Redox Titrations:

- *Imagine a system with all redox couples in an oxidized form, and then titrating with electrons*
  - *All oxidized species combine with the newly available electrons, but species with greatest affinity for electrons get reduced first; these are species with highest "local" pe*
  - *To a good approximation, all of one oxidized species becomes reduced before the next most attractive species (with the next highest local pe) starts acquiring electrons*
  - *Process continues until pe of all couples is so low that newly added electrons are at same energy level as existing ones*

Redox Titrations: How to "add electrons"?

- *To add H^+ in an acid titration, we add a strong acid – one that has a strong tendency to donate its* H^+*, as indicated by a very low pK_a, so…*
- *To add electrons, we add a strong reductant – one that has a strong tendency to donate its e^-, as indicated by a very low local pe.*
- *In nature, organic matter is the most commonly available reductant with a very low local pe, and the oxidized species with progressively lower local pe's tend to be* O_2(*aq*), NO_3^-, Fe(III)*,* Mn(IV)*,* SO_4^{2-}*, and other organic molecules.*
- *Similarly, a titration with an electron acceptor* (*e.g.,* O_2) *would oxidize organic matter,* S(–II), Mn(II), Fe(II), *and* NH_4^+ *in sequence, if thermodynamics controlled behavior.*

Sequential Redox Reactions in Time and Space

- *Wastewater treatment – Oxidation of organics coupled to reduction of O_2, and then coupled to reduction of NO_3^- once almost all the O_2 is consumed.*
- *Diffusion of organics, oxygen, nitrate, and sulfate into sediments, where Fe(III) and Mn(IV) already reside (as $Fe(OH)_3(s)$ and $MnO_2(s)$, respectively).*

	pe^o	pe^o (W)
$O_2(aq)$/ H_2O	21.5	14.5
NO_3^-/ $N_2(g)$	21.02	12.63
$MnO_2(s)$ / Mn^{2+}	20.80	6.80
$Fe(OH)_3(s)$ / Fe^{2+}	17.92	–3.08
SO_4^{2-}/ HS^-	4.21	–3.67
Ac^-/ CH_4 + HCO_3^-	2.89	–4.98

Example: Problem 9.8

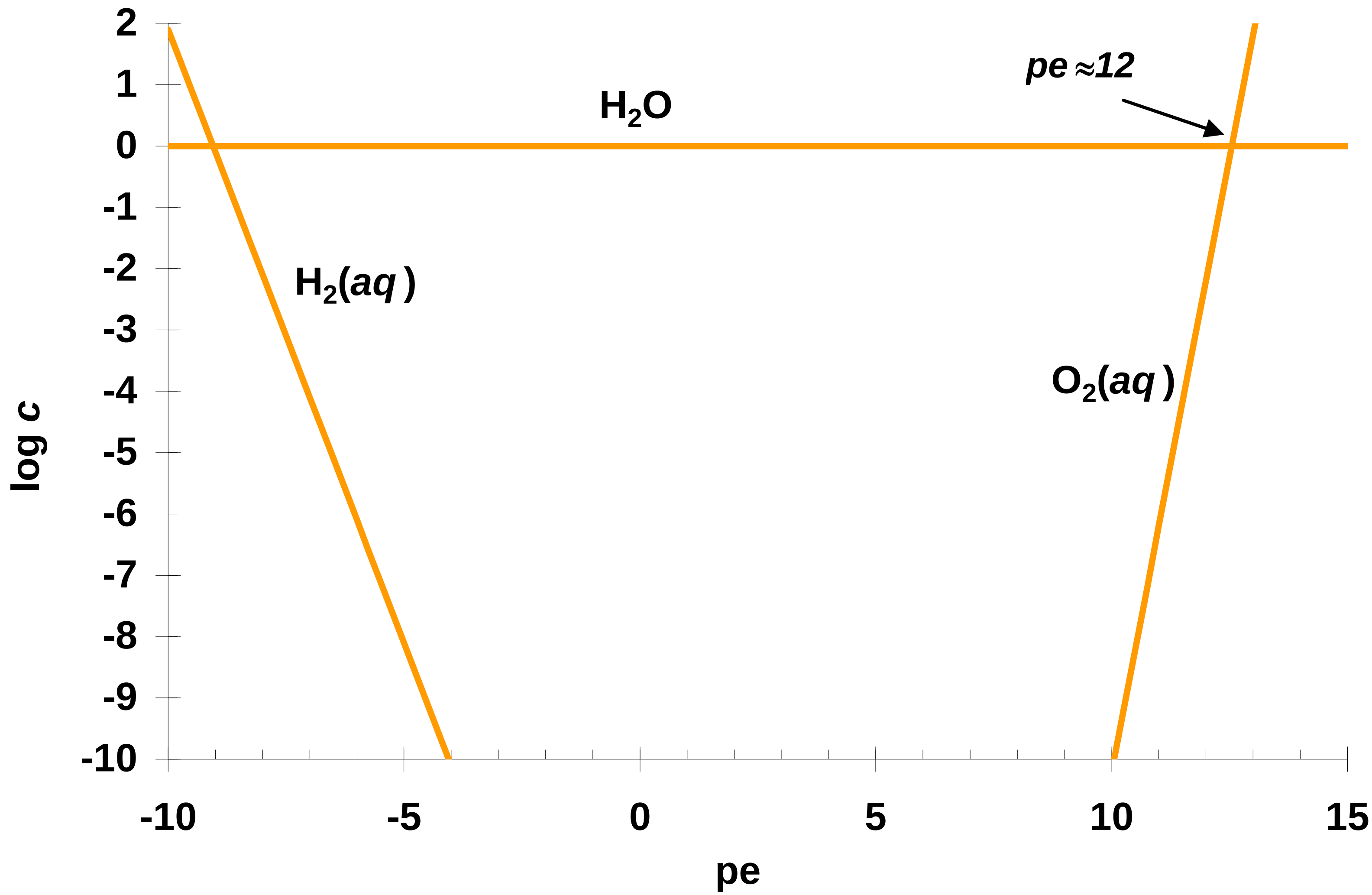
During turnover of a lake, reduced bottom water is mixed with oxidized surface water. Some major constituents of each solution are:

- *Bottom water: 1.5e–3 TOTFe(II), 3.0e–4 TOTS(–II), 1.0e–3 TOTS(VI)*
- *Surface water: 3.0e–4 O_2(aq), 1.2e–4 TOTN(V), 1.3e–3 TOTS(VI)*

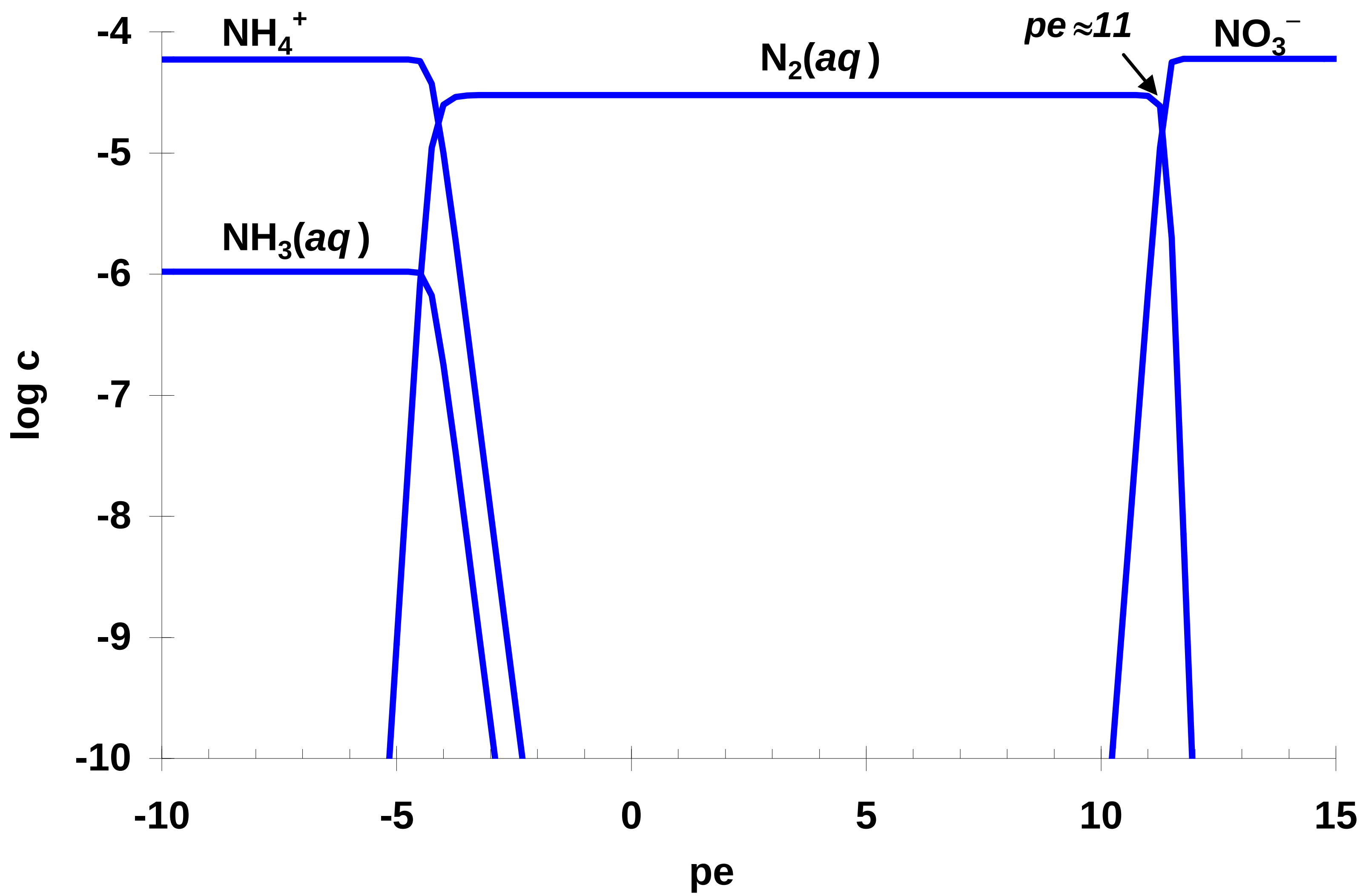
Plot a log c – pe diagram a 1:1 mixture of surface and bottom water, assuming the pH is 7.5 and no gas/liquid exchange. Consider Fe(II), Fe(III), S(–II), S(VI), N(–III), N(0), and N(V).

Write the TOTe equation using H_2O, Fe^{2+}, SO_4^{2-}, and N_2(aq) as components, and find the equilibrium composition of the solution.

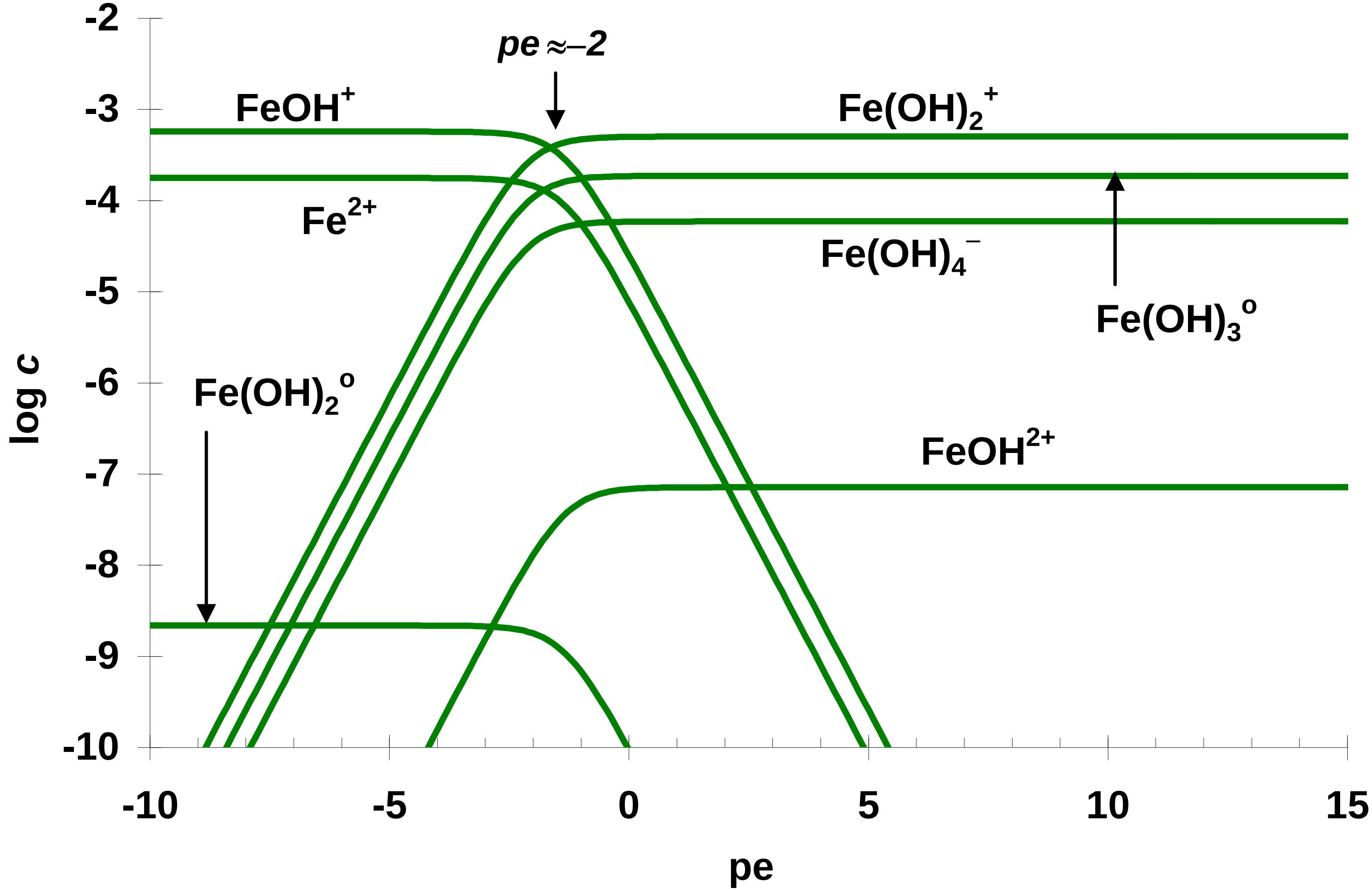
O(0)/O(–II) and H(I)/H(0) Redox Groups



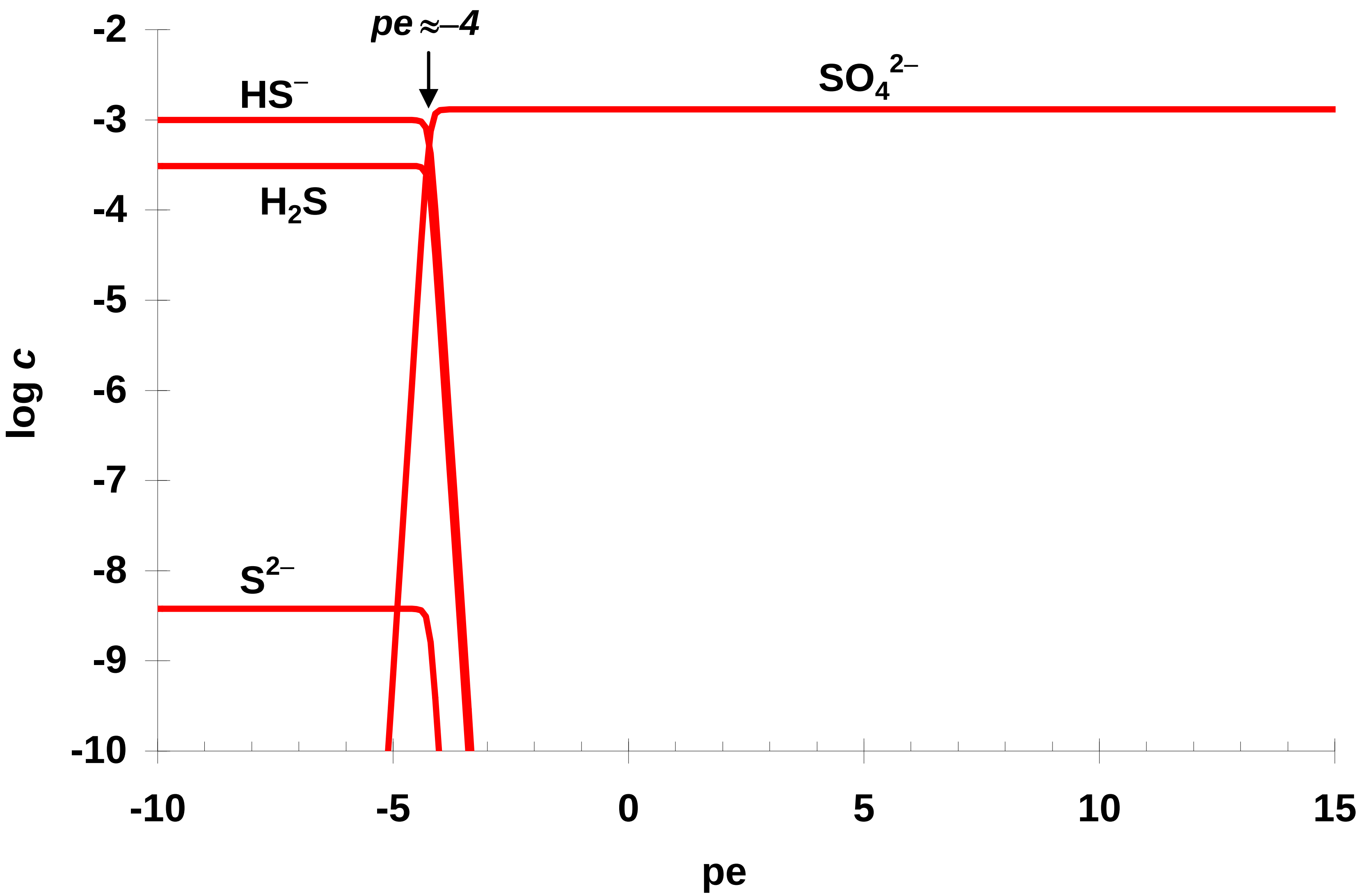
N(V)/N(0)/N(–III) Redox Group

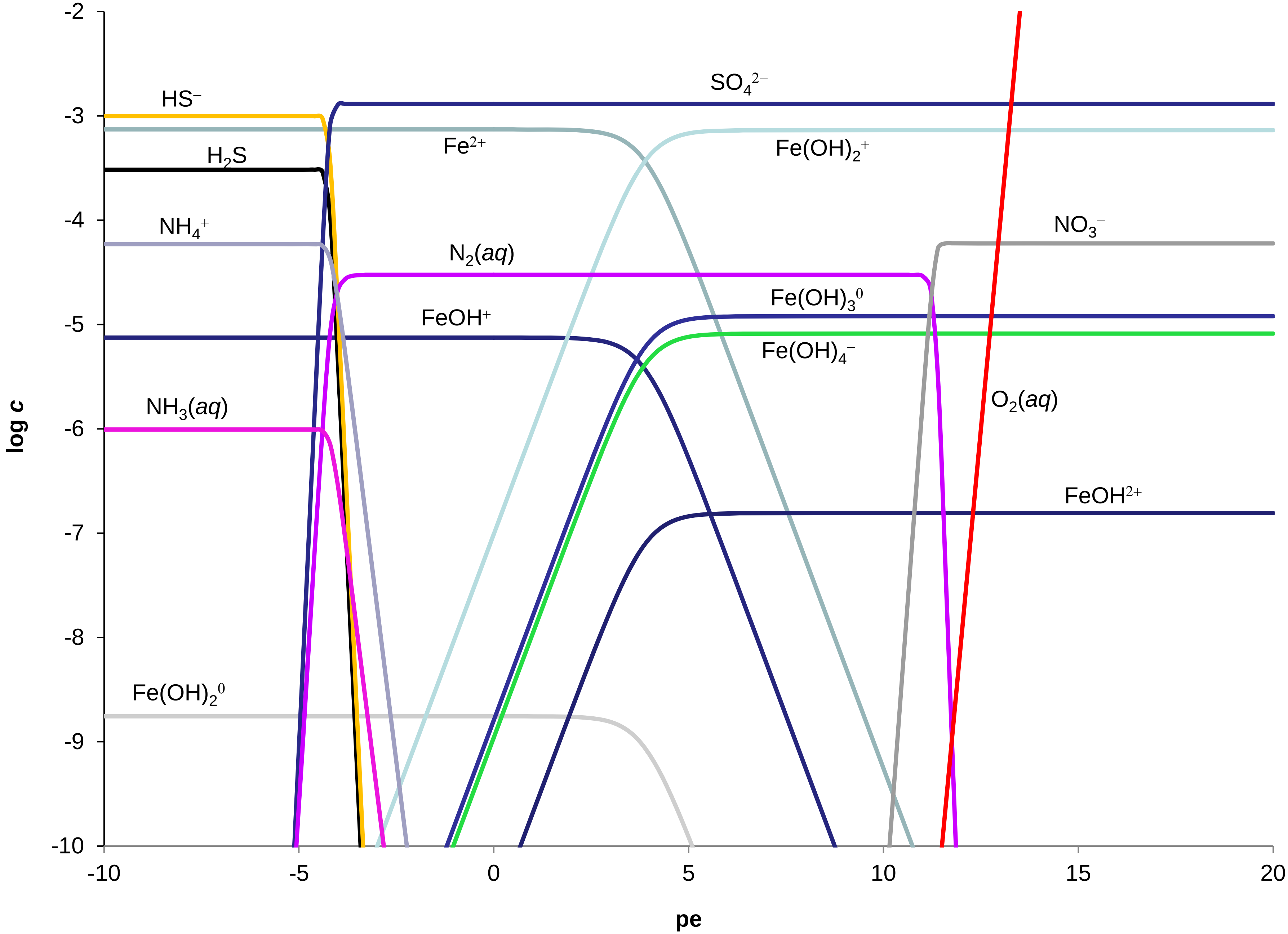


Fe(III)/Fe(II) Redox Group



S(VI)/S(–II) Redox Group





log c
pe
-2
-3
-4
-5
-6
-7
-8
-9
-10
-10
-5
0
5
10
15
20
HS⁻
H₂S
NH₄⁺
NH₃(aq)
Fe(OH)₂⁰
SO₄²⁻
Fe²⁺
N₂(aq)
FeOH⁺
Fe(OH)₂⁺
Fe(OH)₃⁰
Fe(OH)₄⁻
NO₃⁻
O₂(aq)
FeOH²⁺

Equilibrium species tableau

	H_2O	H^+	e^-	Fe^{2+}	SO_4^{2-}	$N_2(aq)$
H_2O	1	0	0	0	0	0
H^+	0	1	0	0	0	0
e^-	0	0	1	0	0	0
Fe(II)	*var*	*var*	0	1	0	0
S(VI)	0	0	0	0	1	0
$N_2(aq)$	0	0	0	0	0	1
OH^-	1	–1	0	0	0	0
$O_2(aq)$	2	–4	–4	0	0	0
$H_2(aq)$	0	2	2	0	0	0
Fe(III)	*var*	*var*	–1	1	0	0
S(–II)	*var*	*var*	8	0	1	0
N(–III)	0	*var*	3	0	0	0.5
N(V)	3	–6	–5	0	0	0.5

$$TOTe_{\mathrm{eq}} = (-4)\left(\mathrm{O}_2\left(aq\right)\right) + 2\left(\mathrm{H}_2\left(aq\right)\right) - \left(\mathrm{Fe}\left(\mathrm{III}\right)\right) + 8\left(\mathrm{S}\left(-\mathrm{II}\right)\right)$$
$$+3\left(\mathrm{N}\left(-\mathrm{III}\right)\right) - 5\left(\mathrm{N}\left(-\mathrm{V}\right)\right)$$

Input species tableau

	H_2O	H^+	e^-	Fe^{2+}	SO_4^{2-}	$N_2(aq)$	*Conc'n*
H_2O	1	0	0	0	0	0	0
H^+	0	1	0	0	0	0	0
e^-	0	0	1	0	0	0	0
Fe(II)	*var*	*var*	0	1	0	0	$7.5\text{x}10^{-4}$
S(VI)	0	0	0	0	1	0	$1.15\text{x}10^{-3}$
$N_2(aq)$	0	0	0	0	0	1	0
OH^-	1	–1	0	0	0	0	0
$O_2(aq)$	2	–4	–4	0	0	0	$1.5\text{x}10^{-4}$
$H_2(aq)$	0	2	2	0	0	0	0
Fe(III)	*var*	*var*	–1	1	0	0	0
S(–II)	*var*	*var*	8	0	1	0	$1.5\text{x}10^{-4}$
N(–III)	0	*var*	3	0	0	0.5	0
N(V)	3	–6	–5	0	0	0.5	$6.0\text{x}10^{-5}$

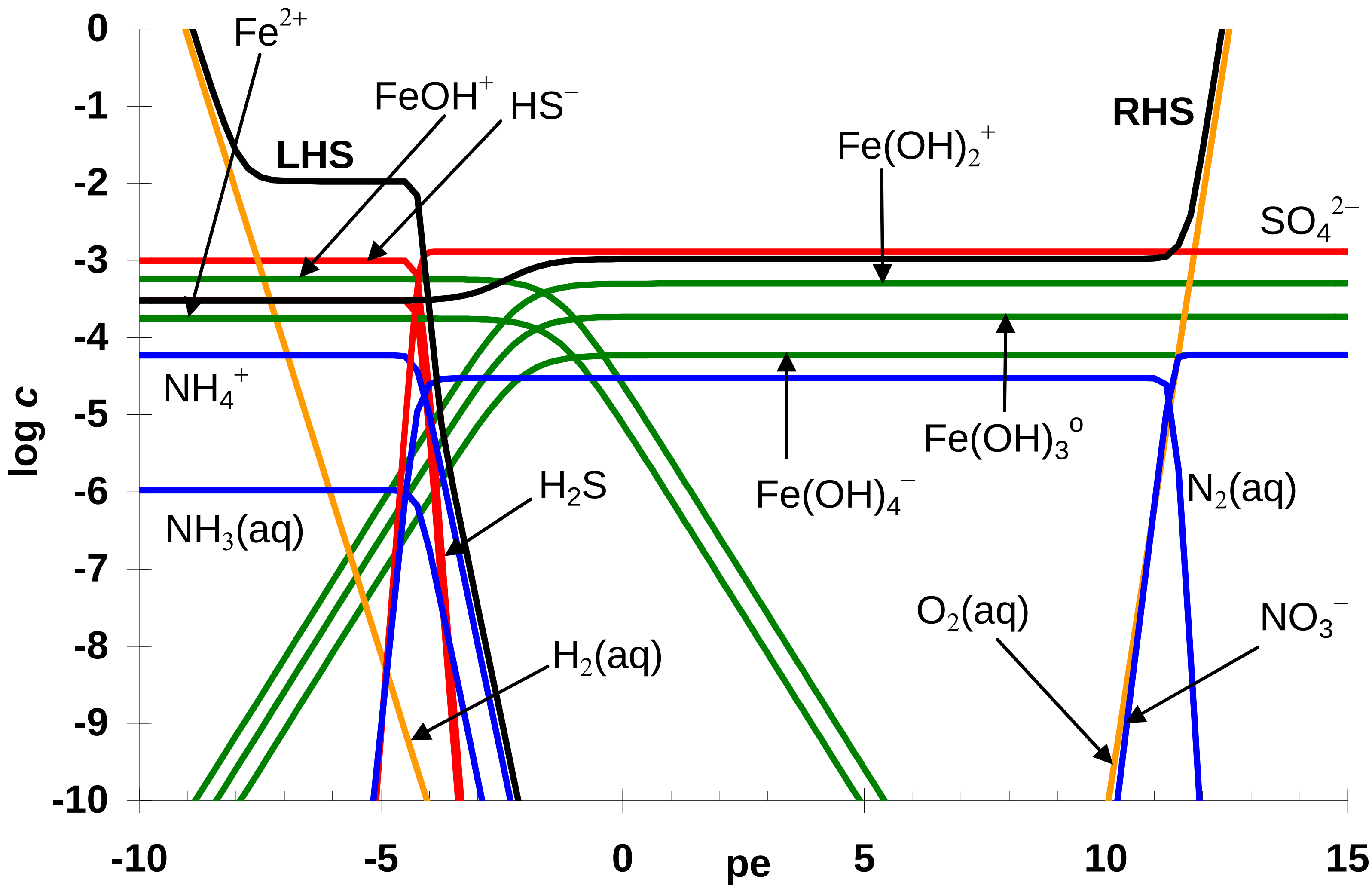
$$TOTe_{\text{in}} = (-4)\left(1.5\text{x}10^{-4}\right) + (8)\left(1.5\text{x}10^{-4}\right) + (-5)\left(6.0\text{x}10^{-5}\right) = 3.0\text{x}10^{-4}$$

TOTe equation: $TOTe_{\mathrm{eq}} = TOTe_{\mathrm{in}}$

$$(-4)\left(\mathrm{O_2}\,(aq)\right) + 2\left(\mathrm{H_2}\,(aq)\right) - \left(\mathrm{Fe}\,(\mathrm{III})\right) + 8\left(\mathrm{S}\,(-\mathrm{II})\right) + 3\left(\mathrm{N}\,(-\mathrm{III})\right) - 5\left(\mathrm{N}\,(-\mathrm{V})\right)$$
$$= 3.0\mathrm{x}10^{-4}$$

$$2\left(\mathrm{H_2}\,(aq)\right) + 8\left(\mathrm{S}\,(-\mathrm{II})\right) + 3\left(\mathrm{N}\,(-\mathrm{III})\right)$$
$$= 3.0\mathrm{x}10^{-4} + \left(\mathrm{Fe}\,(\mathrm{III})\right) + 5\left(\mathrm{N}\,(-\mathrm{V})\right) + 4\left(\mathrm{O_2}\,(aq)\right)$$

$$2\left(\mathrm{H_2}\left(aq\right)\right)+8\left(\mathrm{S}\left(-\mathrm{II}\right)\right)+3\left(\mathrm{N}\left(-\mathrm{III}\right)\right)$$
$$=3.0\mathrm{x}10^{-4}+\left(\mathrm{Fe}\left(\mathrm{III}\right)\right)+5\left(\mathrm{N}\left(-\mathrm{V}\right)\right)+4\left(\mathrm{O_2}\left(aq\right)\right)$$



$$2\left(\mathrm{H_2}\left(aq\right)\right)+8\left(\mathrm{S}\left(-\mathrm{II}\right)\right)+3\left(\mathrm{N}\left(-\mathrm{III}\right)\right)$$
$$=3.0\mathrm{x}10^{-4}+\left(\mathrm{Fe}\left(\mathrm{III}\right)\right)+5\left(\mathrm{N}\left(-\mathrm{V}\right)\right)+4\left(\mathrm{O_2}\left(aq\right)\right)$$