

Practice problems using pe-pH speciation diagrams

1. If a water sample has a pH = 6 and is known to contain H_2S as the dominant form of sulfur, what is the predominant speciation of carbon, nitrogen and manganese?

We will need a set of pe/pH diagrams to work from for this question.

Using Fig. 10.5 (p. 246) textbook, we estimate $\text{SO}_4^{2-}/\text{H}_2\text{S}$ boundary at $\text{pe} \sim -3$ at $\text{pH} = 6$

for carbon; CH_4 predominates at $\text{pH} 6$, $\text{pe} -3$

for nitrogen; NH_4^+ predominates at $\text{pH} 6$, $\text{pe} -3$

for manganese; Mn^{2+} " " "

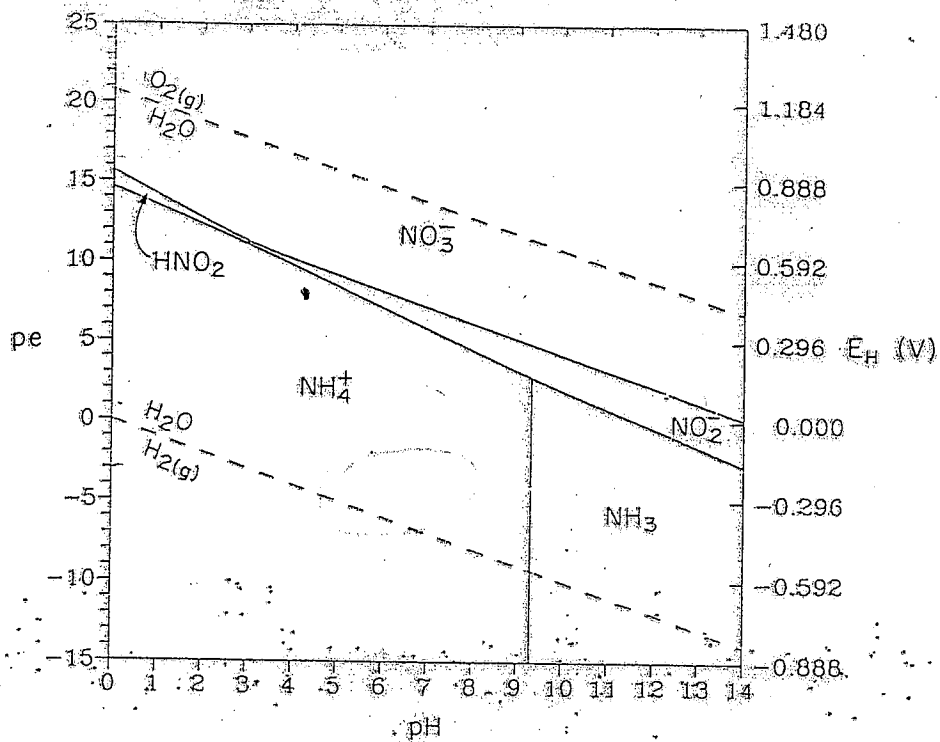


Figure 23.9 pe-pH diagram for aqueous nitrogen at 25°C/1 atm when N₂ is not redox active. Activity corrections are neglected. A line at pH = 3.0 separates the HNO₂ and NO₃⁻ regions. Since all of the forms of nitrogen considered contain the same number of nitrogen atoms (i.e., one), and since no solid forms of nitrogen are considered, the diagram is independent of N_T. The N(II)_T region becomes quite narrow at pH ≈ 3.

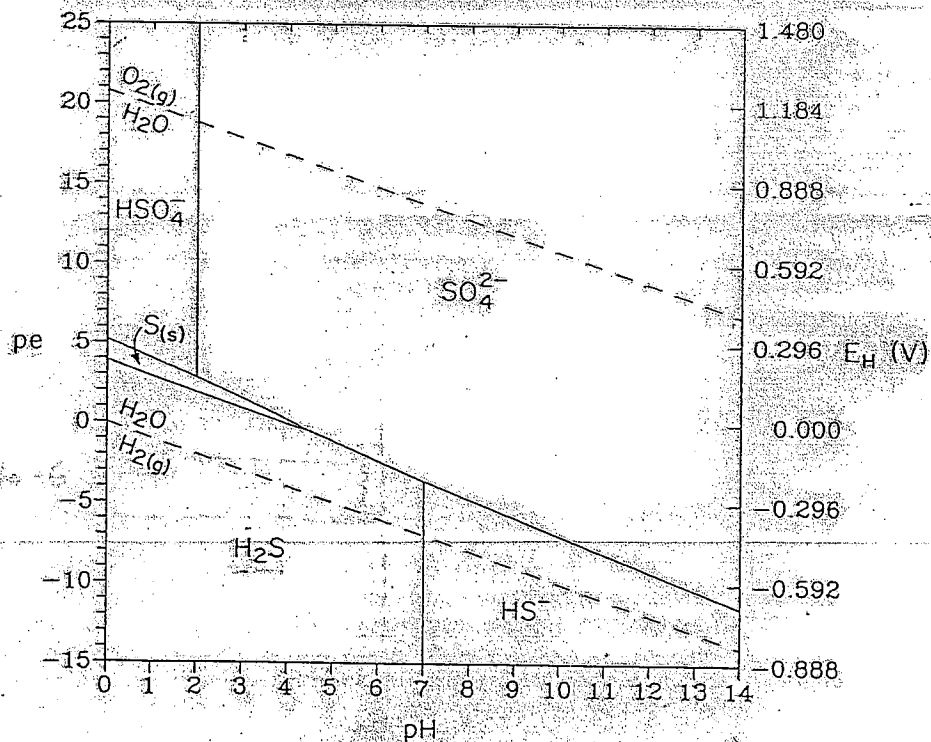


Figure 23.12 pe-pH diagram for aqueous sulfur when S_T = 10⁻³ M and 25°C/1 atm. Activity corrections are neglected. S_(s) is only possible at relatively low pH. As the pe is lowered at any given pH value, the diagram indicates that S(-II) (either as H₂S or as HS⁻) can become the dominant form of sulfur before the in-situ p_{H₂} can reach 1 atm.

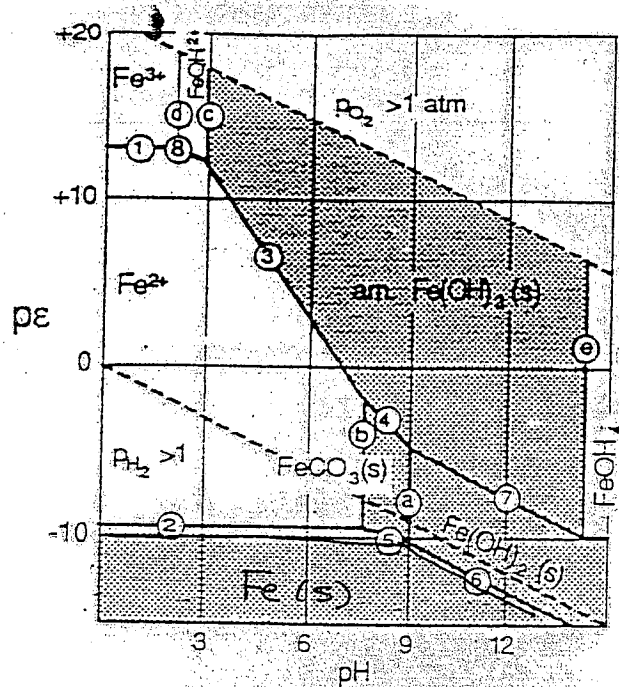


Figure 8.8. Diagram pe versus pH for the system $Fe-CO_2-H_2O$. The solid phases are $Fe(OH)_3$ (amorphous), $FeCO_3$ (siderite), $Fe(OH)_2(s)$, and $Fe(s)$. $C_T = 10^{-3}$ M. Lines are calculated for $Fe(II)$ and $Fe(III) = 10^{-5}$ M ($25^\circ C$). The possible conversion of carbonate to methane at low pe values is ignored.

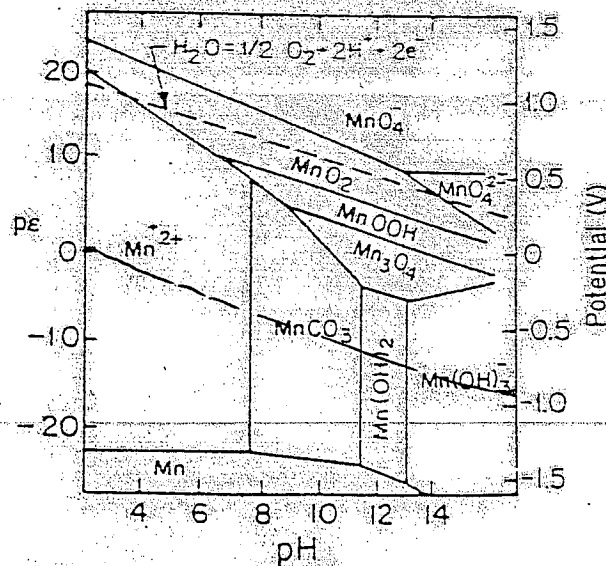


Figure 8.10. pe - pH diagram for the $Mn-CO_2-H_2O$ systems ($25^\circ C$). The solid phases considered are $Mn(OH)_2(s)$ (pyrochroite), $MnCO_3(s)$ (rhodochrosite), $Mn_3O_4(s)$ (hausmannite), γ - $MnOOH(s)$ (manganite), and γ - $MnO_2(s)$ (nsutite). $C_T = 1 \times 10^{-3}$ M and $Mn_T = 1 \times 10^{-5}$ M.

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2. If a sediment contains freshly precipitated $\text{FeCO}_3(\text{s})$ and has a $\text{pH} = 9$, what is the maximum value for the pe of this water?

Using a Pourbaix diagram for iron that includes carbonate species, we see that ~~that~~ the maximum pe value would be

-4

3. Are either iron or manganese metal thermodynamically stable in water? What happens to these metals in water at a pH of 7?

Examining the pourbaix diagrams for iron and manganese, ~~se~~ we see that the metals (oxidation = 0) ~~exist only~~ are thermodynamically stable only well below the reduction boundary for water itself (i.e. $pe = -pH$).

At pH 7, these metals will be oxidized to Fe^{2+} and Mn^{2+} , respectively.

4. Given the speciation diagram for aqueous chlorine species, under what pe/pH conditions is $\text{Cl}_2(\text{aq})$ thermodynamically stable? Are these conditions likely to be maintained in a water sample?

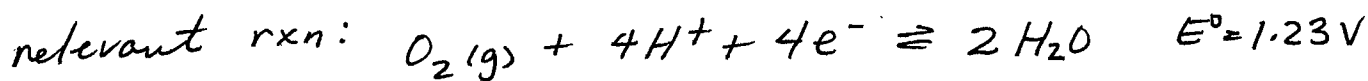
$\text{Cl}_2(\text{aq})$ thermodynamically stable at
 $\text{pH} < 2$ and $\text{pe } 24-26$.

Since this is above the oxidation boundary of water itself, $\text{Cl}_2(\text{aq})$ is not thermodynamically stable in H_2O .

It will react to eventually become Cl^- which is the only speciation for chlorine in water that is thermodynamically stable.

5. Estimate the $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ ratio for water in redox equilibrium with atmospheric $\text{O}_2(\text{g})$ at $\text{pH} = 5.8$.

pe of water in equilibrium w O_2 at $\text{pH} = 5.8$



$$pe^\circ = \frac{1.23\text{V}}{0.0591\text{V}} = 20.8 \quad \text{at std. states}$$

i.e. $P_{\text{O}_2} = 1\text{ atm}$
 $[\text{H}^+] = 1\text{ M}$

but $P_{\text{O}_2} = 0.21\text{ atm}$ at sea-level in dry atmos.

and $[\text{H}^+] = 10^{-5.8} = 1.6 \times 10^{-6}\text{ M}$

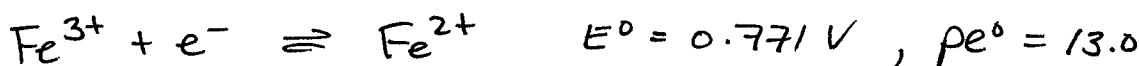
Use $pe = pe^\circ - \frac{1}{n_e} \log Q$

$$= 20.8 - \frac{1}{4} \log \frac{1}{P_{\text{O}_2} \cdot [\text{H}^+]^4}$$

$$= 20.8 - \frac{1}{4} \log (7.6 \times 10^{23})$$

$$= 20.8 - \frac{1}{4} (23.8) = \boxed{14.8 = pe}$$

Now, use this pe to calculate the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio



$$pe = pe^\circ - \frac{1}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

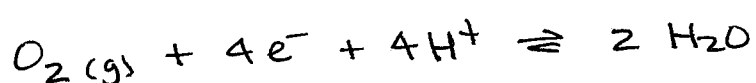
and $\boxed{\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = 0.016}$

14.8 \uparrow \uparrow 13.0

$$\therefore \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = -1.8$$

6. Can Cr^{3+} be oxidized to the more toxic form $\text{Cr}_2\text{O}_7^{2-}$ by aerated water at $\text{pH} = 6.5$? If a water sample originally containing 26 mg/L Cr^{3+} was allowed to equilibrate with aerated water at this pH , estimate the final $[\text{Cr}^{3+}]$.

pe of aerated water at $\text{pH} = 6.5$



$$E^\circ = 1.23 \text{ V}$$

$$pe^\circ = 20.8$$

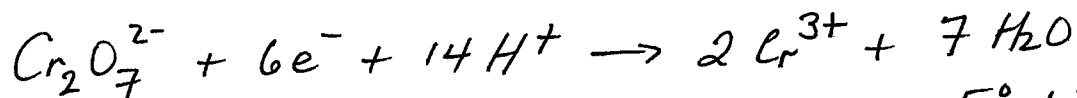
$$pe = pe^\circ - \text{pH} - \frac{1}{4} \log \frac{1}{P_{\text{O}_2}}$$

$$= 20.8 - 6.5 - \frac{1}{4} \left(\log \frac{1}{P_{\text{O}_2}} \right)$$

$$\leftarrow 0.21$$

$pe = 14.1$

Now consider $\text{Cr}_2\text{O}_7^{2-} / \text{Cr}^{3+}$ couple



$$E^\circ = 1.36 \text{ V}$$

$$pe^\circ = 23.0$$

$$pe = pe^\circ - \frac{14}{6} \text{pH} - \frac{1}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}]}$$

14.1

↑
23.0

↑
6.5

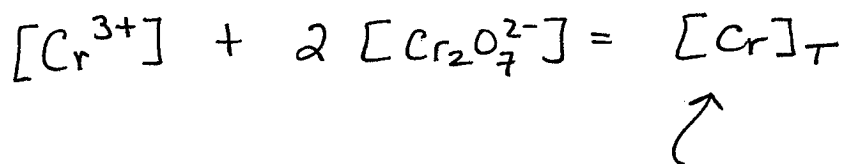
(from above)

$$\therefore \log \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}]} = -37.6$$

$$\text{and } \frac{[\text{Cr}^{3+}]}{[\text{Cr}_2\text{O}_7^{2-}]} = 10^{-37.6} = 1.6 \times 10^{-38}$$

To calculate $[Cr^{3+}]$, we will need another independent equation relating $[Cr^{3+}]$ & $[Cr_2O_7^{2-}]$.

If we assume that these are the only two forms of Cr present, we can write



$$\frac{26 \text{ mg}}{L} \times \frac{1 \text{ mol}}{51,990 \text{ mg}} = 5.0 \times 10^{-4} \text{ M}$$

$$\therefore [Cr^{3+}] + 2 [Cr_2O_7^{2-}] = 5.0 \times 10^{-4} \text{ M}$$

$$\text{and } [Cr_2O_7^{2-}] = \left(\frac{5.0 \times 10^{-4} - [Cr^{3+}]}{2} \right)$$

$$\text{So } \frac{([Cr^{3+}])^2}{(2.5 \times 10^{-4} - 0.5 [Cr^{3+}])} = 1.6 \times 10^{-38}$$

$$\text{let } x = [Cr^{3+}]$$

$$\text{then } \frac{x^2}{2.5 \times 10^{-4} - 0.5x} = 1.6 \times 10^{-38}$$

$$x^2 = 4.0 \times 10^{-42} - 0.80 \times 10^{-38} x$$

$$x^2 + 8.0 \times 10^{-39} - 4.0 \times 10^{-42} = 0$$

Use quadratic formula to solve for x

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where

$$a = 1$$

$$b = 8.0 \times 10^{-39}$$

$$c = -4.0 \times 10^{-42}$$

$$x = \frac{-8.0 \times 10^{-39} \pm \left[(8.0 \times 10^{-39})^2 - 4(-4.0 \times 10^{-42}) \right]^{1/2}}{2}$$

$$= \frac{-8.0 \times 10^{-39} \pm 4.0 \times 10^{-21}}{2}$$

$$= 2.0 \times 10^{-21} \text{ M} \leftarrow [\text{Cr}^{3+}]$$

$$\cancel{[\text{Cr}_2\text{O}_7^{2-}]} = 2.5 \times 10^{-4} \text{ M}$$

(i.e. essentially all Cr^{3+} has been converted to $\text{Cr}_2\text{O}_7^{2-}$ in aerated water!)