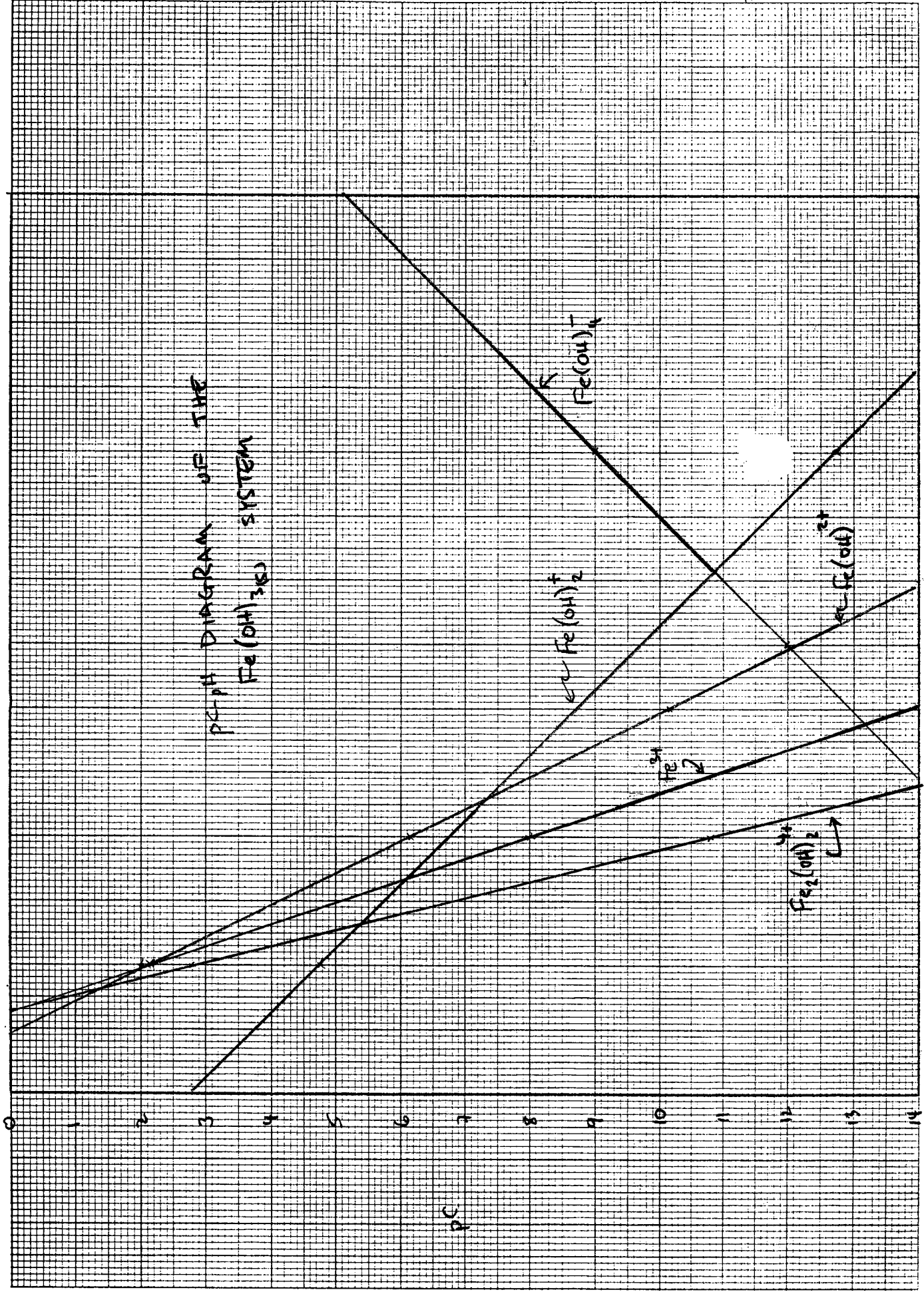


Figure 6.18 Macrocyclic complex formers. (a) Structure of a ferrichrome (desferriferrichrome). One of the strongest complex formers presently known for Fe(III). The iron-binding center is an octahedral arrangement of six oxygen donor atoms of trihydroxamate. It has been suggested that such naturally occurring ferrichromes play an important role in the biosynthetic pathways involving iron. (b) The vitamin B₁₂ (or cyanocobalamin) as a macrocyclic multidentate complex of cobalt in the porphyrin-resembling part. The cyanide group CN⁻ can be exchanged for Cl⁻ or OH⁻. Vitamin B₁₂ is an essential growth factor for several bacteria and auxotrophic phytoplankton.

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

PC-PH DIAGRAM OF THE
 $Fe(OH)_3(s)$ SYSTEM



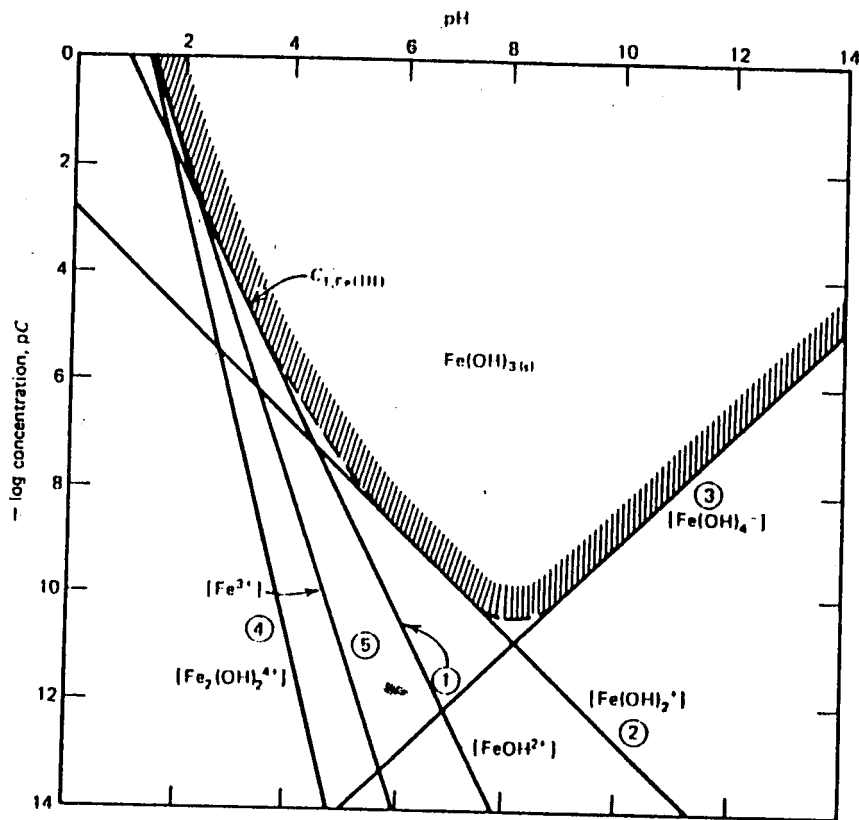


Fig. 6-7. Equilibrium concentrations of hydroxo iron(III) complexes in a solution in contact with freshly precipitated $Fe(OH)_3(s)$ at 25°C.

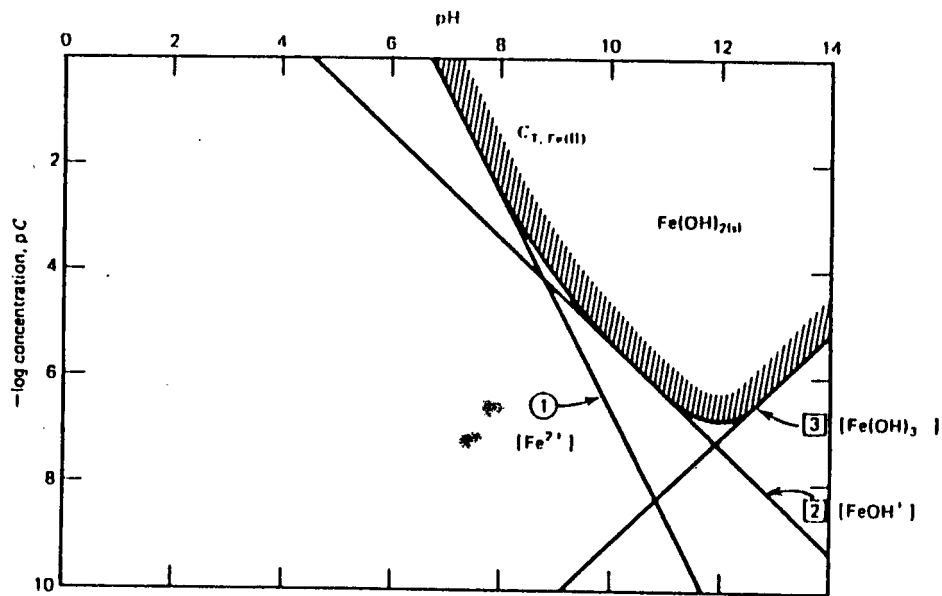


Fig. 6-9. The pC-pH diagram for soluble Fe(II) in equilibrium with $Fe(OH)_2(s)$, $T = 25^\circ C$.

Fig. 11.4 Dissolution equilibrium constant values at 25°C/1 atm for the solids in Figures 11.3-11.7. All constants for initially pure water.

Dissolution Equilibrium	log K
$(am)Fe(OH)_{3(s)} + 3H^+ = Fe^{3+} + 3H_2O$ $\log[Fe^{3+}] = 3.2 - 3pH$	$\log K_{s0} = 3.2$
$(am)Fe(OH)_{3(s)} + 2H^+ = FeOH^{2+} + 2H_2O$ $\log[FeOH^{2+}] = 1.0 - 2pH$	$\log K_{s1} = 1.0$
$(am)Fe(OH)_{3(s)} + H^+ = Fe(OH)_2^+ + H_2O$ $\log[Fe(OH)_2^+] = -2.5 - pH$	$\log K_{s2} = -2.5$
$(am)Fe(OH)_{3(s)} = Fe(OH)_3^0$ $\log[Fe(OH)_3^0] < -12.0$	$\log K_{s3} < -12.0$
$(am)Fe(OH)_{3(s)} + H_2O = Fe(OH)_4^- + H^+$ $\log[Fe(OH)_4^-] = -18.4 + pH$	$\log K_{s4} = -18.4$

Sec. 11.5 Solubility of Metal Oxides, Hydroxides, and Oxyhydroxides

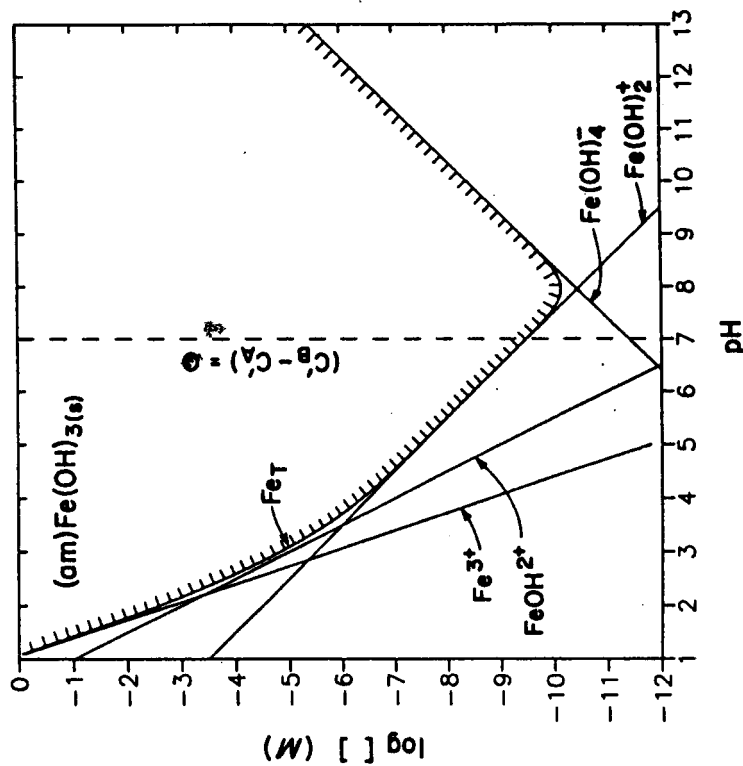


Figure 11.3 Log concentration (M) vs. pH for various Fe(III) species and Fe_T in equilibrium with (am)Fe(OH)3(s) at 25°C/1 atm. Dashed vertical line gives speciation for dissolution into initially pure water (i.e., for (C'_B - C'_A) = 0). Polynuclear species like Fe2(OH)2^4+ have been neglected. Activity corrections neglected (not valid at very low or very high pH).

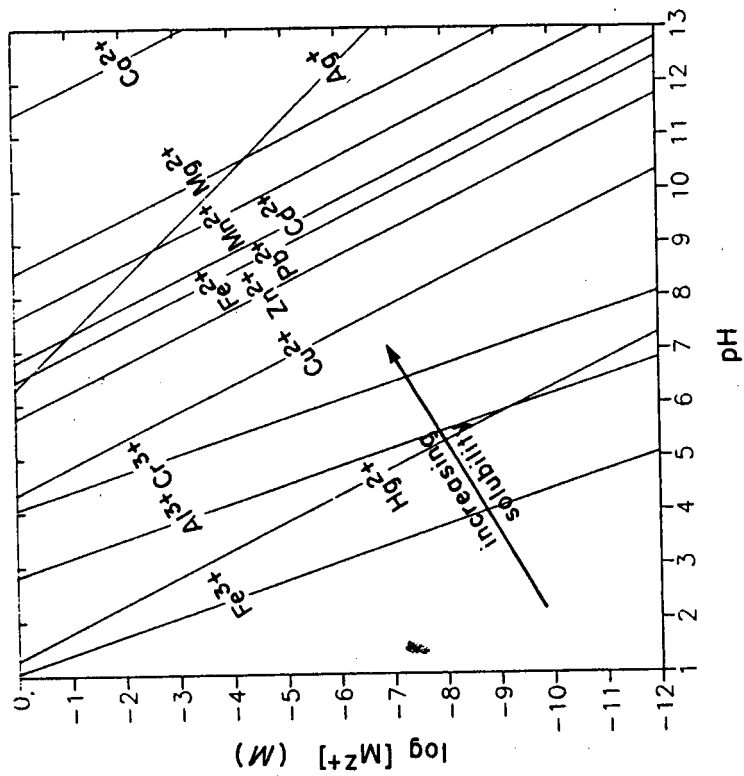


Figure 11.2 Solubility of various metal ions as controlled by their oxides or hydroxides as a function of pH at 25°C/1 atm. Activity corrections neglected (not valid at very low or very high pH).

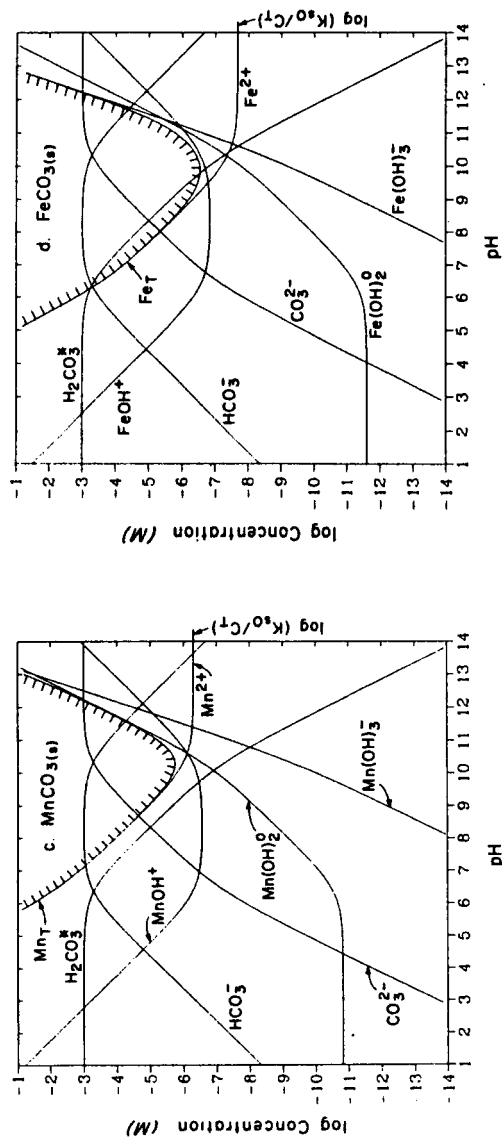
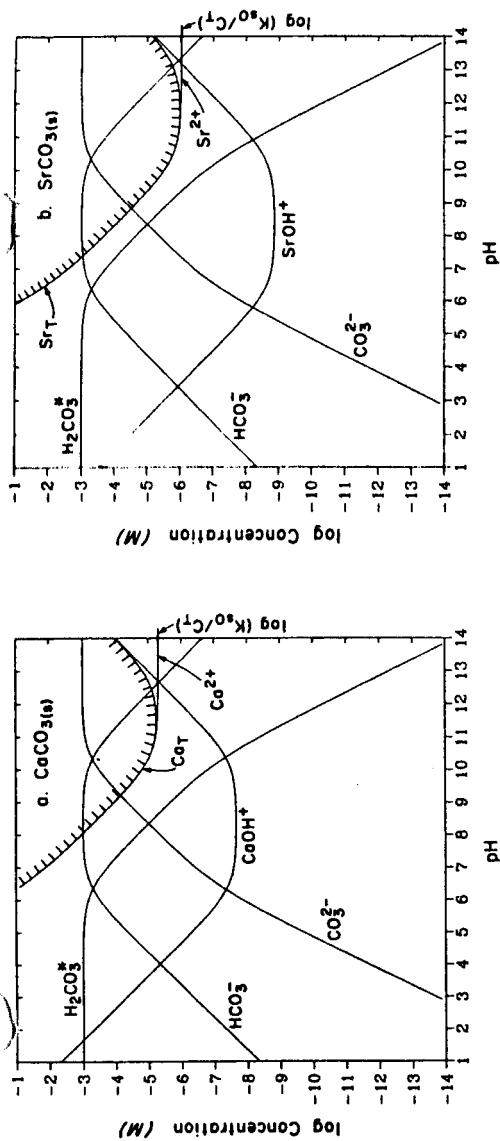


Figure 12.3 Log concentration (M) vs. pH diagrams with $C_T = 10^{-3} M$ (closed system) for four divalent metal carbonates in equilibrium with water at $25^\circ C/1$ atm. Activity corrections neglected (not valid at very low or very high pH). Note that the solubility ($\log M_T$) increases both when the pH becomes very low, and when it becomes very high. When the metal-hydroxo complexes can be neglected in a portion of the region $pH \gg pK_2$, then $\log M_T \approx \log(K_{sp}/C_T)$ in that portion. This type of behavior is observed for $CaCO_{3(s)}$ and $SrCO_{3(s)}$; it is not observed for either $MnCO_{3(s)}$ or $FeCO_{3(s)}$. In this type of $C_T = 10^{-3} M$ system, at $25^\circ C/1$ atm, the four solids are unstable relative to their corresponding solid hydroxides at pH values above 14.1, >14, 10.7, and 10.1, respectively.

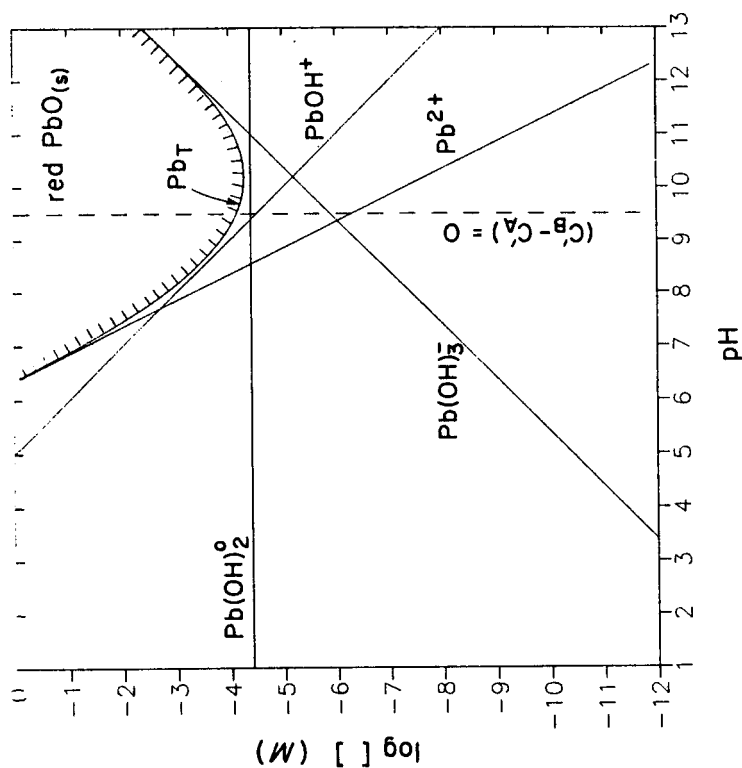


Figure 11.5 Log concentration (M) vs. pH for various Pb(II) species and Pb_T in equilibrium with red $PbO_{(s)}$ at $25^\circ C/1$ atm. Dashed vertical line gives speciation for dissolution into initially-pure water (i.e., for $(C'_B - C'_A) = 0$). Activity corrections neglected (not valid at very low or very high pH).

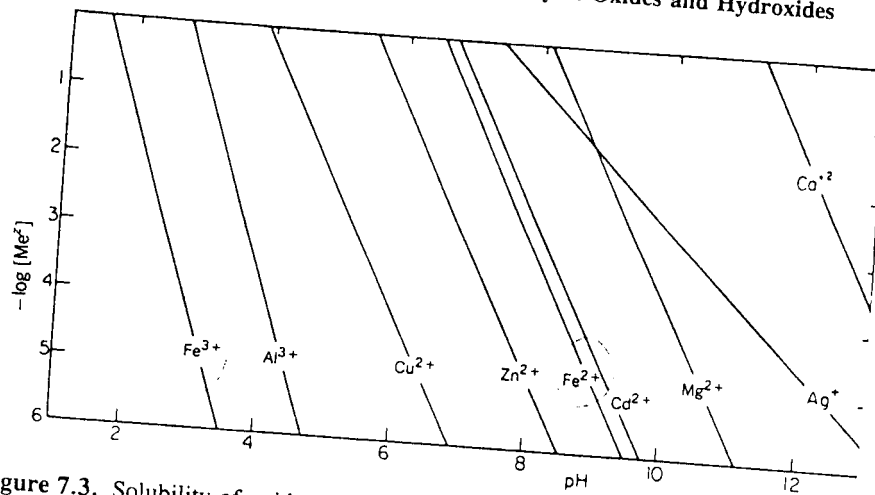


Figure 7.3. Solubility of oxides and hydroxides. Free metal-ion concentration in equilibrium with solid oxides or hydroxides. The occurrence of hydroxo metal complexes must be considered for evaluation of complete solubility.

Component	Reaction	$\log K (I = 0)$	$\log K (I = 0.01)$
	$Cr(OH)_3(s) = Cr^{3+} + 3 OH^-$	-30.0	-29.4
	$Cr^{3+} + OH^- = CrOH^{2+}$	10	9.8
	$Cr^{3+} + 2 OH^- = Cr(OH)_2^+$	18.3	17.9
	$Cr^{3+} + 3 OH^- = Cr(OH)_3(aq)$	24.0	23.7
	$Cr^{3+} + 4 OH^- = Cr(OH)_4^-$	28.6	28.1
	$3 Cr^{3+} + 4 OH^- = Cr_3(OH)_4^{5+}$	47.8	47.5
	$H^+ + OH^- = H_2O$	14.0	13.91

and establish Tableau 7.1.

Figure 7.4 gives the solubility of amorphous $Cr(OH)_3(s)$ in accordance with the equilibria given in Tableau 7.1. In line with the equations in this tableau, the lines characterizing the logarithmic concentrations of Cr^{3+} , $CrOH^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$, $Cr(OH)_4^-$, and $Cr_3(OH)_4^{5+}$, as a function of pH, have slopes of -3 , -2 , -1 , 0 , $+1$, and -5 . The intercepts are also defined readily; for example, for $Cr(OH)_2^+$, $\log [Cr(OH)_2^+] = 0$ when $pH = \log *K_{s2}$; for $CrOH^{2+}$, $\log [CrOH^{2+}] = 0$ when $pH = \frac{1}{2} \log *K_{s1}$. Summing up all the soluble Cr(III) species indicated by a thick line gives the overall solubility as a function of pH. The solubility of $Cr(OH)_3(s)$ is affected markedly on the acid side by the polynuclear species $Cr_3(OH)_4^{5+}$.

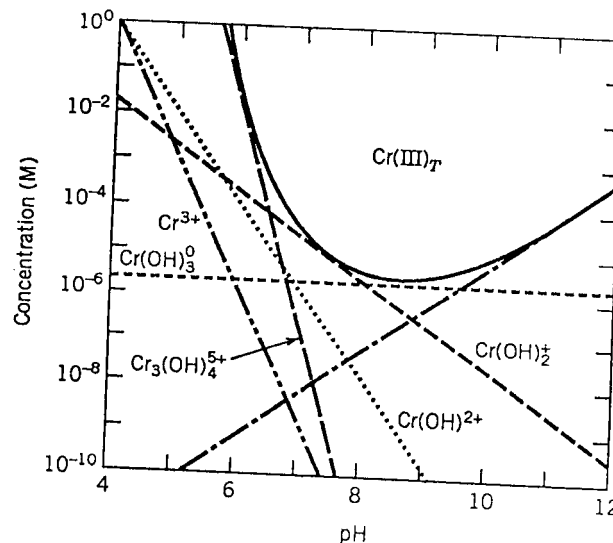


Figure 7.4. Solubility of precipitated $Cr(OH)_3(s)$ ($25^\circ C, I = 10^{-2} M$) in accord with Tableau 7.1.