Log C – pH Diagrams for Diprotic Acids

Everything is more or less the same. But we just have more species, more equations and more plots.

α (alpha) notation for monoprotic acids

Ex. Consider a 10^{-2} M solution of the weak diprotic acid H_2A ($pK_{a,1} = 4$, $pK_{a,2} = 8$). Neglecting ionic strength effects and T = 25°C:

<u>equilibria:</u>

H_2O <=====> OH^- + H^+ pK_w

H_2A <=====> HA^- + H^+ pK_{a1}

HA^- <=====> A^{2-} + H^+ pK_{a2}

<u>species present at equilibrium:</u> H_2A, HA^-, $A^=$, H^+, OH^-

$$\alpha_0 = \frac{[H_2A]}{TOTA} = \frac{1}{1+\frac{K_{a,1}}{[H^+]}+\frac{K_{a,1}K_{a,2}}{[H^+]^2}}$$

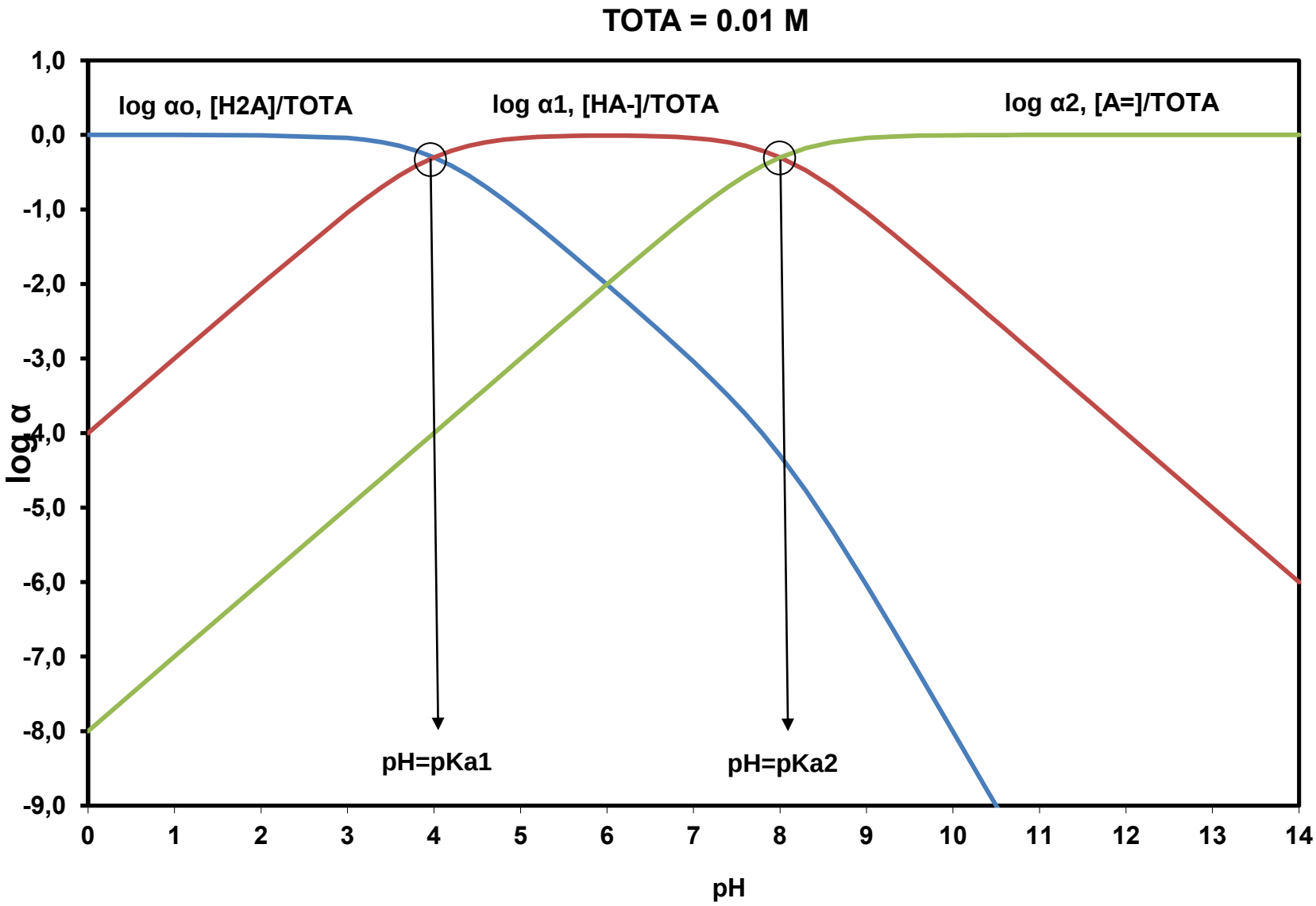
$$\alpha_1 = \frac{[HA^-]}{TOTA} = \frac{1}{1+\frac{[H^+]}{K_{a,1}}+\frac{K_{a,2}}{[H^+]}}$$

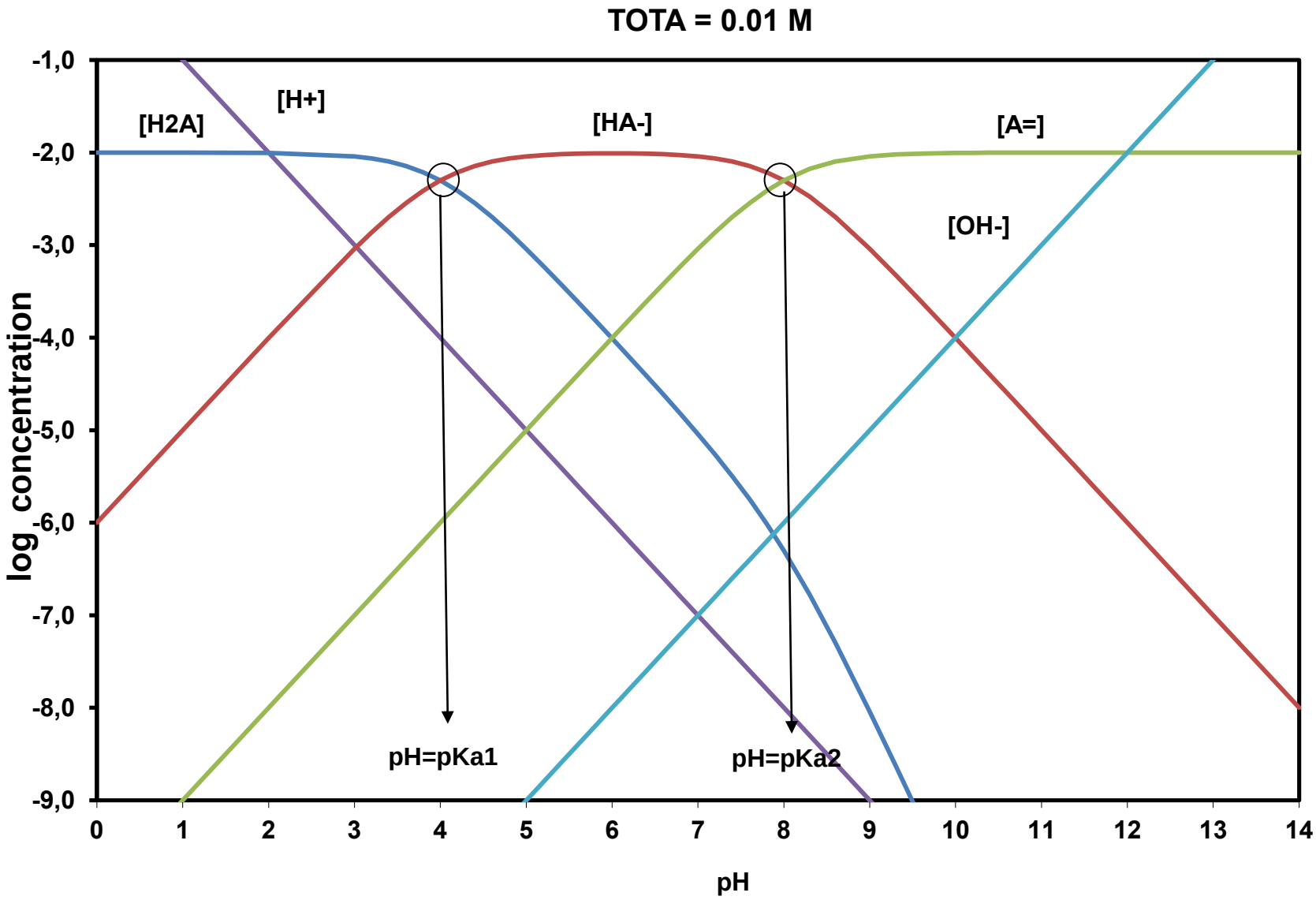
$$\alpha_2 = \frac{[A^-]}{TOTA} = \frac{1}{1+\frac{[H^+]^2}{K_{a,1}K_{a,2}}+\frac{[H^+]}{K_{a,2}}}$$

10-2 M H2A

pKa1=	4	Ka1=	1,00E-04
pKa2=	8	Ka2=	1,00E-08
TOTA=	0,01		
log TOTA=	-2		

pH	H+	OH-	log α0	log α1	log α2
0	1	1E-14	0,000	-4,000	-8,000
1	0,1	1E-13	0,000	-3,000	-7,000
2	1E-02	1E-12	-0,004	-2,004	-6,000
3	1E-03	1E-11	-0,041	-1,041	-5,000
3,2	6E-04	1,6E-11	-0,064	-0,864	-4,800
3,4	4E-04	2,5E-11	-0,097	-0,697	-4,600
3,6	3E-04	4,0E-11	-0,146	-0,546	-4,400
3,8	2E-04	6,3E-11	-0,212	-0,412	-4,200
4	1E-04	1E-10	-0,301	-0,301	-4,000
4,2	6E-05	1,6E-10	-0,412	-0,212	-3,800


TOTA = 0.01 M
log αo, [H2A]/TOTA
log α1, [HA-]/TOTA
log α2, [A=]/TOTA
pH=pKa1
pH=pKa2
log α
pH
1,0
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
-6,0
-7,0
-8,0
-9,0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14

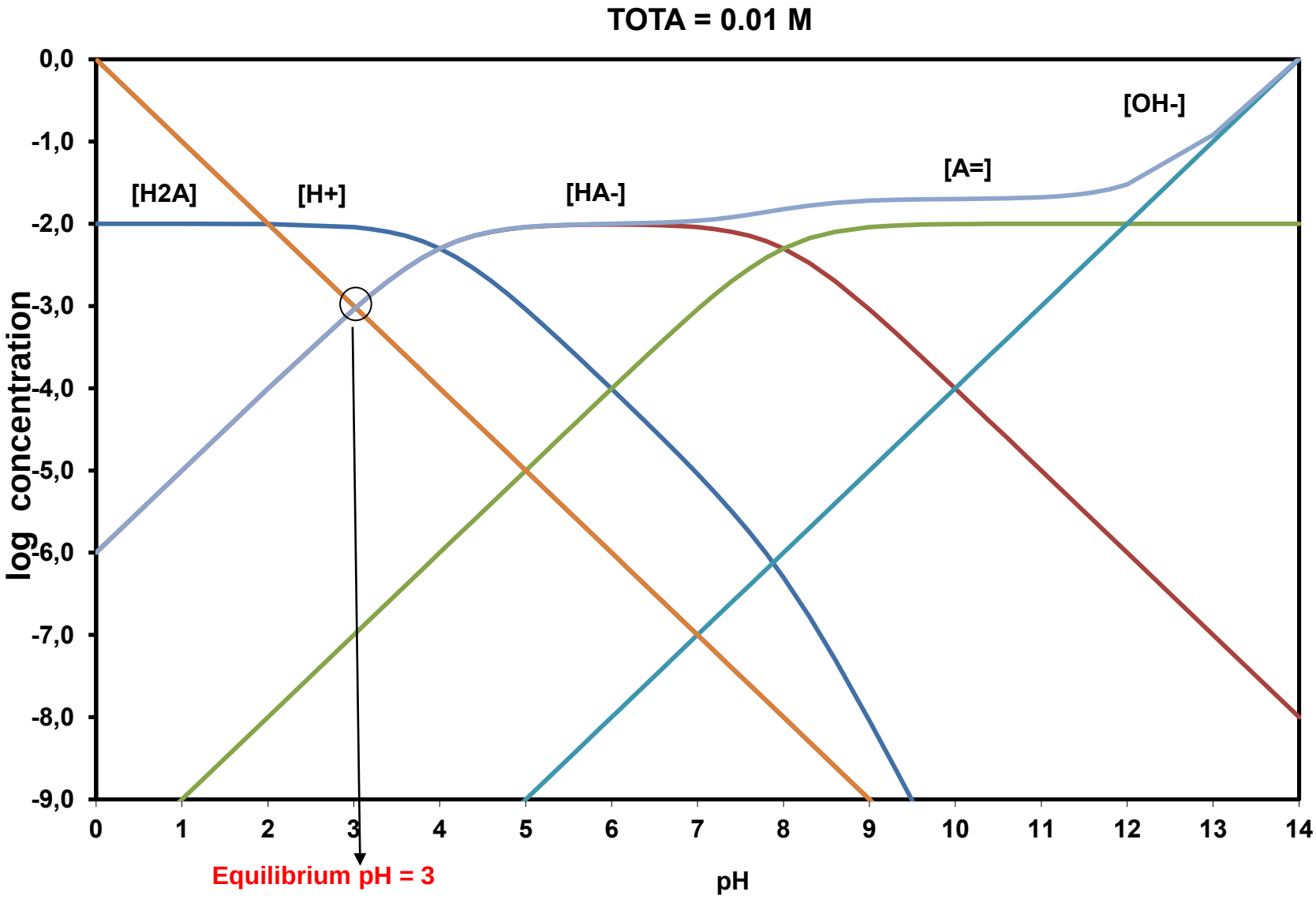

TOTA = 0.01 M
[H2A]
[H+]
[HA-]
[A=]
[OH-]
pH=pKa1
pH=pKa2
log concentration
pH
-1,0
-2,0
-3,0
-4,0
-5,0
-6,0
-7,0
-8,0
-9,0
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14

- **Ex. What are the pH and the concentrations of all species at equilibrium in this 10^{-2} M H_2A solution?**
- Equilibrium species: H^+ OH^- H_2A HA^- $A^=$
- K's: K_w $K_{a1} = 10^{-4}$ $K_{a1} = 10^{-8}$
- MB's TOTA = $[H_2A] + [HA^-] + [A^=] = 10^{-2}$ M

- CB: $[H^+] = [OH^-] + [HA^-] + 2[A^=]$

  $\log (2[A^=]) = \log 2 + \log [A^=]$

  $= 0.3 + \log [A^=]$



CB : $[H^+]$ = $[OH^-] + [HA^-] + 2[A^=]$

LHS RHS

Equilibrium Concentrations of 10^{-2} M H_2A

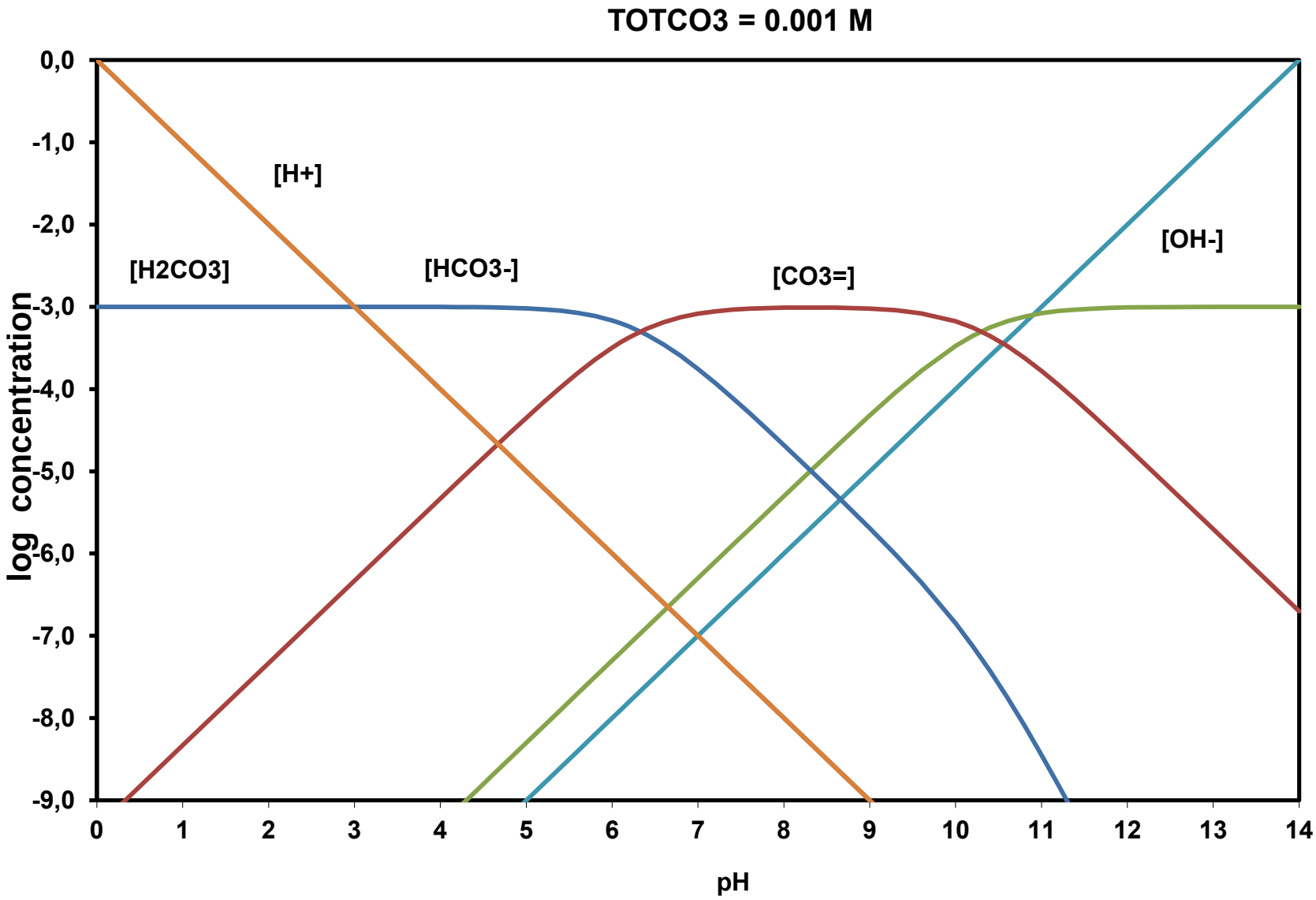
- $[H^+] = 10^{-3}$ M
- $[OH^-] = 10^{-11}$ M
- $[H_2A] = 10^{-2}$ M
- $[HA^-] = 9x10^{-4}$ M
- $[A^=] = 10^{-7.0}$ M

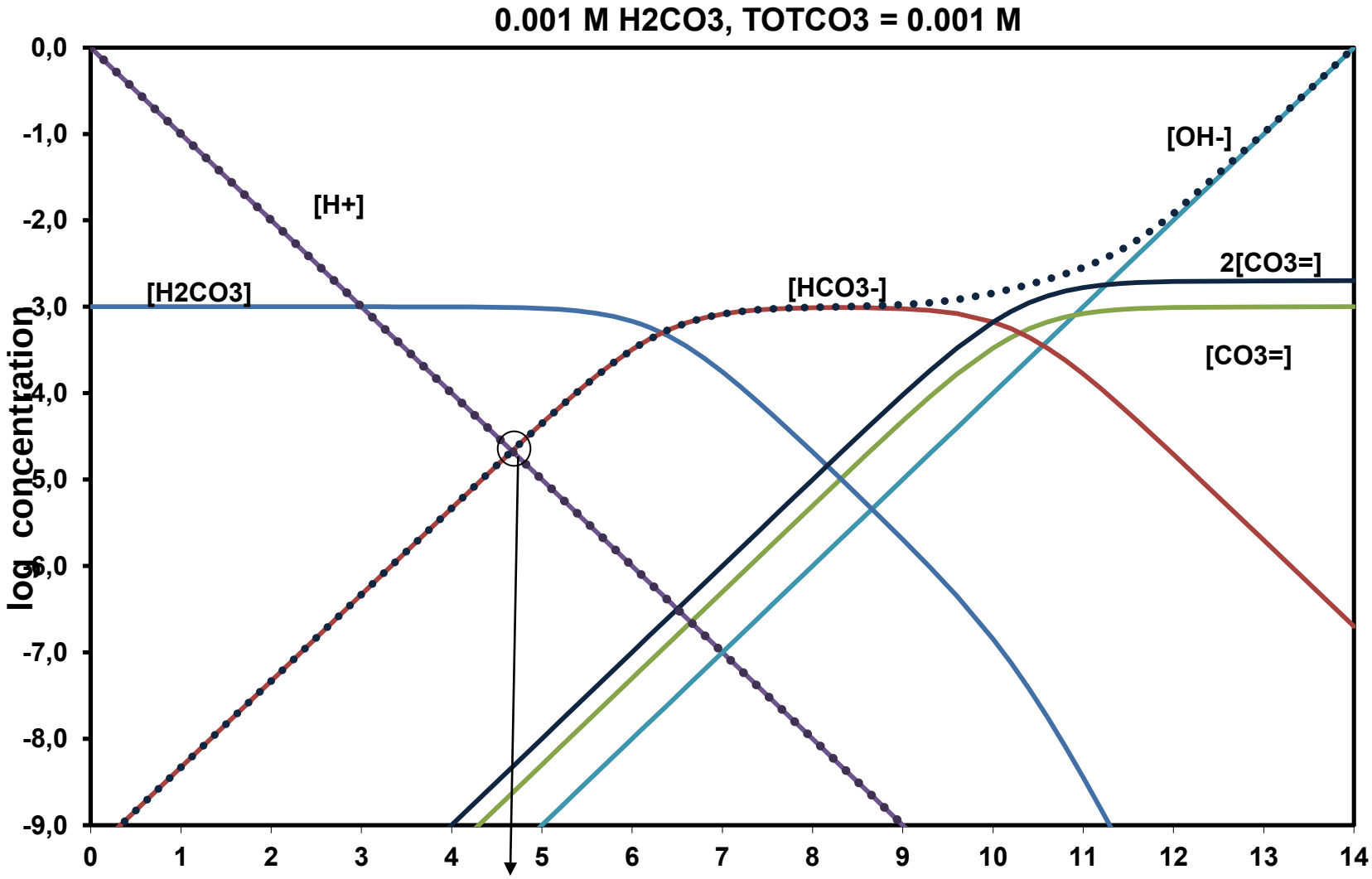
➢ Now, the last step is to check the charge balance:

$10^{-3} = 10^{-11} + 9x10^{-4} + 2\ (10^{-7.0})$ ok

- **Ex. What are the pH and the concentrations of all species at equilibrium in 10^{-3} M H_2CO_3 solution?**
- Equilibrium species: H^+ OH^- H_2CO_3 HCO_3^- $CO_3^=$
- K's: K_w $K_{a1} = 10^{-6.33}$ $K_{a1} = 10^{-10.3}$
- MB's $TOTCO_3 = [H_2CO_3]+[HCO_3^-] + [CO_3^=] = 10^{-3}$ M

- CB: $[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^=]$


TOTCO3 = 0.001 M
log concentration
0,0
-1,0
-2,0
-3,0
-4,0
-5,0
-6,0
-7,0
-8,0
-9,0
[H+]
[H2CO3]
[HCO3-]
[CO3=]
[OH-]
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH



CB : $[H^+]$ = $[OH^-] + [HCO_3^-] + 2[CO_3^=]$

LHS RHS

Does this solution have any alkalinity?

Alkalinity is the ability of water to neutralize acids.

If there is any species present in water that can react with acids, then the water is said to have alkalinity.

Therefore, check if there is any species at equilibrium that can react with acids.

- **Ex. What are the pH and the concentrations of all species at equilibrium in 10^{-3} M $NaHCO_3$ solution?**
- Equilibrium species: H^+ OH^- H_2CO_3 HCO_3^- $CO_3^=$
- K's: K_w $K_{a1} = 10^{-6.33}$ $K_{a1} = 10^{-10.3}$
- MB's $TOTCO_3 = [H_2CO_3]+[HCO_3^-] + [CO_3^=] = 10^{-3}M$

- CB: $[Na^+] +[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^=]$

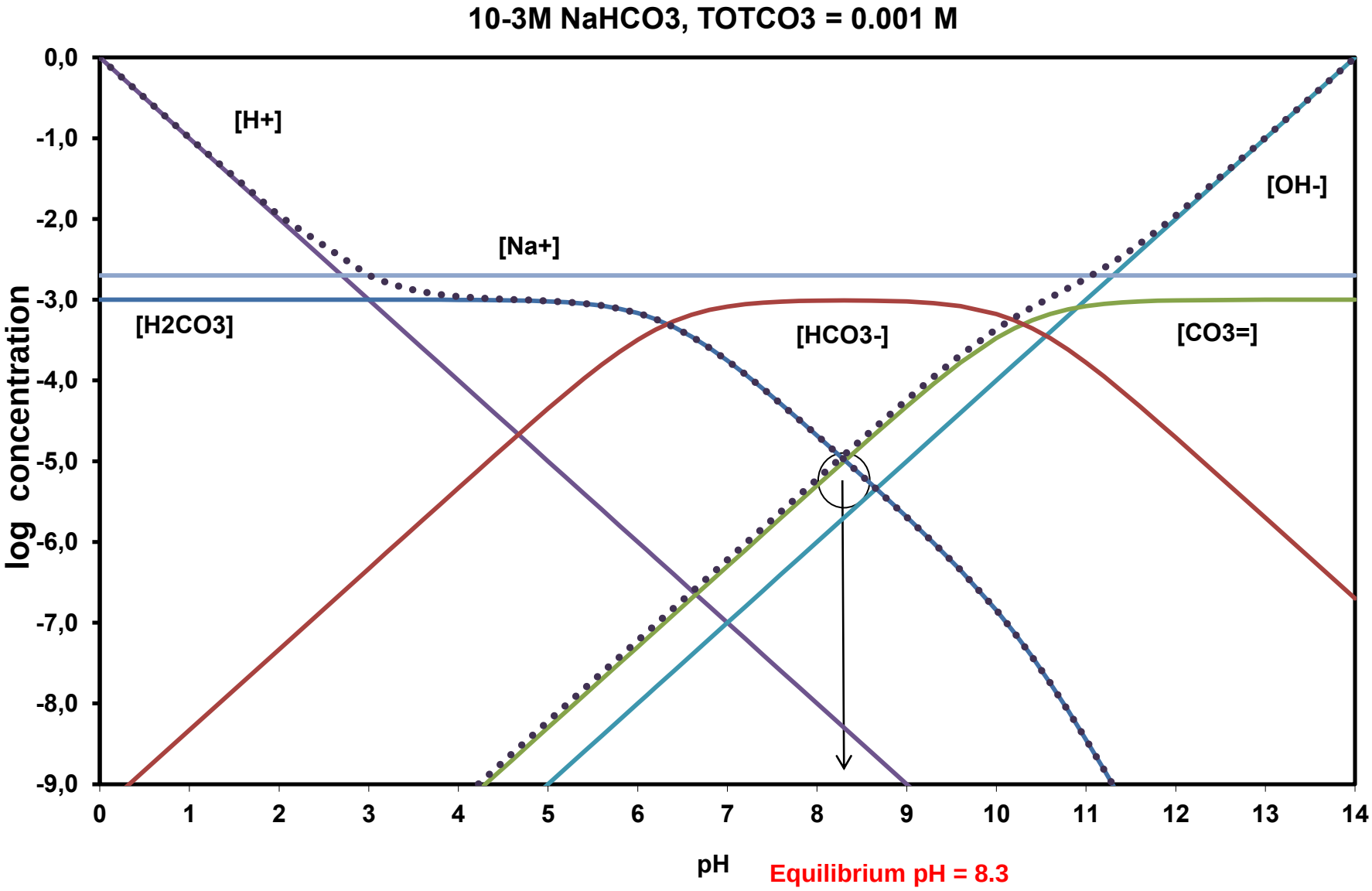
$[Na^+] = 10^{-3}$ M

- CB: $[Na^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^=]$

  $[Na^+] = TOTCO_3$

Modified CB:

$$[H_2CO_3] + [H^+] = [OH^-] + [CO_3^=]$$



MODIFIED CB : $[H_2CO_3] + [H^+] = [OH^-] + [CO_3^{=}]$

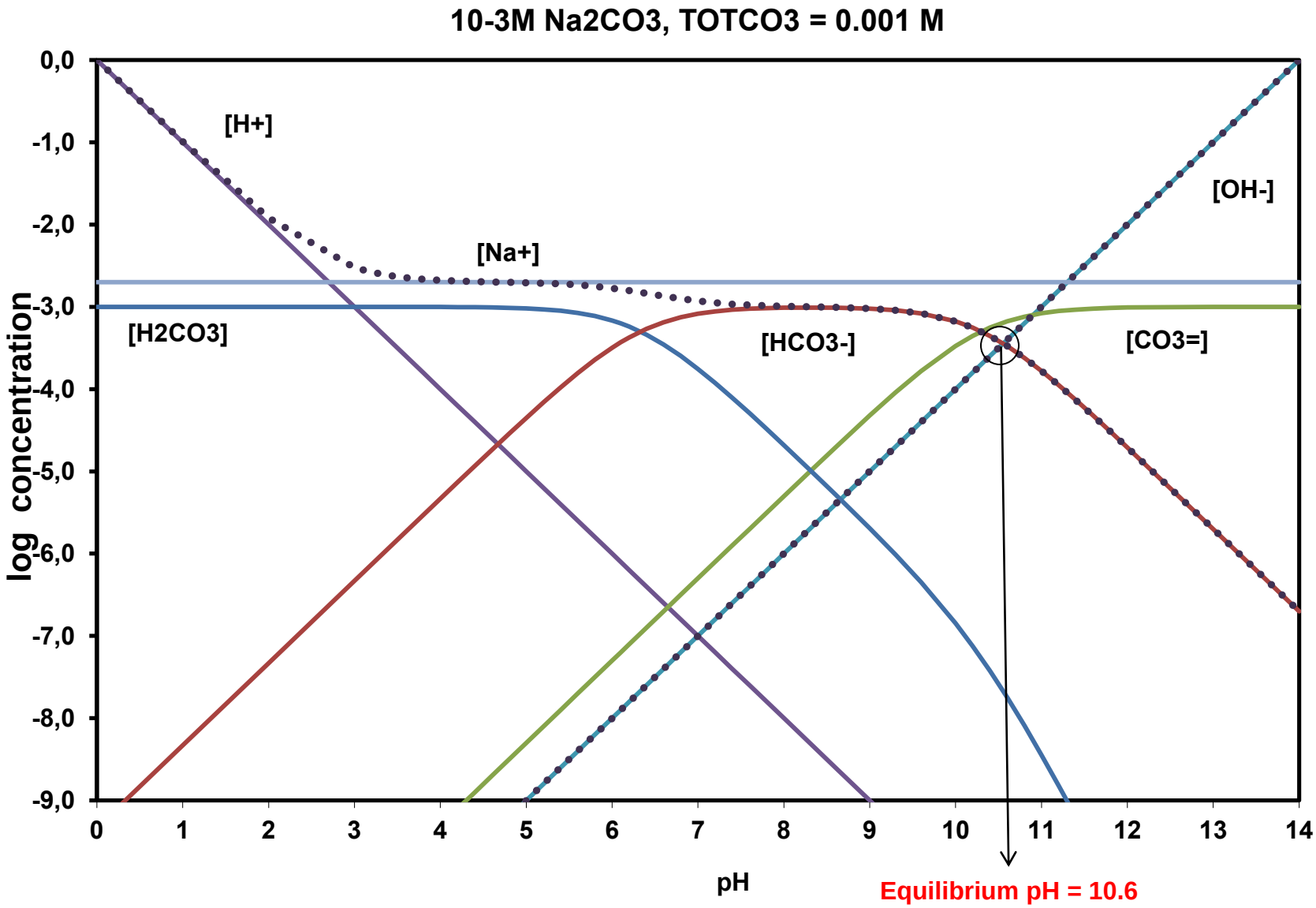
LHS RHS

Does this solution have any alkalinity?

- **Ex. What are the pH and the concentrations of all species at equilibrium in 10^{-3} M Na_2CO_3 solution?**
- Equilibrium species: H^+ OH^- H_2CO_3 HCO_3^- $CO_3^=$
- K's: K_w $K_{a1} = 10^{-6.33}$ $K_{a1} = 10^{-10.3}$
- MB's $TOTCO_3 = [H_2CO_3]+[HCO_3^-] + [CO_3^=] = 10^{-3}M$

- CB: $[Na^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^=]$

$[Na^+] = 2X10^{-3}$ M



MODIFIED CB : $2[H_2CO_3] + [HCO_3^{=}] + [H^+] = [OH^-] + [CO_3^{=}]$

LHS RHS

Does this solution have any alkalinity?

	pH
10^{-3} M H_2CO_3	4.6
10^{-3} M $NaHCO_3$	8.3
10^{-3} M Na_2CO_3	10.6