/Fe^{2+}, $pe^o=13.03$*

To draw speciation diagram, MBs and K's must be satisfied; One approach for Fe(III) *and* Fe(II) *species:*

- *Compute α_0 for* Fe(III) *and* Fe(II) *based on pH*

- *Compute* $\{Fe^{3+}\}/\{Fe^{2+}\}$ *ratio as fcn of pe from Nernst Eq*

- *Use preceding results to find TOTFe(III)/TOTFe(II) as function of pe*

- *Use preceding result to find TOTFe(III)/**TOTFe** and TOTFe(II)/**TOTFe** as function of pe, and then use α values to find concentration of each species vs. pe*

(c) Draw a log c–pe diagram showing species in the Fe(III)/Fe(II) *and* O(0)/O(–II) *couples. Treat* H_2O *and* OH^- *as possible* O(–II) *species*

Relevant issues for O(0)/O(–II) speciation :

- *2 mg/L O_2(aq) = 6.25×10^{-5} = $10^{-4.20}$*

- *Activities of H_2O, OH^- are fixed (i.e., independent of pe)*

- *For O_2(aq)/H_2O, pe^o=21.50*

In this case, the lines for activity of OH⁻ and H₂O are easy to draw. The line for O₂(aq) can then be developed directly from the Nernst equation:

$$pe_{O_2(aq)/H_2O} = pe^o - \frac{1}{4}\log\frac{\{H_2O\}^2}{\{O_2(aq)\}} - \frac{4}{4}pH$$

$$= 21.50 - \frac{1}{4}\log\frac{(1.0)^2}{\{O_2(aq)\}} - 7.5$$

$$\log\{O_2(aq)\} = -56.00 + 4\,pe$$