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

	H_2O	H^+	e^-	Fe^{2+}	log K
H_2O	1	0	0	0	0.00
H^+	0	1	0	0	0.00
e^-	0	0	1	0	0.00
Fe^{2+}	0	0	0	1	0.00
OH^-	1	–1	0	0	–14.00
$FeOH^+$	1	–1	0	1	–9.40
$Fe(OH)_2^o$	2	–2	0	1	–20.49
$Fe(OH)_3^-$	3	–3	0	1	–30.99
Fe^{3+}	0	0	–1	1	–13.03
$FeOH^{2+}$	1	–1	–1	1	–15.05
$Fe(OH)_2^+$	2	–2	–1	1	–18.78
$Fe(OH)_3^o$	3	–3	–1	1	–28.03
$Fe(OH)_4^-$	4	–4	–1	1	–35.73
$O_2(aq)$	2	–4	–4	0	–86.00

	H_2O	H^+	e^-	Fe^{2+}
H_2O	1	0	0	0
H^+	0	1	0	0
e^-	0	0	1	0
Fe(II)	n_{OH}	$-n_{OH}$	0	1
OH^-	1	–1	0	0
Fe(III)	n_{OH}	$-n_{OH}$	–1	1
$O_2(aq)$	2	–4	–4	0

Equilibrium species tableau

	H_2O	**H^+**	**e^-**	**Fe^{2+}**
H_2O	1	0	0	0
H^+	0	1	0	0
e^-	0	0	1	0
Fe(II)	n_{OH}	$-n_{OH}$	0	1
OH^-	1	–1	0	0
Fe(III)	n_{OH}	$-n_{OH}$	–1	1
$O_2(aq)$	2	–4	–4	0

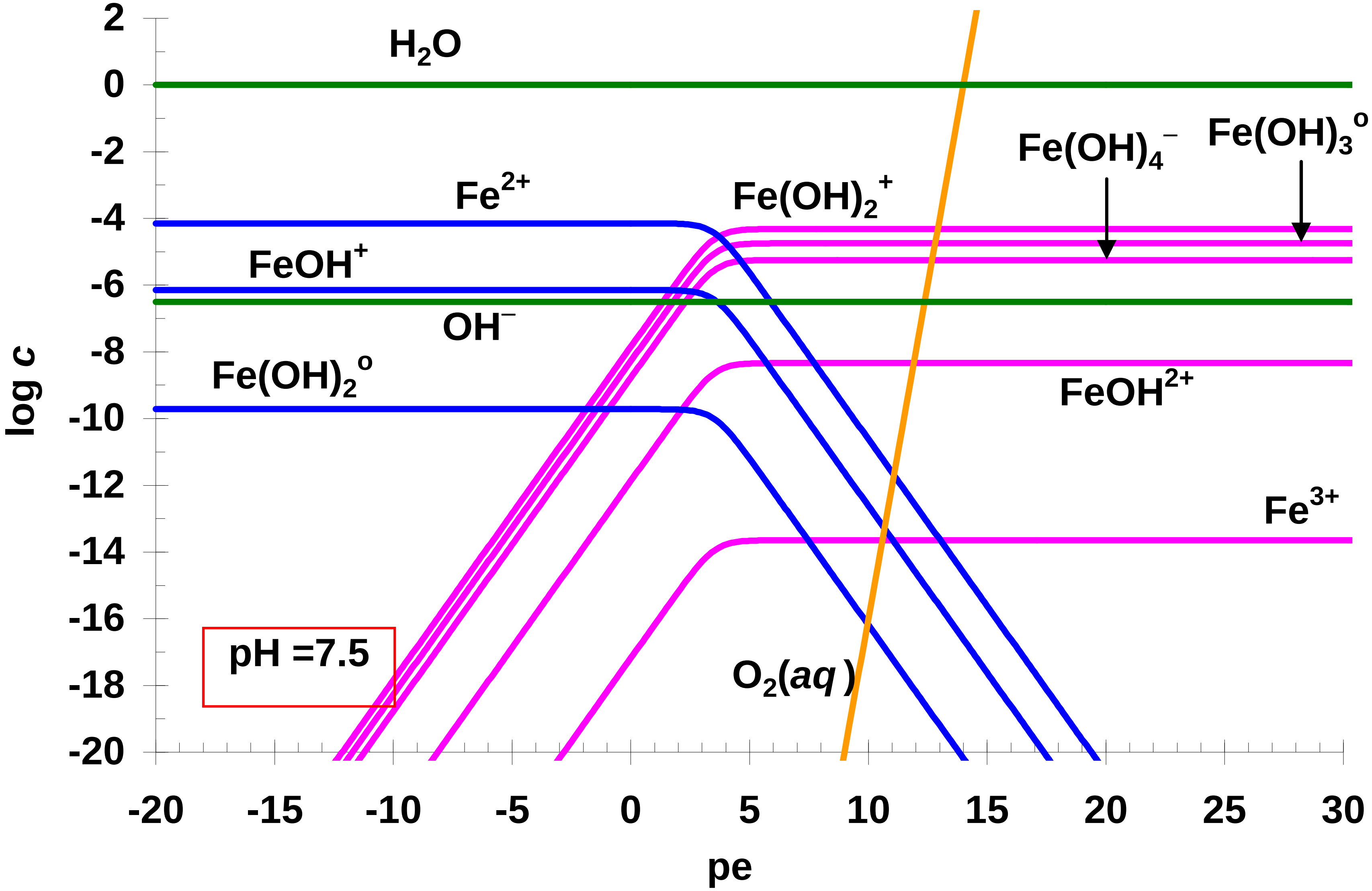
Input species tableau

	H_2O	**H^+**	**e^-**	**Fe^{2+}**	**Conc**
Inputs					
H^+	0	1	0	0	$10^{-7.50}$
OH^-	1	–1	0	0	$10^{-6.50}$
Fe(II)	n_{OH}	$-n_{OH}$	0	1	$10^{-4.14}$
Fe(III)	n_{OH}	$-n_{OH}$	–1	1	$10^{-6.75}$
$O_2(aq)$	2	–4	–4	0	$10^{-4.20}$

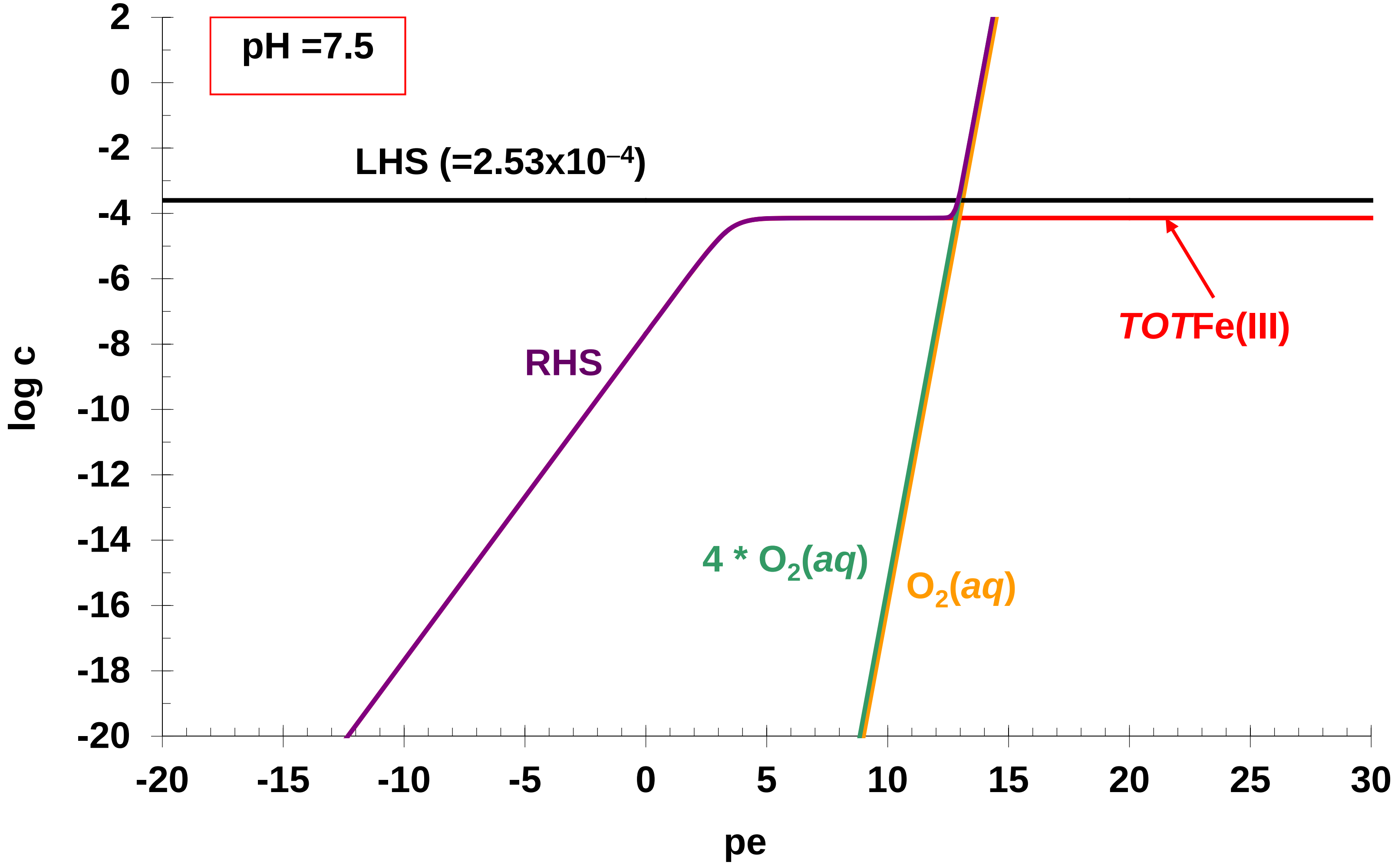
TOTe equation:

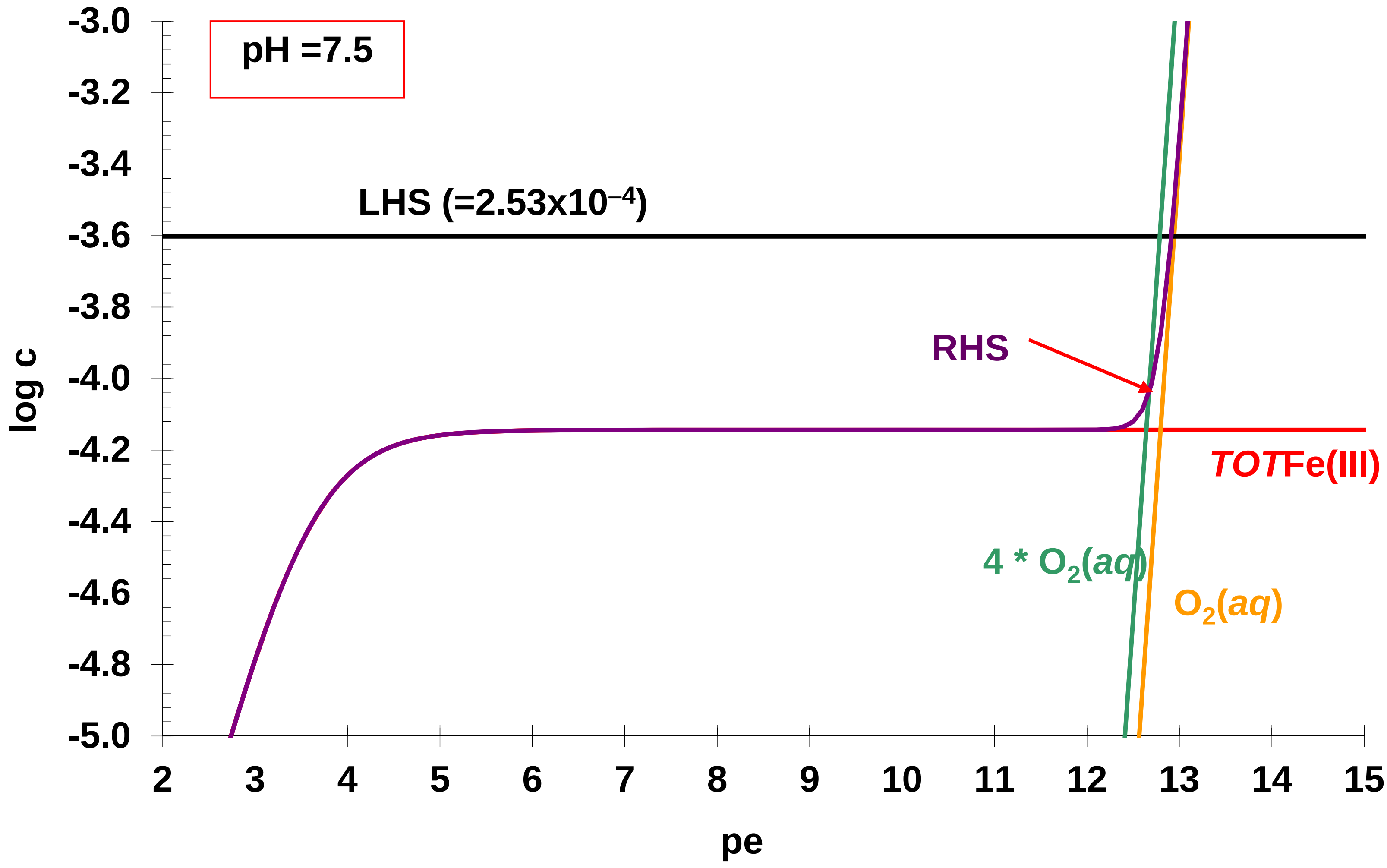
$$(-1)\left(10^{-6.75}\right)+(-4)\left(10^{-4.20}\right)=\cancel{\left[e^-\right]_{eq}}-TOT\mathrm{Fe}\left(\mathrm{III}\right)_{eq}-4\left[\mathrm{O}_2\left(aq\right)\right]_{eq}$$

$$2.53\mathrm{x}10^{-4}=TOT\mathrm{Fe}\left(\mathrm{III}\right)_{eq}+4\left[\mathrm{O}_2\left(aq\right)\right]_{eq}$$



pH =7.5
H_2O
Fe^{2+}
$FeOH^+$
OH^-
$Fe(OH)_2^o$
$Fe(OH)_2^+$
$Fe(OH)_4^-$
$Fe(OH)_3^o$
$FeOH^{2+}$
Fe^{3+}
$O_2(aq)$
log c
pe
2
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
-20
-15
-10
-5
0
5
10
15
20
25
30


pH =7.5
LHS (=2.53x10⁻⁴)
RHS
TOTFe(III)
4 * O2(aq)
O2(aq)
log c
2
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
-20
-15
-10
-5
0
5
10
15
20
25
30
pe



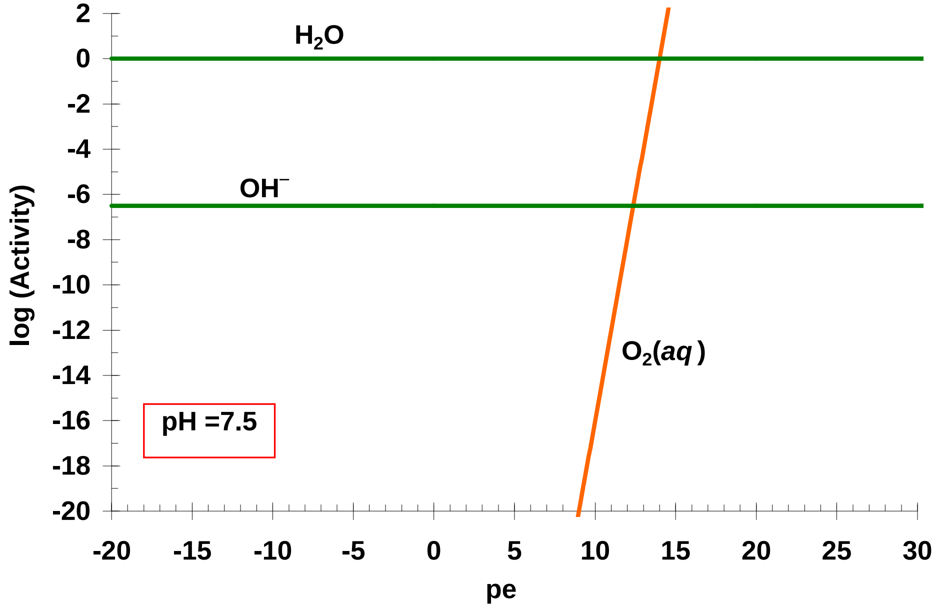
Equilibrium pe = 12.91;

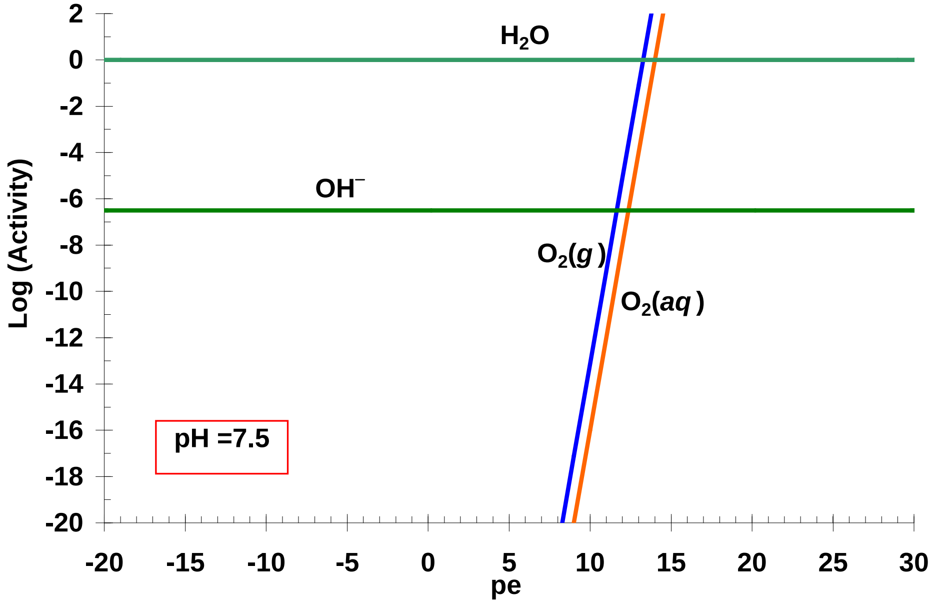
Essentially all Fe(II) *oxidized, most* $O_2(aq)$ *unreacted*

Consider again the $O_2(aq)/H_2O$ equilibrium. The reaction can be combined with log K for the $O_2(aq)/O_2(g)$ reaction to yield:

$$pe = pe^{o}_{O_2(g)/H_2O} - \frac{1}{4}\log\frac{\{\cancel{H_2O}\}}{\{O_2(g)\}} - \frac{4}{4}\mathrm{pH}$$

$$\log\{O_2(g)\} = -4pe^{o}_{O_2(g)/H_2O} + 4pe + 4\mathrm{pH}$$





The preceding application of the Nernst equation indicates the activity (i.e., partial pressure) of $O_2(g)$ *that is in equilibrium with an aqueous solution at any pe and pH. For* $\{O_2(g)\} = 0.21$, *we find the pe that a solution must have at any given pH to be in equilibrium with atmospheric* O_2:

$$pe = \frac{1}{4}\log\left\{O_2\left(g\right)\right\} + pe^{o}_{O_2(g)/H_2O} - \mathrm{pH}$$

$$= \frac{1}{4}\log\left(0.21\right) + 20.78 - \mathrm{pH}$$

$$= 20.61 + \mathrm{pH}$$

Similarly, if $\{O_2(g)\}$=1.0, *we find the pe that a solution must have at any given pH to be in equilibrium with pure* O_2 *at* P_{tot} *= 1.0 atm*

$$pe = \frac{1}{4}\log\left(1.0\right) + 20.78 - \mathrm{pH}$$

$$= 20.78 - \mathrm{pH}$$

If P_{tot} *is less than the* $P_{O2(g)}$ *that would be in equilibrium with the solution,* $O_2(g)$ *bubbles form spontaneously. As long as this situation persists, the process continues, with the water becoming oxidized and being removed from the solution. The process is similar to boiling, in which case the partial pressure of* H_2O *exceeds the total pressure on the solution, and bubbles of water vapor form spontaneously.*

An analogous process occurs if the pe is lowered, and the water is reduced to $H_2(g)$ *via the* $H_2O/H_2(g)$ *couple. The reaction is commonly combined with* K_w *to show it as reduction of* H^+*:*

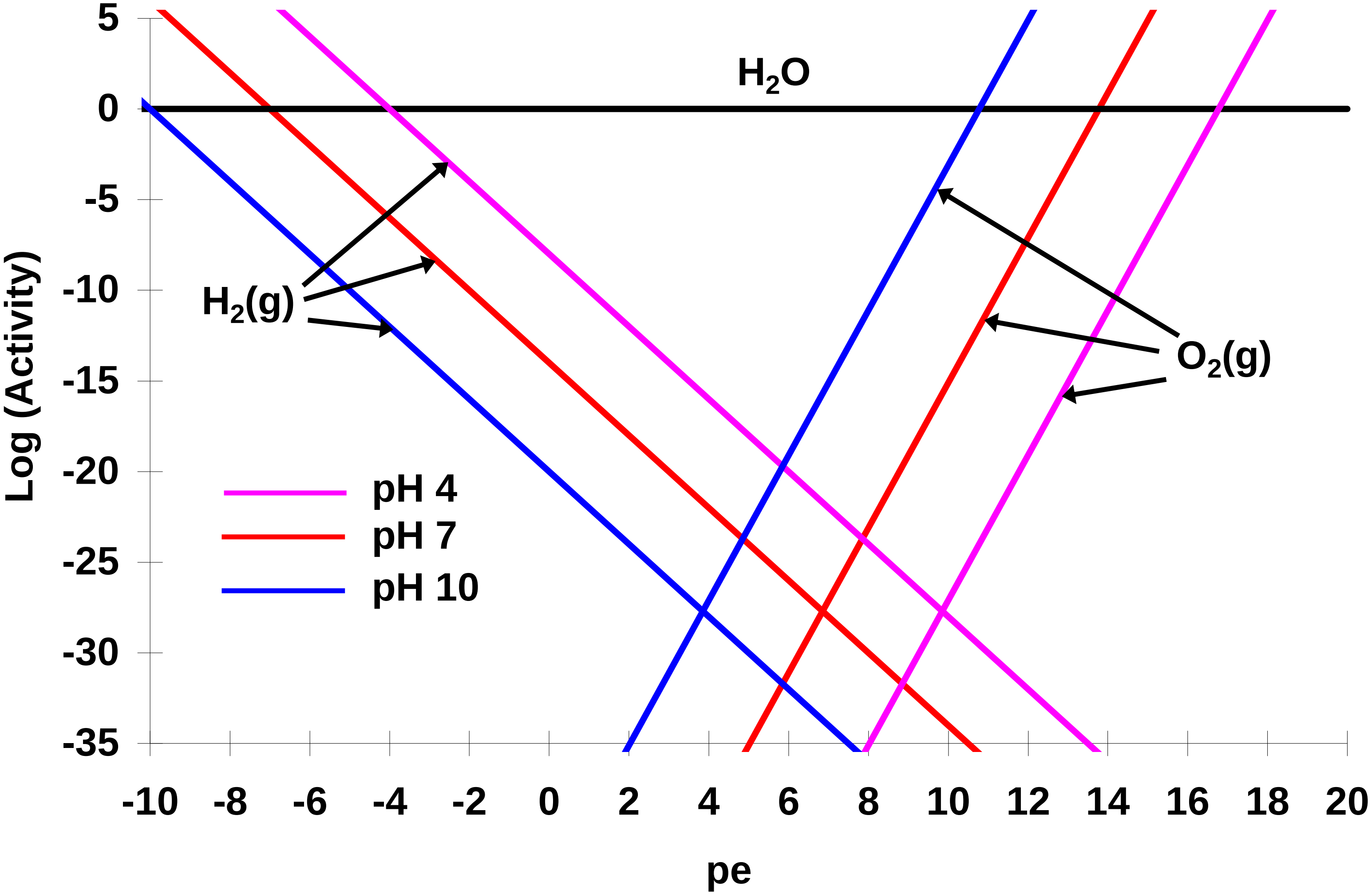
$$\begin{array}{l} 2H_2O + 2e^- \leftrightarrow H_2(g) + 2OH^- \\ 2H^+ + 2OH^- \leftrightarrow 2H_2O \\ \hline 2H^+ + 2e^- \leftrightarrow H_2(g) \end{array}$$

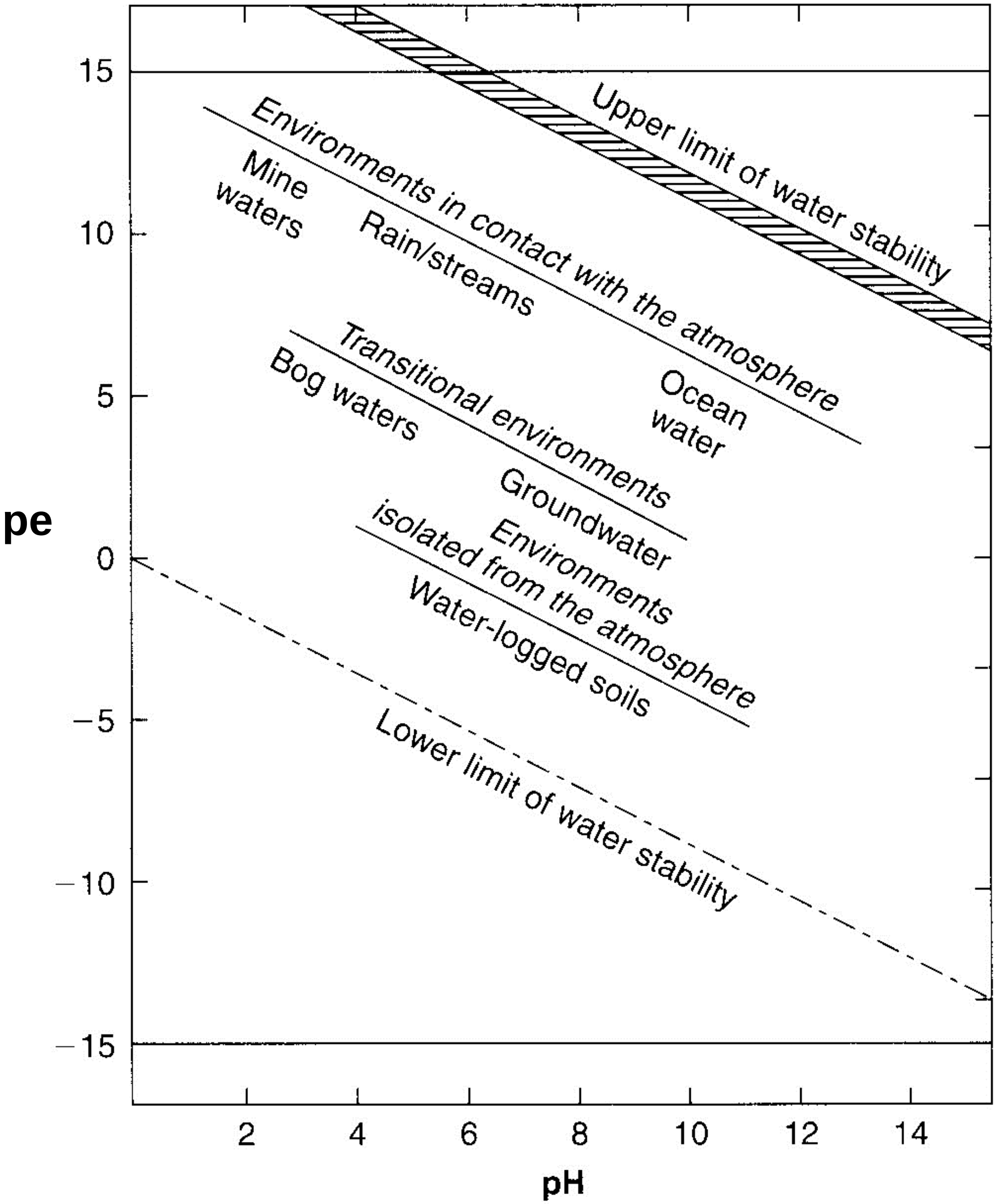
$$pe = \cancel{pe^o_{H^+/H_2(g)}} - \frac{1}{2}\log\{H_2(g)\} - \frac{2}{2}pH$$

$$= -\frac{1}{2}\log\{H_2(g)\} - pH$$

$$\log\{H_2(g)\} = -2pe - 2pH$$

Lines indicate equilibrium activity of $H_2(g)$ *or* $O_2(g)$ *at given pe and pH. Limit of stability of water is where this activity equals 1.0*





Lines for upper and lower stability limits of water are collections of (pe, pH) points where activities of O_2(*g*) *and* H_2(*g*) *equal 1.0 on previous figure*

$$pe = -\frac{1}{2}\log\{\mathrm{H}_2(g)\} - \mathrm{pH}$$

For equilibrium with atmospheric $H_2(g)$ $(P_{H2}=5x10^{-7})$ *or* $H_2(g)$ *at a partial pressure of 1.0 atm, the pe's are:*

For equilibrium with atmospheric $H_2(g)$*:* $$pe = -3.15 - \mathrm{pH}$$

For equilibrium with $H_2(g)$ *at* $P_{H2}=1$ *atm:* $$pe = -\mathrm{pH}$$

Again, if the partial pressure of the gas (in this case, $H_2(g)$*) is greater than the total pressure on the solution, bubbles will form spontaneously and the solution is unstable*

The pe's that a solution must have at any given pH to be in equilibrium with atmospheric $H_2(g)$ *and* $O_2(g)$ *are:*

For equilibrium with atmospheric $H_2(g)$*:* $pe = -3.15 - \mathrm{pH}$

For equilibrium with atmospheric $O_2(g)$*:* $pe = 20.78 - \mathrm{pH}$

Conclusion: A solution can never be in redox equilibrium with both $O_2(g)$ *and* $H_2(g)$ *at the partial pressures that those gases have in the normal atmosphere. If the concentrations of* $O_2(aq)$ *and* $H_2(aq)$ *are in equilibrium with the atmosphere, those concentrations strongly favor oxidation of the* $H_2(aq)$ *and reduction of the* $O_2(aq)$ *to destroy those species and form* H_2O. *However, if that occurs, the gas/liquid equilibrium replenishes the lost solutes, so the driving force for the redox reaction remains.*

If all the reactions proceeded indefinitely, the $H_2(g)$ *partial pressure would eventually decline by orders of magnitude. In reality, however, the redox reaction is very slow in the absence of a catalyst, and the solution remains out of redox equilibrium.*