Environmental Chemistry

Part 3 Hydrospheric Chemistry

3.6 Dissolution and Precipitation

- 迁移能力与溶解性

溶解度大，迁移能力强

溶解与迁移

热力学原因 动力学原因

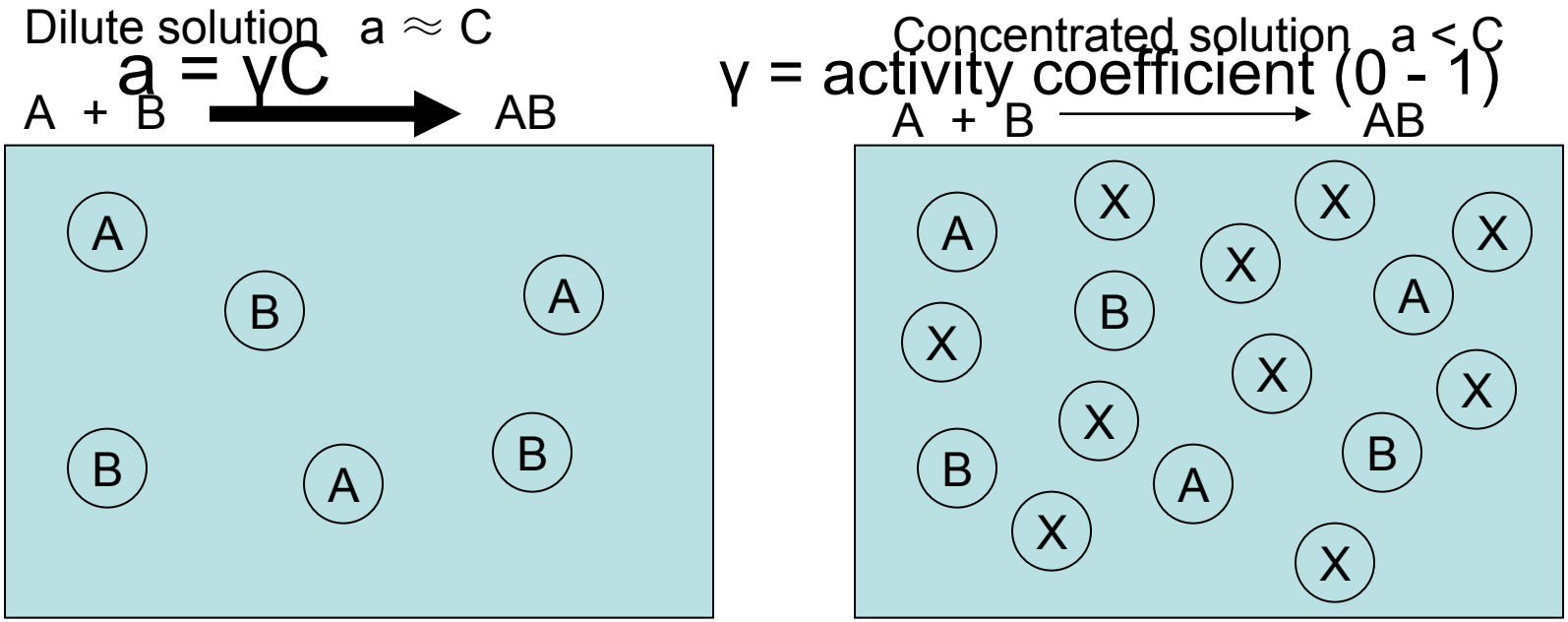
- SiO_2
- Fe_2O_3 $Al(OH)_3$
- $CaCO_3$ $MgCO_3$
- Mica (K)(云母)
- Feldspar (K)长石
- Apatite (P)磷灰石

- Kaolinite
- Montmorillonite蒙脱石, 胶岭石, 高岭石

Intensity = Solution Activity

- Dissolved in the solution
- Activity (a，活度)

  = effective concentration (C)



γ 活度系数

Activity vs Concentration in Solution

Ion	Concentration	Activity
	mM	mM
Ca^{2+}	1.68	0.98
Mg^{2+}	0.71	0.43
K^{+}	2.60	2.23
NH_4^{+}	4.98	4.26
SO_4^{2-}	0.75	0.42
Al^{3+}	0.0255	0.0085

溶度积
Solubility Product, K_{sp}

- Smaller the Ksp the lower the solubility
  - $CaSO_4$ Gypsum Ksp = 1.95 x 10-4
  - $Al(OH)_3$ Aluminum Hydroxide Ksp = 1.6 x 10^{-34}

- Calcium Carbonate
  - K_{sp} $CaCO_3$ = 0.87 x10^{-8}
- Aluminum Hydroxide
  - K_{sp} $Al(OH)_3$ = 1.6x 10^{-34}
- Iron Hydroxide
  - K_{sp} $Fe(OH)_3$ = 1.6x 10^{-37}

The Solubility Product Constant

K_{sp}

Example:

$$AgBr_{(s)} \leftrightarrows Ag^{+}_{(aq)} + Br^{-}_{(aq)}$$

$$K_{sp} = [Ag^{+}][Br^{-}]$$

Example:

$$Ca(OH)_2(s) \leftrightarrows Ca^{2+}(aq) + 2OH^-(aq)$$

$$K_{sp} = [Ca^{2+}][OH^-]^2$$

Example:

$$Ag_2CrO_4(s) \leftrightarrows 2Ag^+(aq) + CrO_4^{2-}(aq)$$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

- Give the K_{sp} expressions for

a) Barium carbonate

b) Silver sulfate

c) Calcium flouride

a)=$[Ba^{2+}][CO_3^{2-}]$

b)=$[Ag+]^2\ [SO_4^{2-}]$

c)=$[Ca^{2+}][F^-]^2$

Solubility and K_{sp}

Solubility = grams of solute / liter of solution

Molar solubility = moles of solute / liter of saturated solution

K_{sp} is the equilibrium constant between the ionic solid and saturated solution.

- K_{sp} has only one value at any specific temperature.

氢氧化物和其他物质溶度积（差别大）

$Al(OH)_3$	1.8×10^{-33}				
$BaCO_3$	8.1×10^{-9}	CuI	5.1×10^{-12}	MnS	3.0×10^{-14}
BaF_2	1.7×10^{-6}	$Cu(OH)_2$	2.2×10^{-20}	Hg_2Cl_2	3.5×10^{-18}
$BaSO_4$	1.1×10^{-10}	CuS	6.0×10^{-37}	HgS	4.0×10^{-54}
Bi_2S_3	1.6×10^{-72}	$Fe(OH)_2$	1.6×10^{-14}	NiS	1.4×10^{-24}
CdS	8.0×10^{-28}	$Fe(OH)_3$	1.1×10^{-36}	AgBr	7.7×10^{-13}
$CaCO_3$	8.7×10^{-9}	FeS	6.0×10^{-19}	Ag_2CO_3	8.1×10^{-12}
CaF_2	4.0×10^{-11}	$PbCO_3$	3.3×10^{-14}	AgCl	1.6×10^{-10}
$Ca(OH)_2$	8.0×10^{-6}	$PbCl_2$	2.4×10^{-4}	Ag_2SO_4	1.4×10^{-5}
$Ca_3(PO_4)_2$	1.2×10^{-26}	$PbCrO_4$	2.0×10^{-14}	Ag_2S	6.0×10^{-51}
$Cr(OH)_3$	3.0×10^{-29}	PbF_2	4.1×10^{-8}	$SrCO_3$	1.6×10^{-9}
CoS	4.0×10^{-21}	PbI_2	1.4×10^{-8}	$SrSO_4$	3.8×10^{-7}
CuBr	4.2×10^{-8}	PbS	3.4×10^{-28}	SnS	1.0×10^{-26}
		$MgCO_3$	4.0×10^{-5}	$Zn(OH)_2$	1.8×10^{-14}
		$Mg(OH)_2$	1.2×10^{-11}	ZnS	3.0×10^{-23}

pH对于溶解度的影响

$Fe(OH)_3 \leftrightarrow Fe^{3+} + 3OH^-$

$K_{sp} = (Fe^{3+})(OH^-)^3 = 10^{-36}$

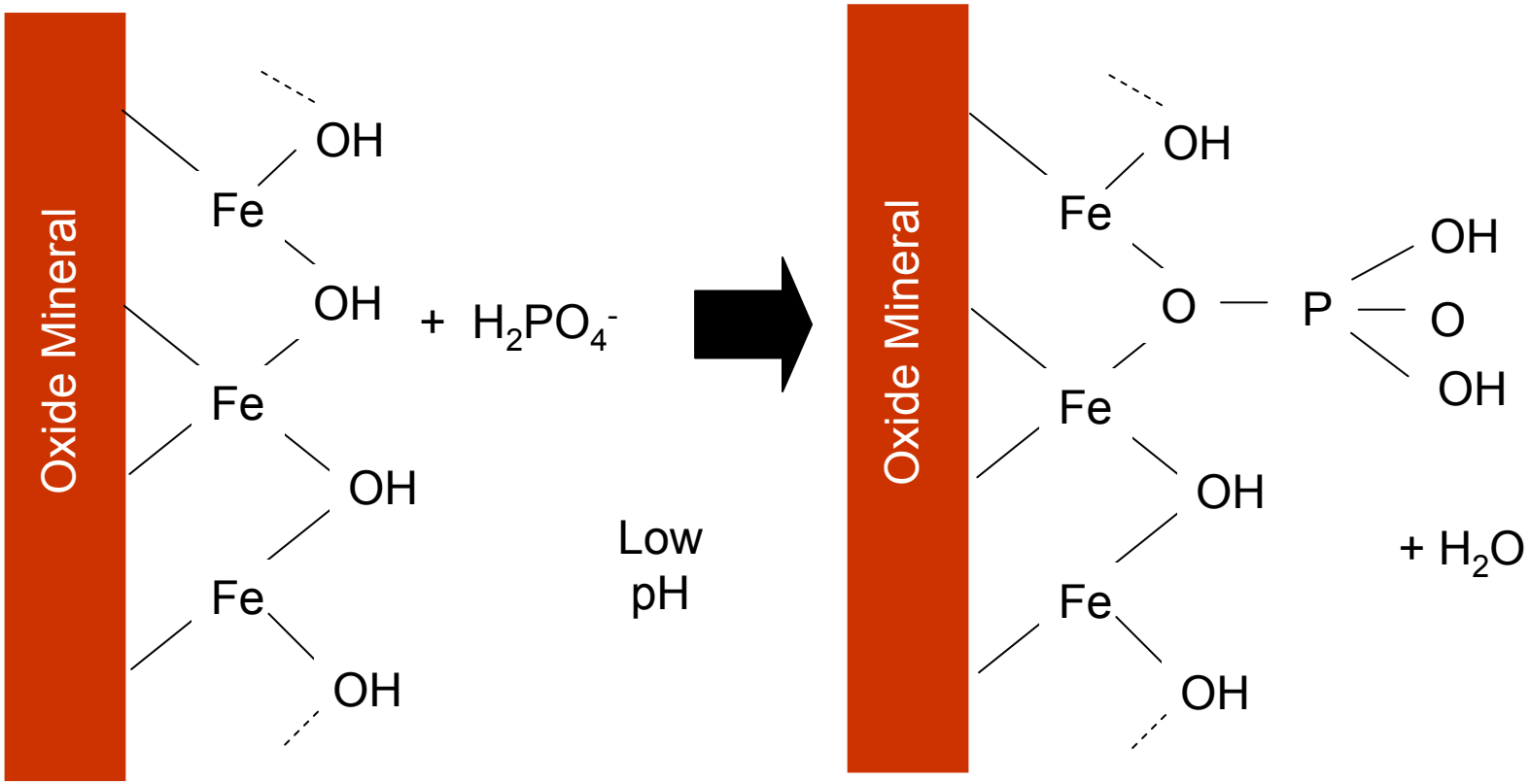
or $(Fe^{3+}) = 10^{-36} / (OH^-)^3$

pH	(OH^-)	(Fe^{3+})
6	10^{-8}	10^{-12}
7	10^{-7}	10^{-15}
8	10^{-6}	10^{-18}

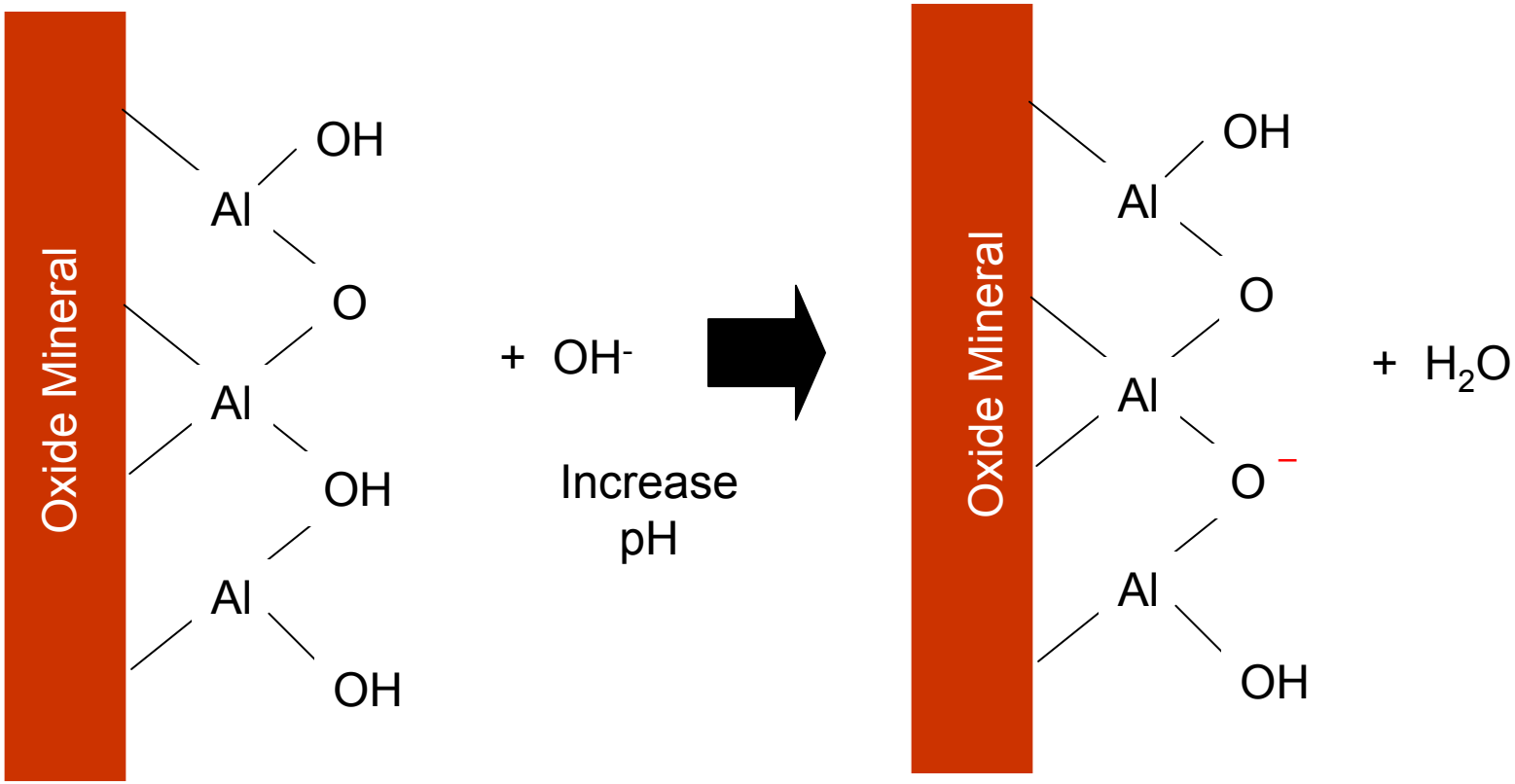
解释南方土壤和水体含铁高的原因

吸附影响Adsorption

– P sorption on oxides



pH Dependent Charge on Oxides



pH Dependent Charge on OM

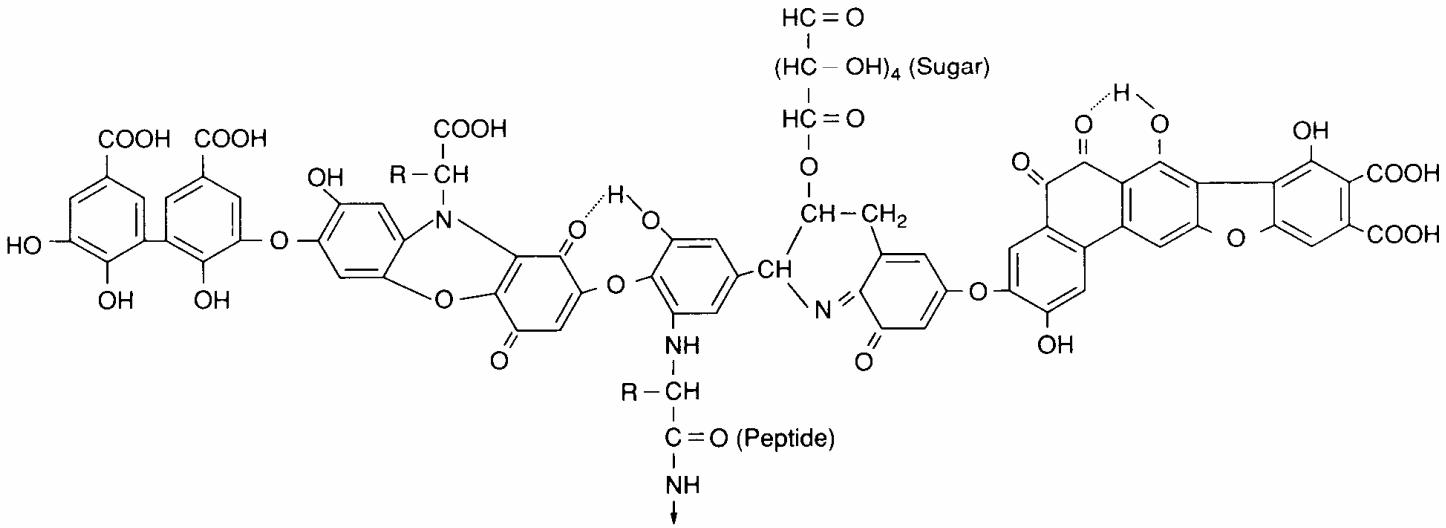
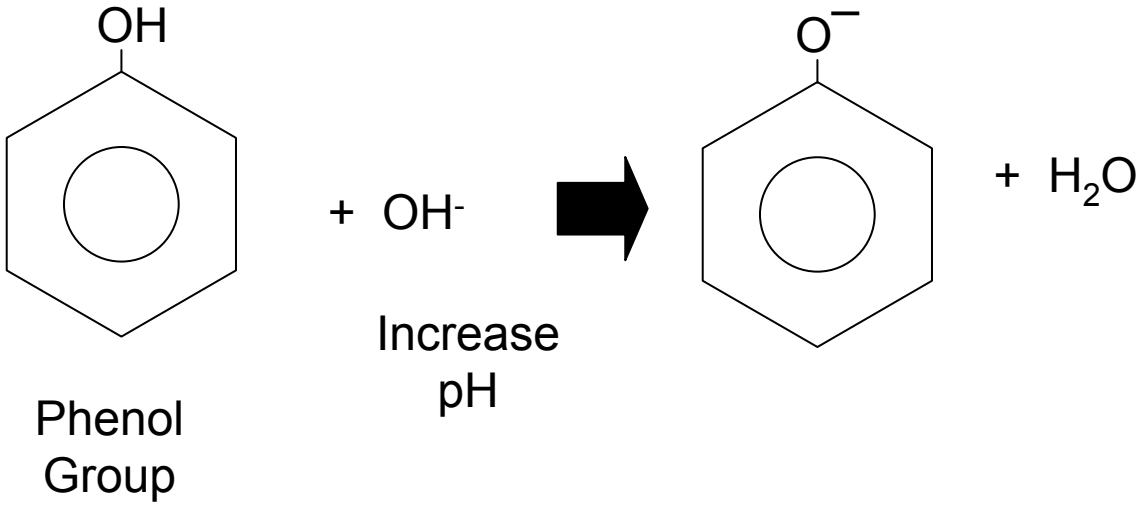
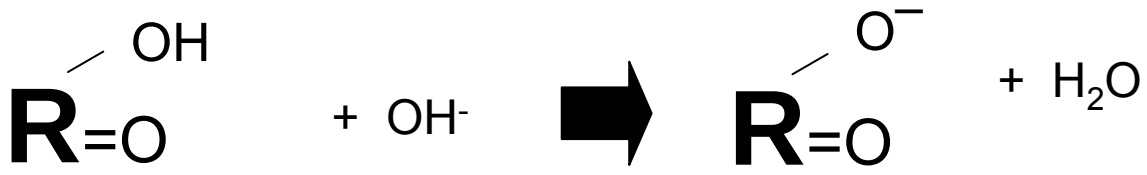


FIGURE 2.8 Suggested structure for humic acid in soil. The COOH and OH groups are the pH-dependent sites. *Mortvedt, Giordano, and Lindsay (Eds.),* Micronutrients in Agriculture, *ASA, 1972.*

pH Dependent Charge on OM

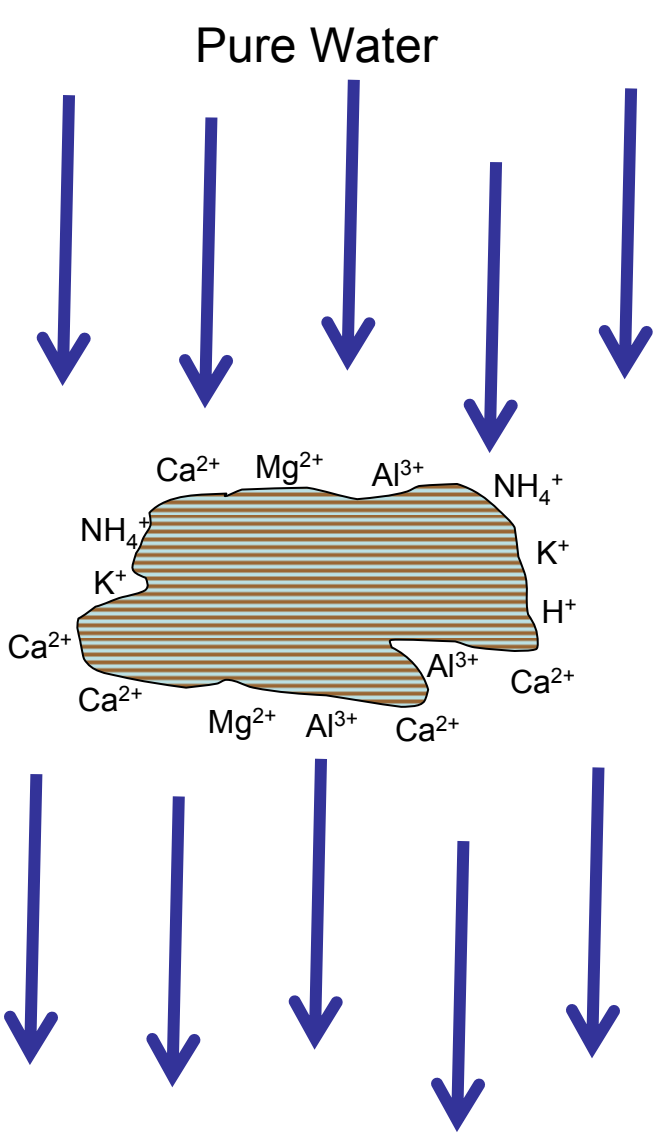


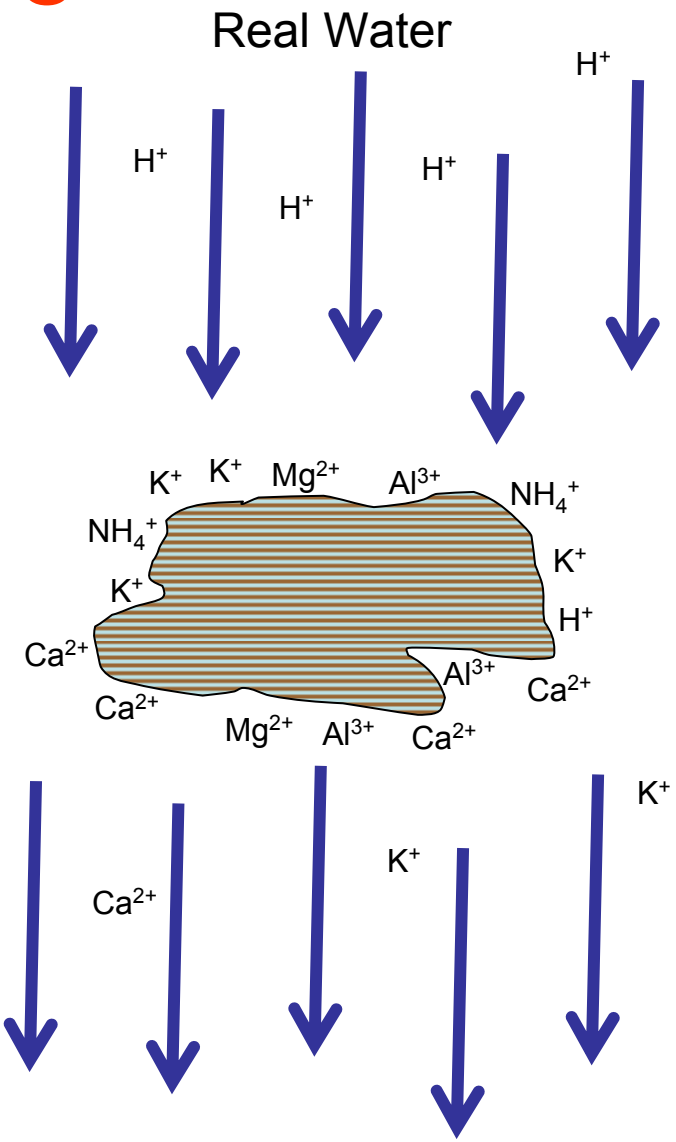
Phenol Group



Carboxyl Group

淋洗过程
Leaching





pH and Solubility

- Example:
  - $Fe(OH)_2$-Add acid

$$Fe(OH)_2(s) <=> Fe^{2+}(aq) + 2OH^-(aq)$$

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pH and Solubility

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LeChatlier's principle

pH and Solubility

- Example:
  - $Fe(OH)_2$-Add acid

$$Fe(OH)_2(s) \Longleftrightarrow Fe^{2+}(aq) + 2OH^-(aq)$$

More $Fe(OH)_2$ dissolves in response

Solubility increases

Decrease = stress

Stress relief = increase [OH^-]

$$2H_3O^+(aq) + 2OH^-(aq) \rightarrow 4H_2O$$

pH and Solubility

- **Example:**
  - **$Fe(OH)_2$**

$$Fe(OH)_2(s) \Longleftrightarrow Fe^{2+}(aq) + 2OH^-(aq)$$

$$2H_3O^+(aq) + 2OH^-(aq) \rightarrow 4H_2O(l)$$

overall

$$Fe(OH)_2(s) + 2H_3O^+(aq) \Longleftrightarrow Fe^{2+}(aq) + 4H_2O(l)$$

pH and Solubility

- Example:
  - $Fe(OH)_2$

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$$2H_3O^+(aq) + 2OH^-(aq) \rightarrow 4H_2O(l)$$

overall $Fe(OH)_2(s) + 2H_3O^+(aq) \Longleftrightarrow Fe^{2+}(aq) + 4H_2O(l)$

decrease pH → solubility increases

increase pH ← solubility decreases

假如 $[Me^{n+}]=c\ M$

Solubility and equilibria: K_{sp}.

$Me(OH)\ n(s) \quad \sim \quad Me^{n+} + nOH^-$

$Ksp = [Me^{n+}]\ [OH^-]^n$

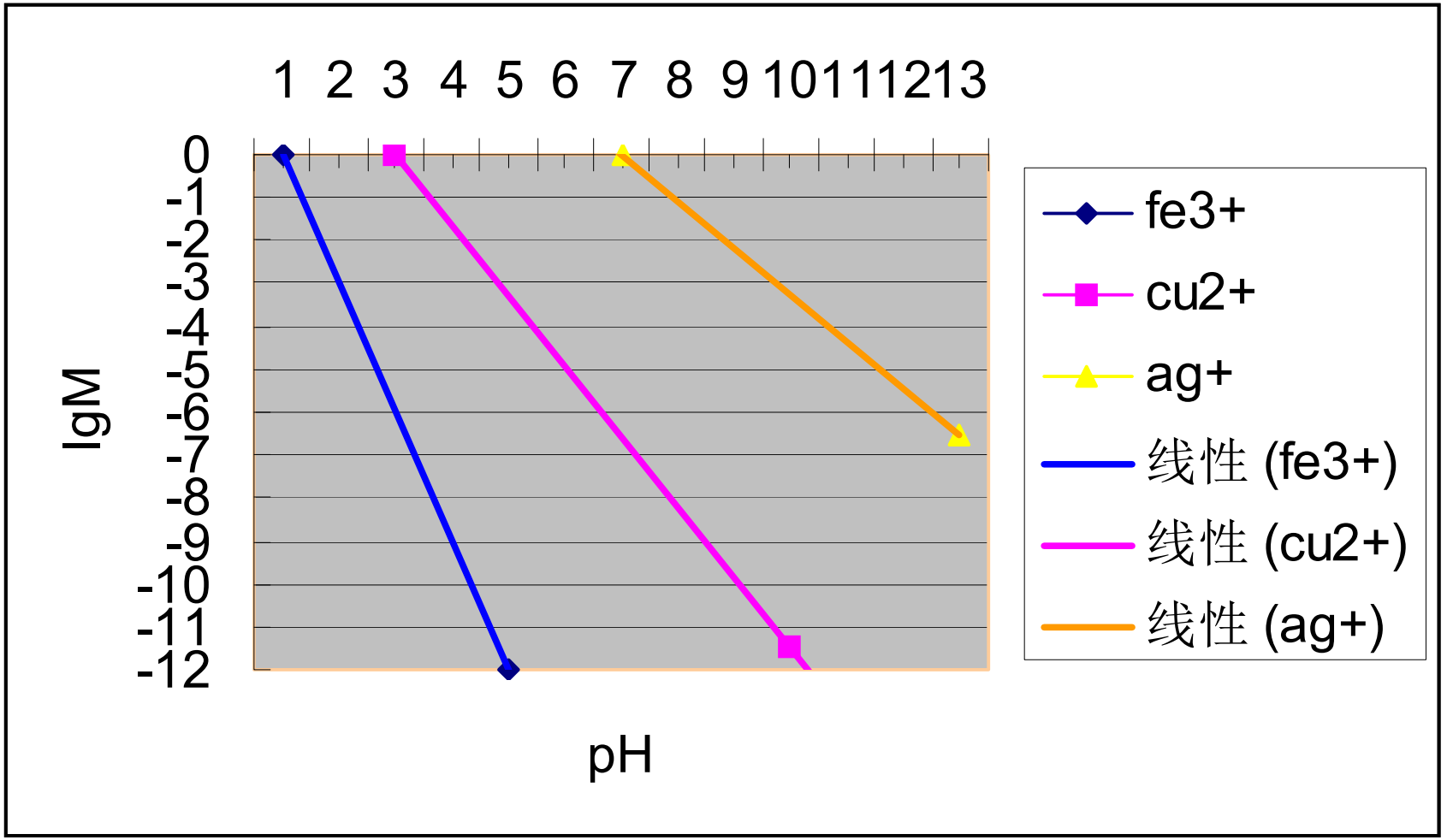
$[Me^{n+}] = Ksp/\ [OH\text{-}]^{n+} = Ksp[H^+]^n/\ Kw^n$

取负对数

$-lg[Me^{n+}] = -lgKsp - nlg\ [H^+] + nlgKw$

$pc = pKsp - npKw + npH$

$-\lg[Me^{n+}] = pc = pKsp - npKw + npH$



分析图3－11的意义？？？

假如 $[Me^{n+}]=1M$

Solubility and equilibria: K_{sp}.

$Me_T = [Me^{n+}] + \Sigma [Me(OH)_n^{z-n}]$ 3-45 p133

以氧化铅为例分析

溶液中物种

$PbOs$ $2H^+$ Pb^{2+} H_2O OH^- $PbOH^+$

$Pb(OH)_2$ $Pb(OH)_3^-$

- $PbOs + 2H^+ = Pb^{2+} + H_2O$ lg Kso=12.7 3-46
- $PbOs + H^+ = PbOH^+$ lg Ks1=5.0 3-47
- PbOs + H2O = Pb(OH) lg Ks2=-4.4 3-48
- $PbOs + H2O = Pb(OH)3^- + H^+$ 3-49

以氧化铅为例分析

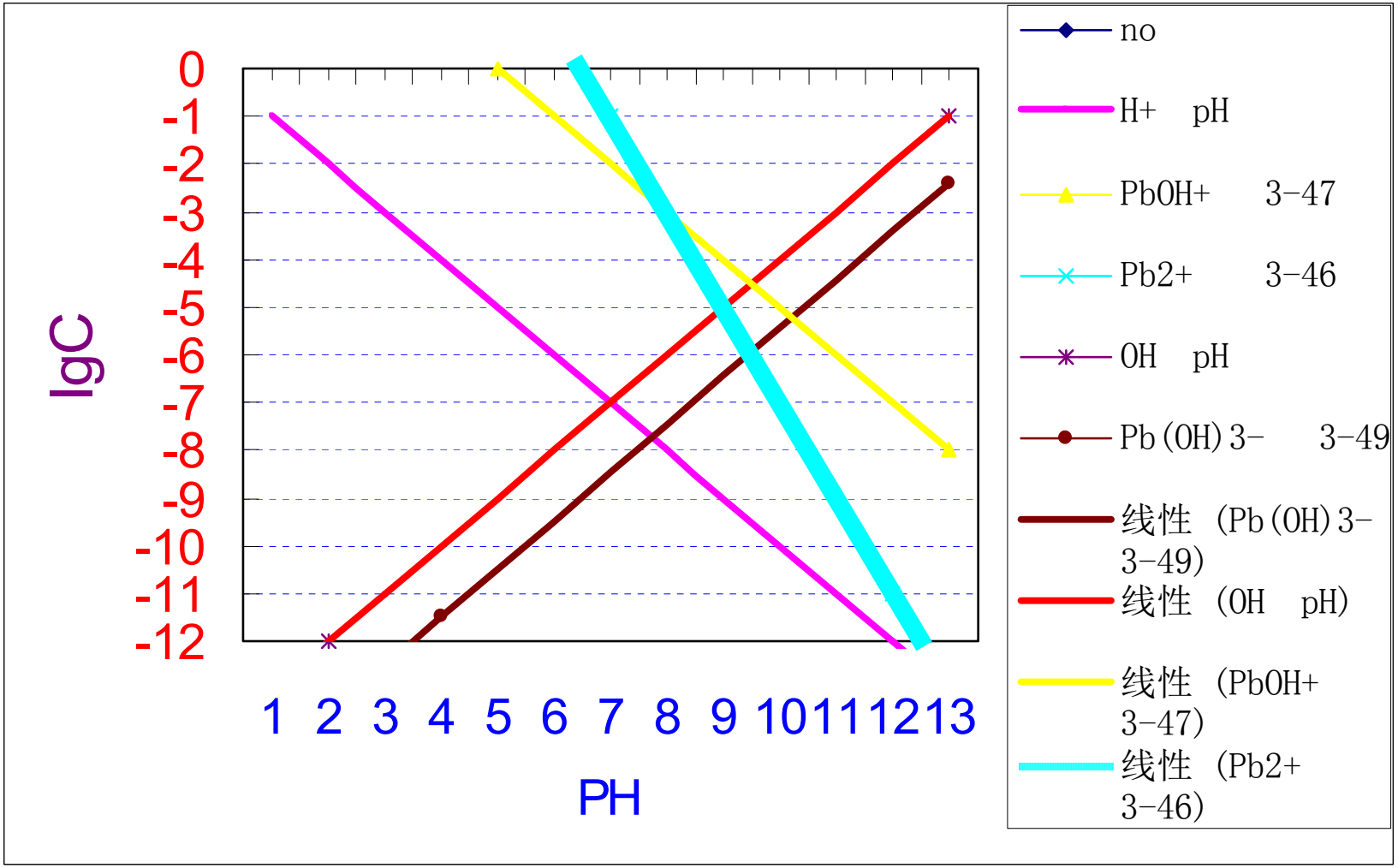
- $PbOs + 2H^+ = Pb^{2+} + H_2O$ lg Kso=12.7 3-46

lg Kso = lg{$[Pb^{2+}]/[H^+]^2$}

$[Pb^{2+}] = 10^{12.7}\ [H^+]^2$ 两边取对数

lg c = 12.7- 2pH

lg c=lg[Pb2+] = 12.7- 2pH



以氧化铅为例分析（2）

- $PbOs + H^+ = PbOH^+$ $\lg Ks1=5.0$ 3-47

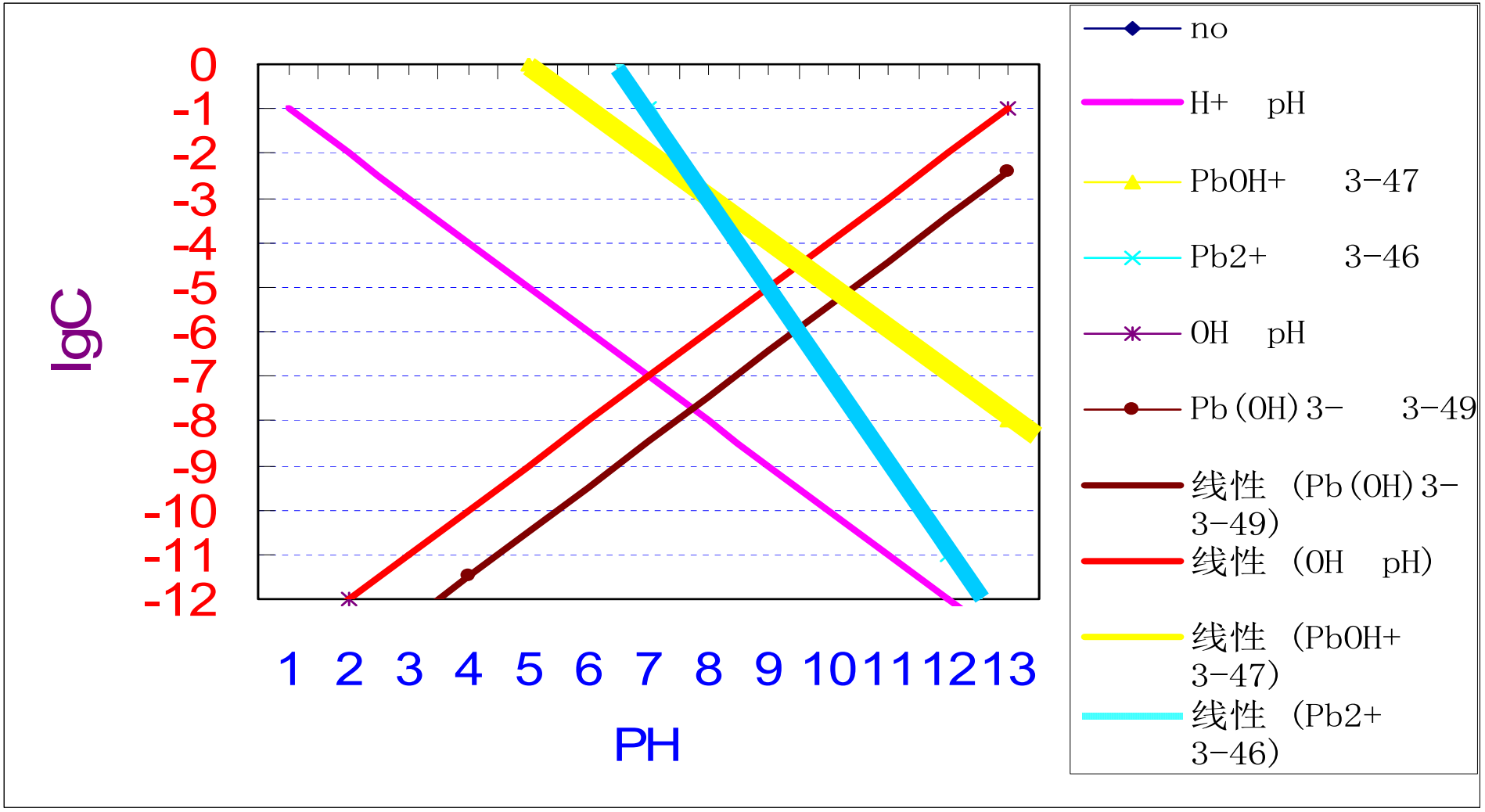
$\lg Ks1 = \lg\{[PbOH^+]/[H^+]\}$

$\lg[PbOH^+] = 10^{5.0}\,[H^+]$ 两边取对数

$\lg[PbOH^+] = \lg c = 5.0 - pH$

$lg[Pb(OH)2] = lgc = -4.4$

方程 3-48



以氧化铅为例分析(3)

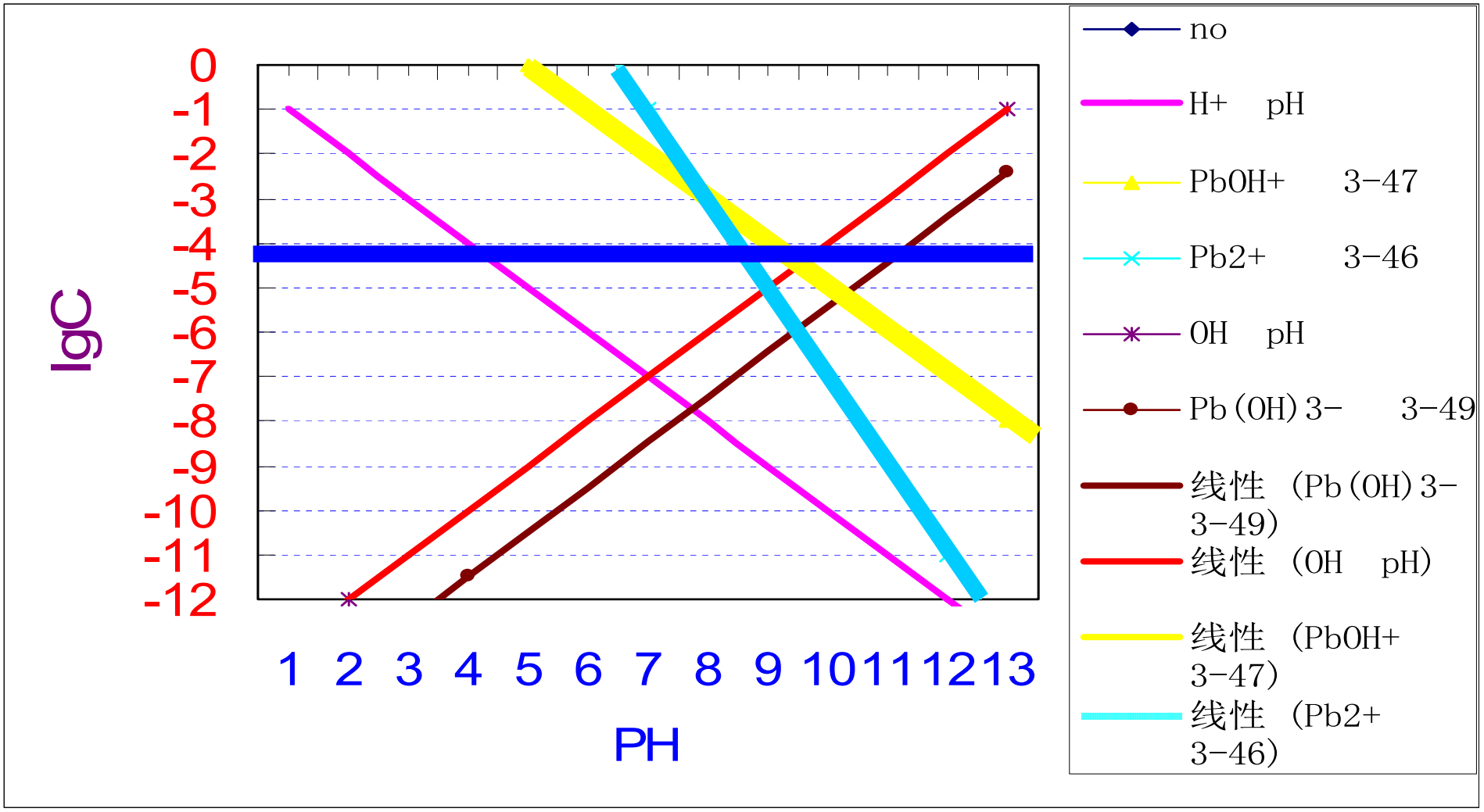
- PbOs + H2O = Pb(OH) lg Ks2=-4.4 3-48

lg Ks2 = lg{[$Pb(OH)_2$] = -4.4

lg[Pb(OH)2] =lgc = -4.4

lg[Pb(OH)2] =lgc =-4.4

方程 3-48



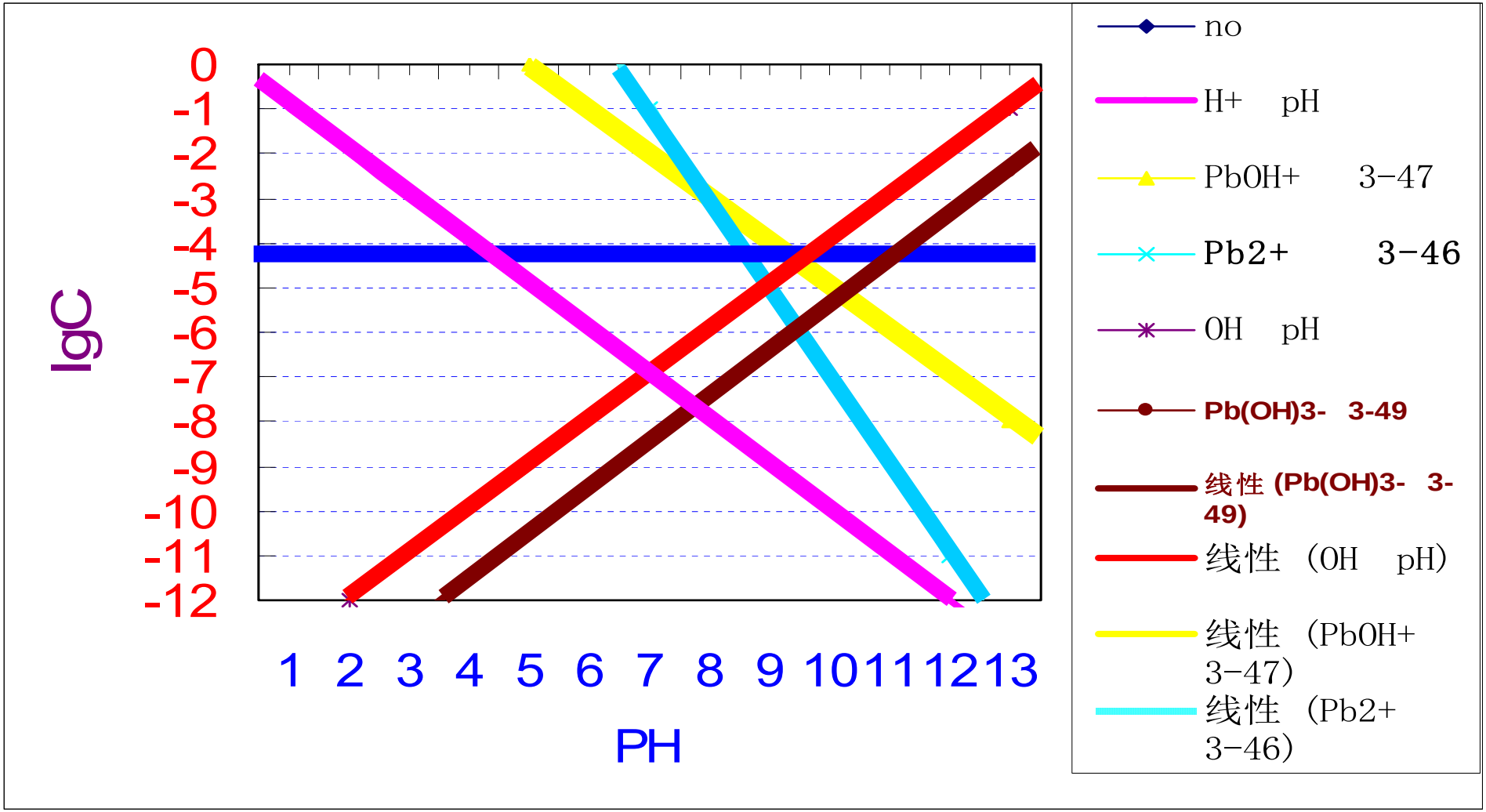
以氧化铅为例分析(3)

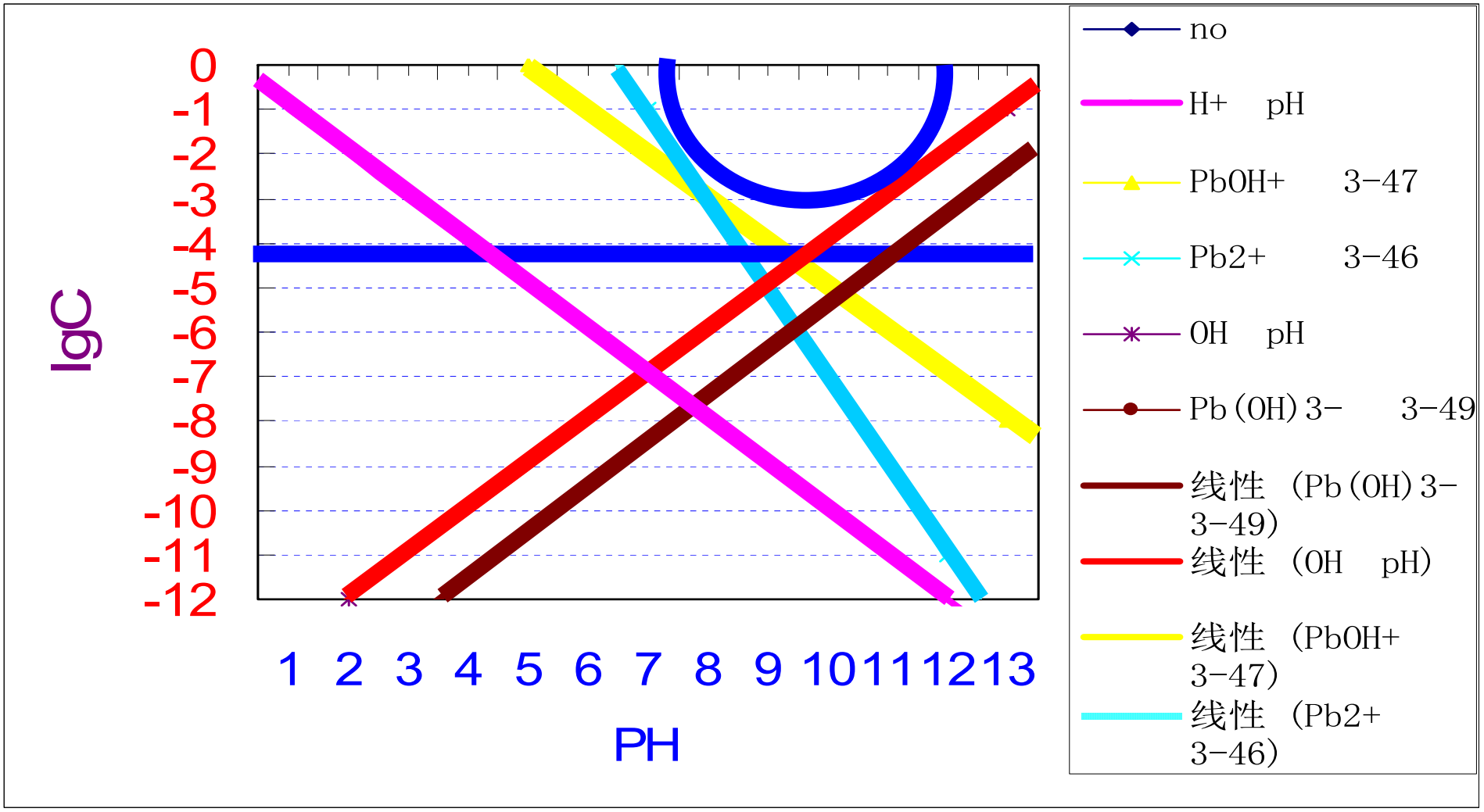
- $PbOs + H_2O = Pb(OH)_3^- + H^+$ 3-49

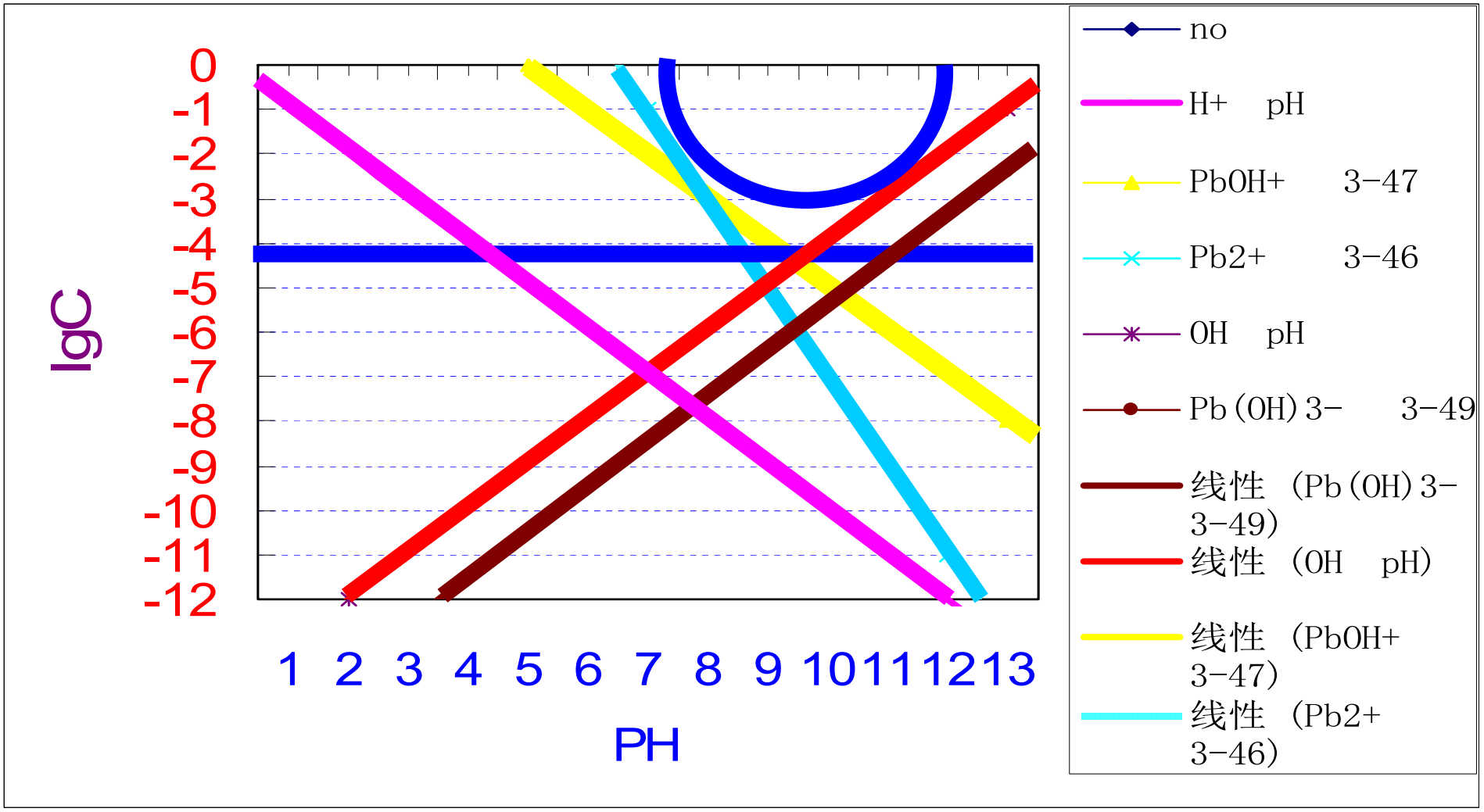
- $$\lg Ks3 = \lg\{[Pb(OH)_3^-][H^+]\} = -15.4$$

$$\lg[Pb(OH)_3^-] = \lg c3 = \lg Ks_3 - \lg[H^+]$$
$$= -15.4 + pH$$

$lg[Pb(OH)_3^-] = lgc3 = -15.4 + pH$ 方程 3-49




lgC
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
1 2 3 4 5 6 7 8 9 10 11 12 13
PH
no
H+ pH
PbOH+ 3-47
Pb2+ 3-46
OH pH
Pb(OH)3- 3-49
线性 (Pb(OH)3- 3-49)
线性 (OH pH)
线性 (PbOH+ 3-47)
线性 (Pb2+ 3-46)


lgC
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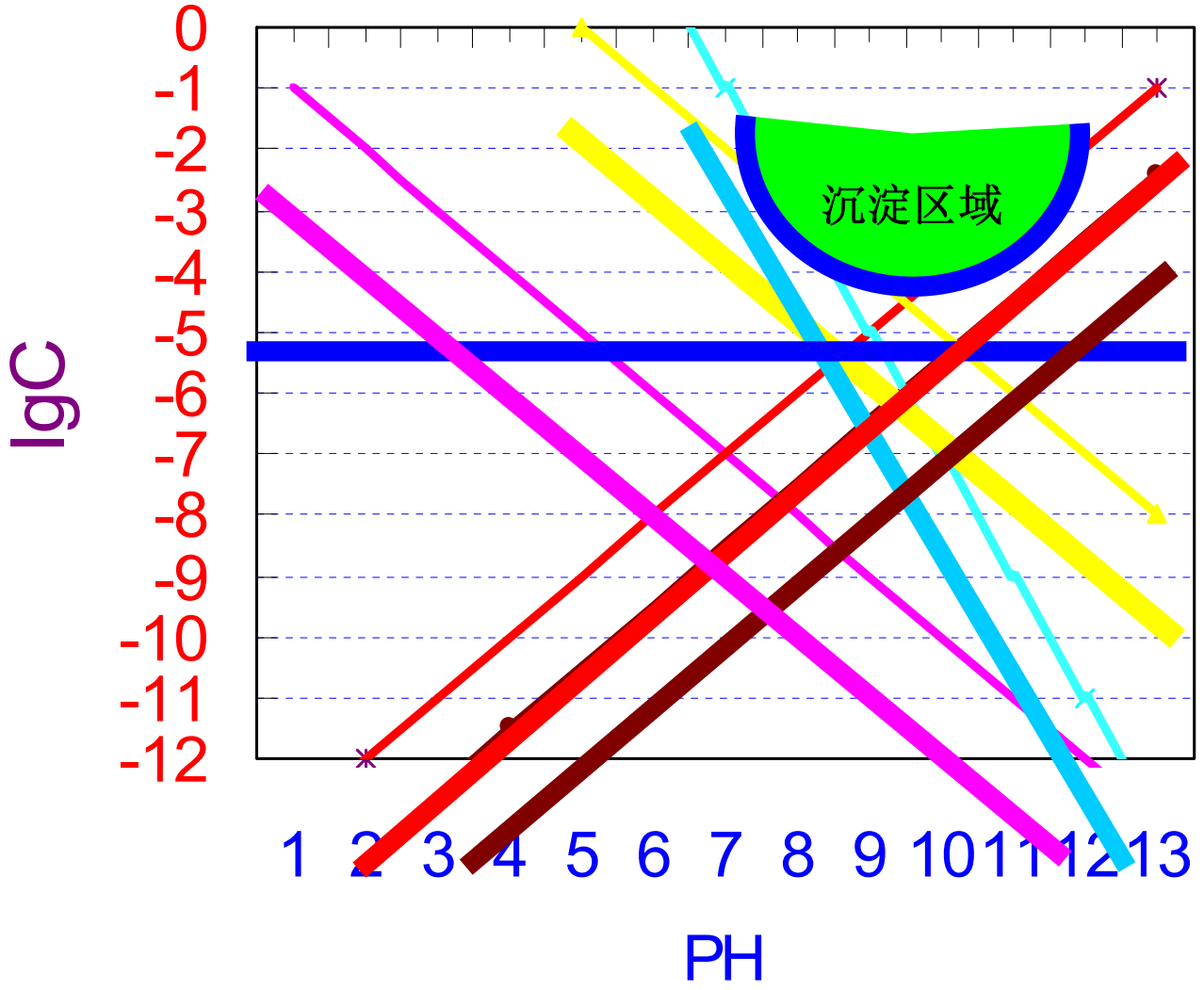
1 2 3 4 5 6 7 8 9 10 11 12 13
PH
no
H+ pH
PbOH+ 3-47
Pb2+ 3-46
OH pH
Pb(OH)3- 3-49
线性 (Pb(OH)3- 3-49)
线性 (OH pH)
线性 (PbOH+ 3-47)
线性 (Pb2+ 3-46)

综合图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lgC
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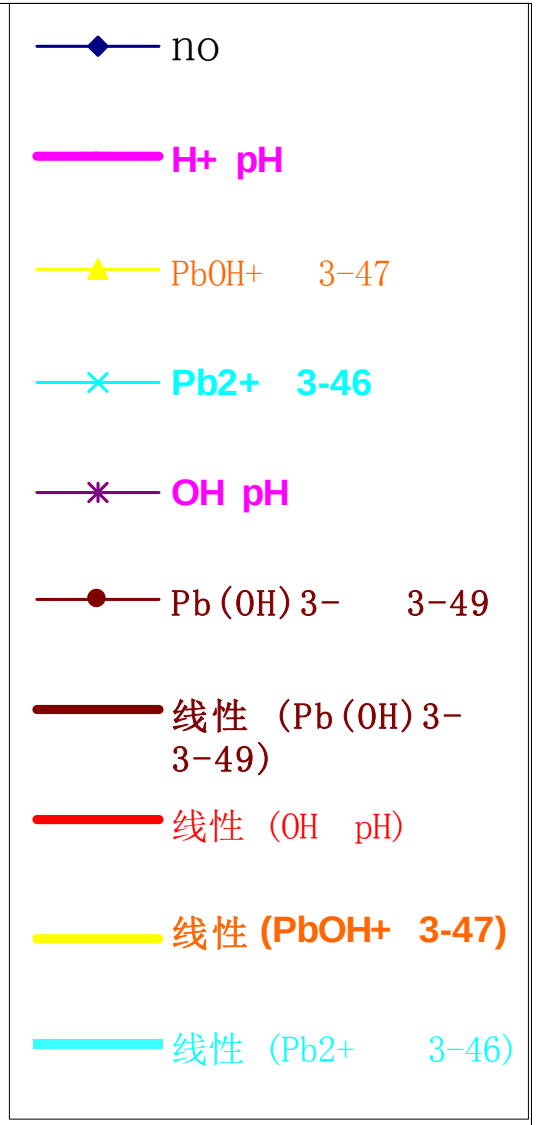
PH
沉淀区域


no
H+ pH
PbOH+ 3-47
Pb2+ 3-46
OH pH
Pb(OH)3- 3-49
线性 (Pb(OH)3- 3-49)
线性 (OH pH)
线性 (PbOH+ 3-47)
线性 (Pb2+ 3-46)