Log C – pH Diagrams for Monoprotic Acids

To draw the Log C – pH diagram,we must derive equations for each species.

$$[HA] = (TOTA)\alpha_o = (TOTA)\frac{[H^+]}{K_a + [H^+]}$$

$$\log[HA] = \log(TOTA) + \log\alpha_o$$

$$[A^-] = (TOTA)\alpha_1 = (TOTA)\frac{[K_a]}{K_a + [H^+]}$$

$$\log[A^-] = \log(TOTA) + \log\alpha_1$$

Log C-pH Diagrams

- The diagram should provide the concentrations of **all the equilibrium species** at all pH values.
- The only equations used to make these graphs are the **acidity constant**, **the mass balance on A**, and K_w.
- The same spreadsheet programs can be used to determine the speciation of **any monoprotic acid** present at **any concentration**.

How to Draw Log C – pH Diagrams Using Excel Spreadsheet

e.g. 5 x 10^{-4} M HAc solution $K_a = 1.8 \times 10^{-5}$

- Set up table with 6 columns:

pH	$[H^+]$	[HA]	$[A^-]$	log[HAc]	$\log[A^-]$

- You will also need 2 cells to input the K_a and *TOTA*.
  - In this example, assume:

    C4 holds K_a (1.8 x 10^{-5}) and

    C5 holds *TOTA* (5.00 x 10^{-4} M)

- Column A pH → go from 0 to 14.
- Column B → $[H^+]$ = 10^-pH
- Column C [HA] → = $C$5 * (1/(1+($C$4/B8)))
- Column D $[A^-]$ → = $C$5 * (1/(1+(B8/$C$4)))
- Calculate **log[HA]** at column E, and **log[A-]** at column F.
- Highlight columns A, E and F, choose XY scatter and plot.
- The pH scale will typically always be 0 – 14, but the log C scale can vary from 0 → -8 0 → -10 or -2 → -10

$$[HA] = (TOTA)\frac{[H^+]}{K_a + [H^+]}$$

$$[A^-] = (TOTA)\frac{[K_a]}{K_a + [H^+]}$$

5×10^{-4} M HAc solution

$K_a = 1.8 \times 10^{-5}$

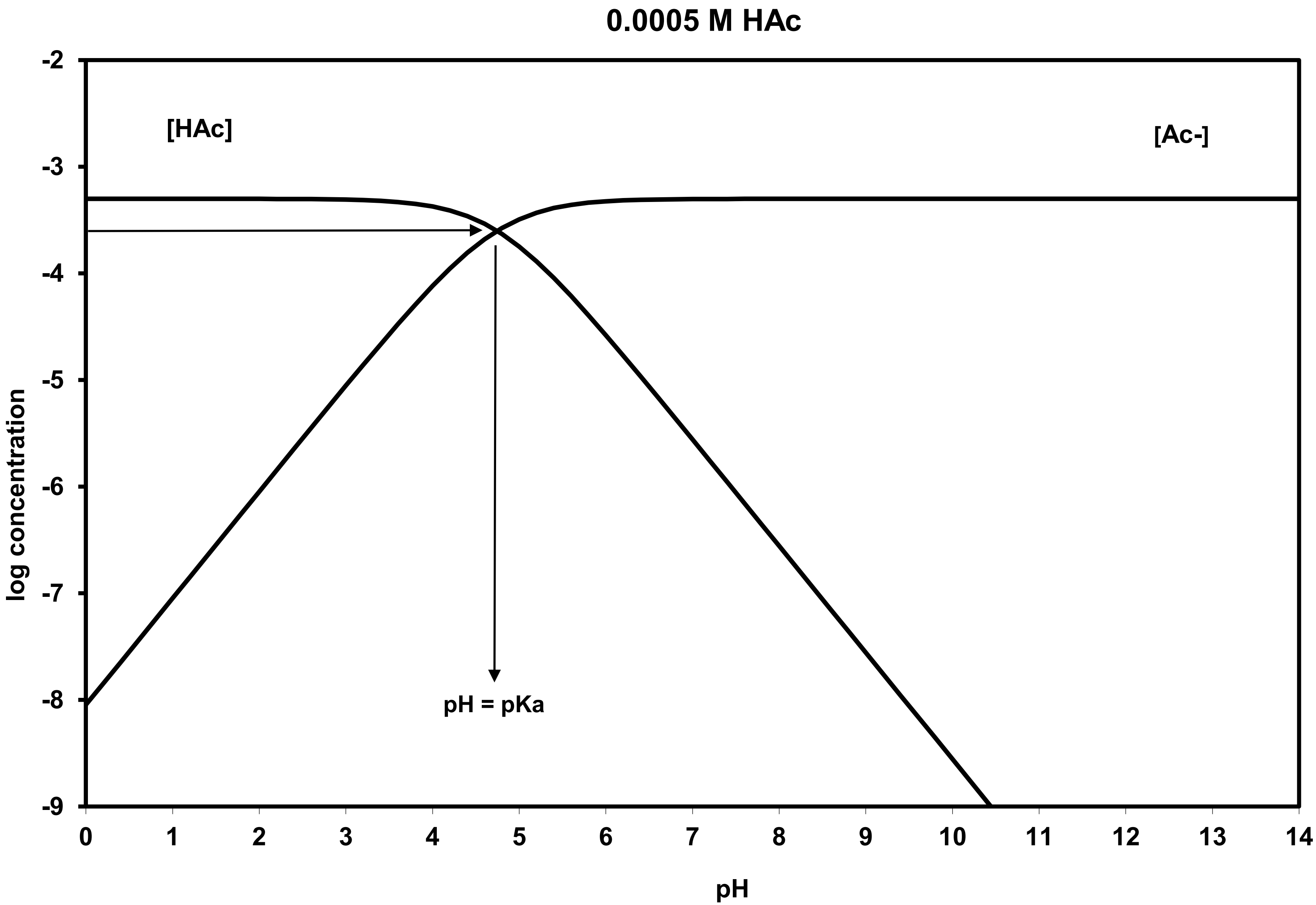
Ka=	1,80E-05
TOTAc=	5,00E-04

pH	[H+]	[HA]	$[A^-]$	log[HAc]	log[A-]
0	1	5,00E-04	9,00E-09	-3,30104	-8,04577
0,2	0,630957	5,00E-04	1,43E-08	-3,30104	-7,84577
0,4	0,398107	5,00E-04	2,26E-08	-3,30105	-7,64578
0,6	0,251189	5,00E-04	3,58E-08	-3,30106	-7,44579
0,8	0,158489	5,00E-04	5,68E-08	-3,30108	-7,24581
1	0,1	5,00E-04	9,00E-08	-3,30111	-7,04584
1,2	0,063096	5,00E-04	1,43E-07	-3,30115	-6,84588
1,4	0,039811	5,00E-04	2,26E-07	-3,30123	-6,64595
1,6	0,025119	5,00E-04	3,58E-07	-3,30134	-6,44607
1,8	0,015849	4,99E-04	5,67E-07	-3,30152	-6,24625
2	0,01	4,99E-04	8,98E-07	-3,30181	-6,04654
2,2	0,00631	4,99E-04	1,42E-06	-3,30227	-5,84699
2,4	3,98E-03	4,98E-04	2,25E-06	-3,30299	-5,64772
2,6	2,51E-03	4,96E-04	3,56E-06	-3,30413	-5,44886
2,8	1,58E-03	4,94E-04	5,61E-06	-3,30593	-5,25066
3	1,00E-03	4,91E-04	8,84E-06	-3,30878	-5,05351
3,2	6,31E-04	4,86E-04	1,39E-05	-3,31325	-4,85797
3,4	3,98E-04	4,78E-04	2,16E-05	-3,32024	-4,66496

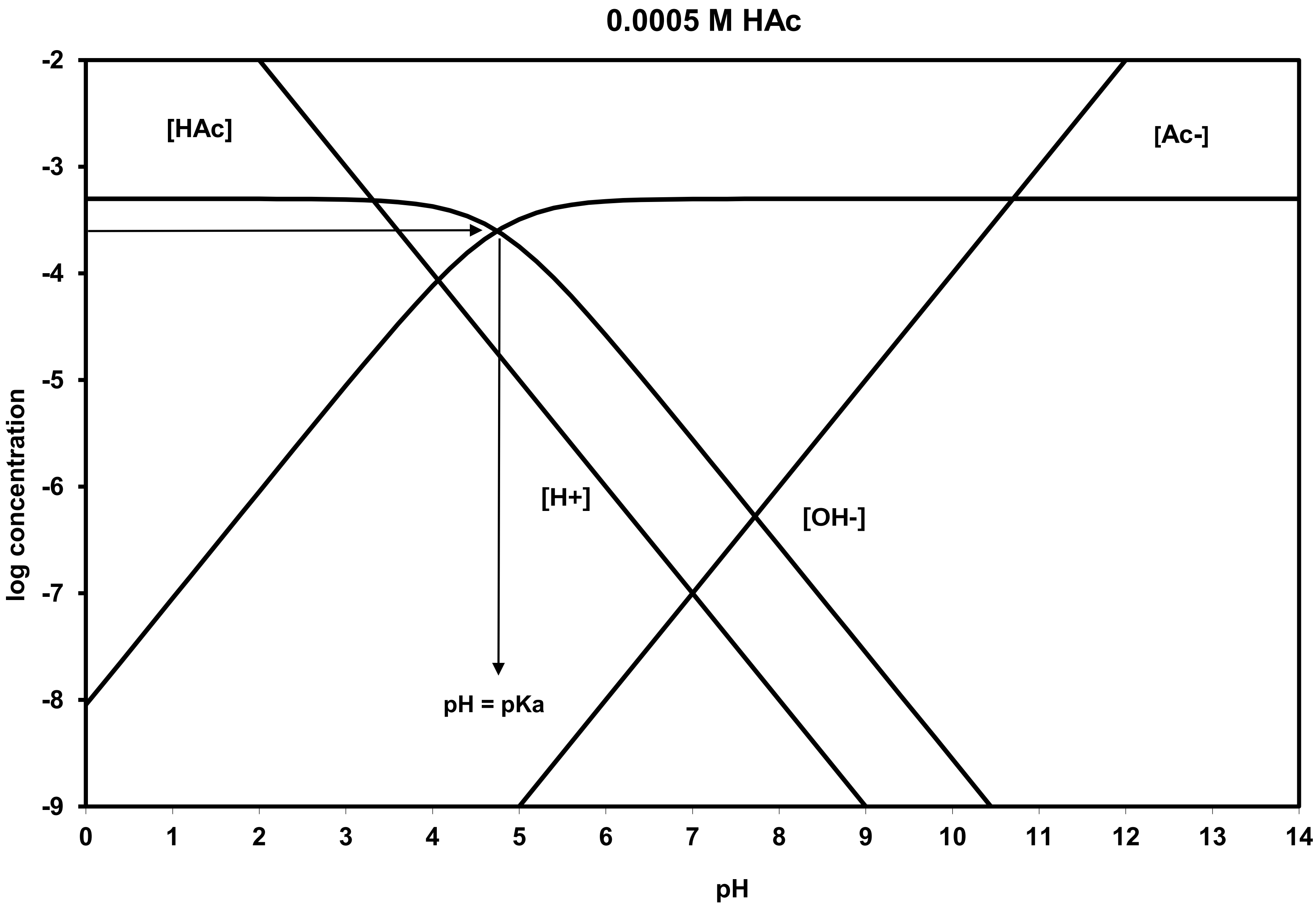
Properties of a Log C-pH Diagram

- Using the plot, one can easily see the speciation of HA over many orders of magnitude of H^+
- Where the HA and A^- lines intersect is where the concentrations of each are equal i.e. when $pH = pK_a$
- at $pH = pK_a$: $[HA] = [A^-] = 0.5(\mathit{TOT}A)$
- $\log [HA] = \log [A^-] = \log 0.5 + \log (\mathit{TOT}A) = -0.3 + \log (\mathit{TOT}A)$
- For a monoprotic acid, the point of intersection will always be at a point that is 0.3 units below the *TOT*A when plotted on a log scale
- The only 2 equations used to make these graphs are the acidity constant and the mass balance on A
- The same spreadsheet programs can be used to determine the speciation of any monoprotic acid present at any concentration
- In general: acids dissociate almost completely if $pH > pK_a + 1$

- A log C-pH diagram helps visualize the speciation of acids and bases over a wide range of conditions.
- We can use these diagrams to determine the pH and the speciation of the whole solution at equilibrium.
- Before computers were widely accessible, this was the only way to solve acid/base problems.
- A log C-pH diagram contains information about the
  - relevant acidity constants (indicated by the intersection points of conjugate acid/base pairs),
  - the dissociation of water (indicated by the relative positions of the H^+ and OH^- lines),
  - and the total amount of each weak acid/base group in the system (indicated by the largest value that log C approaches for the individual acid and base species)
- Once the graph is drawn, we determine the equilibrium speciation of the system by finding the unique pH where the charge balance is satisfied.



0.0005 M HAc
[HAc]
[Ac-]
pH = pKa
log concentration
pH
-2
-3
-4
-5
-6
-7
-8
-9
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14



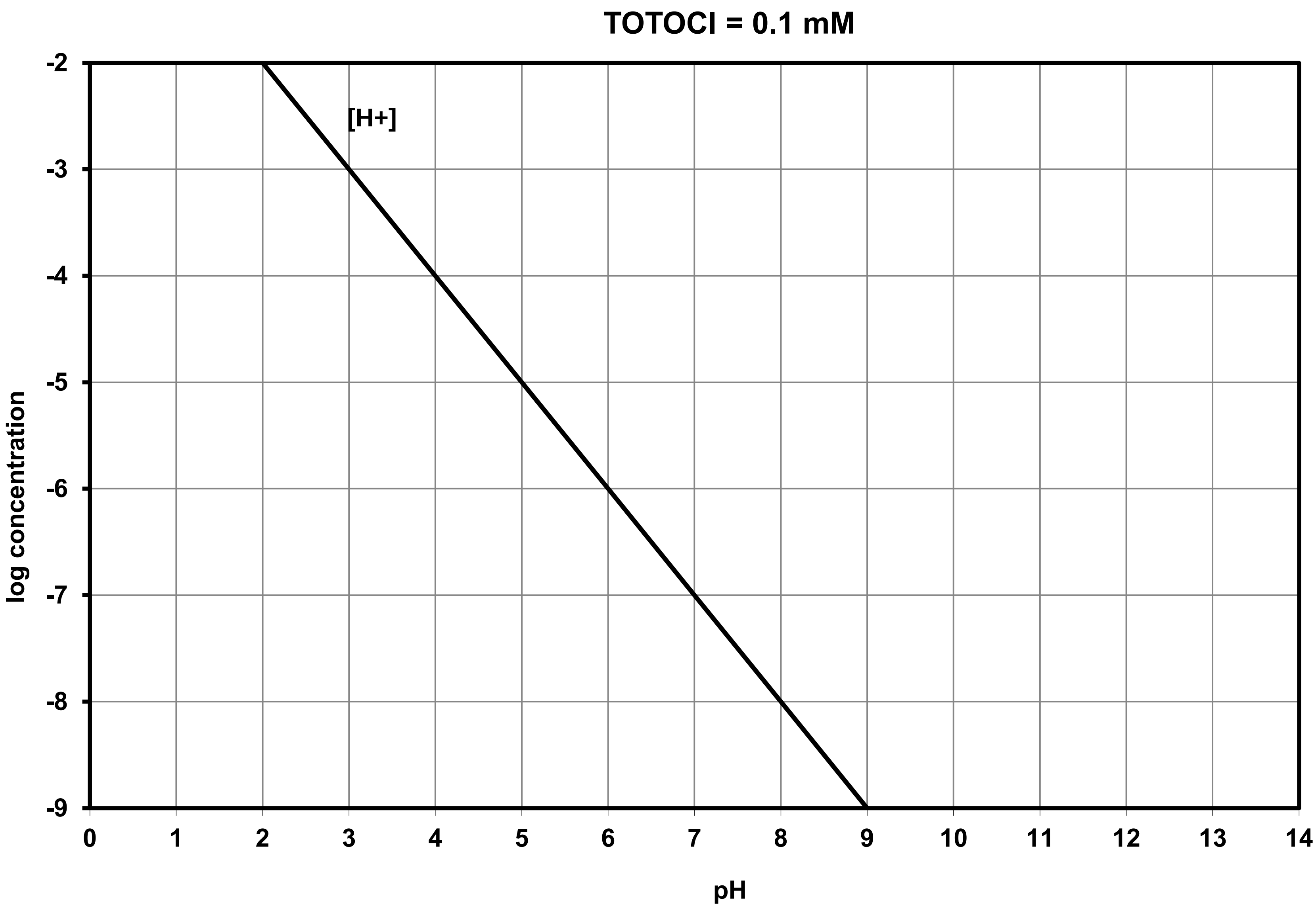
0.0005 M HAc
[HAc]
[Ac-]
[H+]
[OH-]
pH = pKa
log concentration
pH
-2
-3
-4
-5
-6
-7
-8
-9
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14

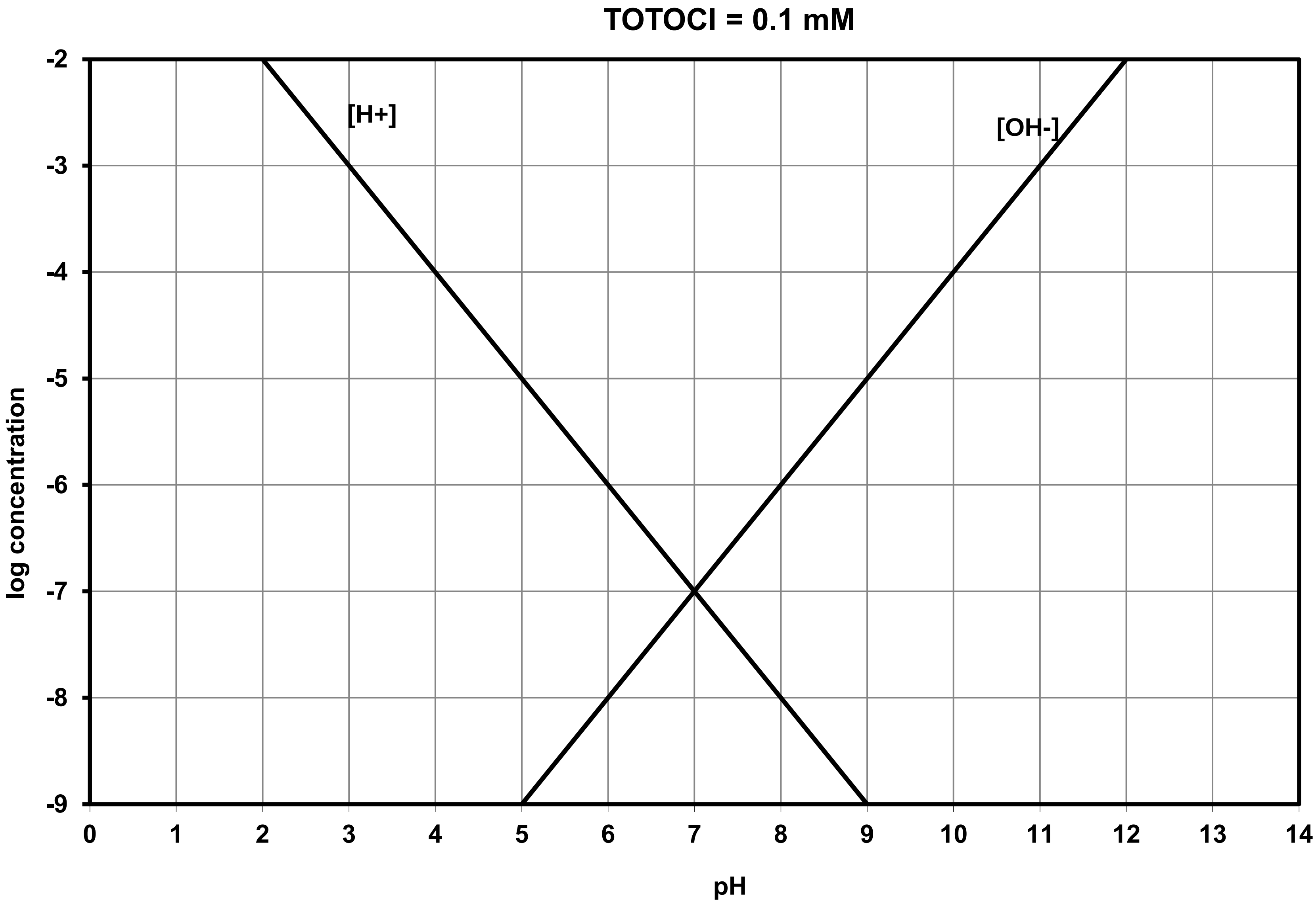
How to Draw log C-pH Diagrams on Graph Paper

1. The y axis is log C and it can have different scales, 0 to -8 or -2 to -9.
2. pH is on the x axis → 0 to 14
3. Plot H^+ line → it will pass through 0,0 and 7,7 (and will have a slope of –1)
4. Plot OH^- line → it will pass through14,0 and 7,7 (and will have a slope of +1)
5. Plot weak acid/base MB line (or TOTA line) → straight line at log C
6. Identify pH=pKa line.
7. Plot HA line → before pKa it will be horizontal at log C
8. Past pKa it will have slope of –1 (ie it will be parallel to the H^+ line)
9. Plot A^- line → past pKa it will be horizontal at log C
10. Before pKa, it will have a slope of +1 (ie it will be parallel to the OH^- line)
11. Plot the intersection of the HA and A^- lines → which will occur at 0.3 log C units below the MB line at the pKa
12. When pH = pKa, [HA] = [A-] = 0.5TOTA
13. ∴ log [HA] = log [A-] = log (0.5) + log (TOTA) = -0.3 + log (TOTA)
14. i.e. both are 0.3 log units below the MB line
15. Join the 2 parts of the HA and A^- lines with a nice smooth curve

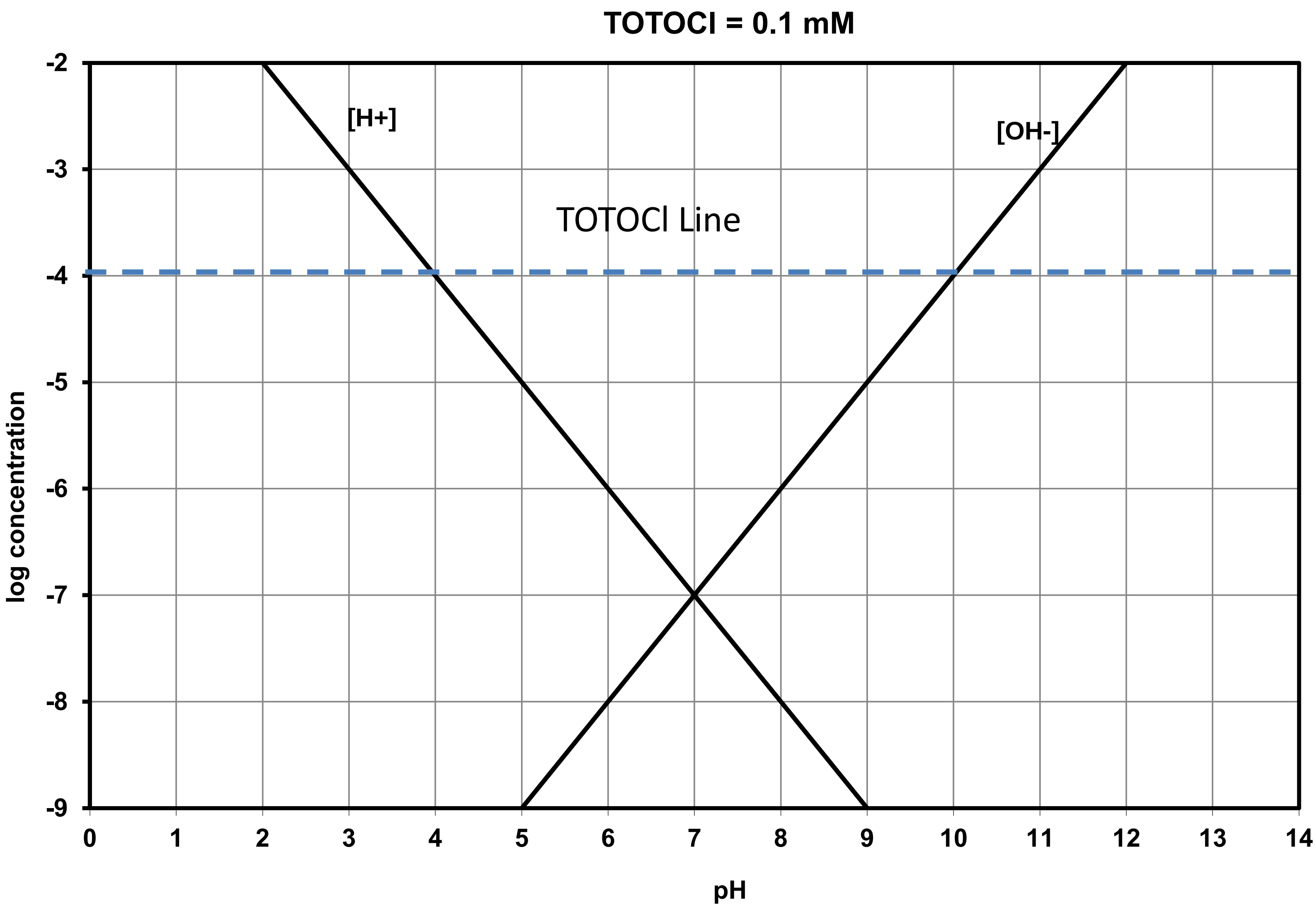
e.g. 0.1m M HOCl Solution pKa = 7.6

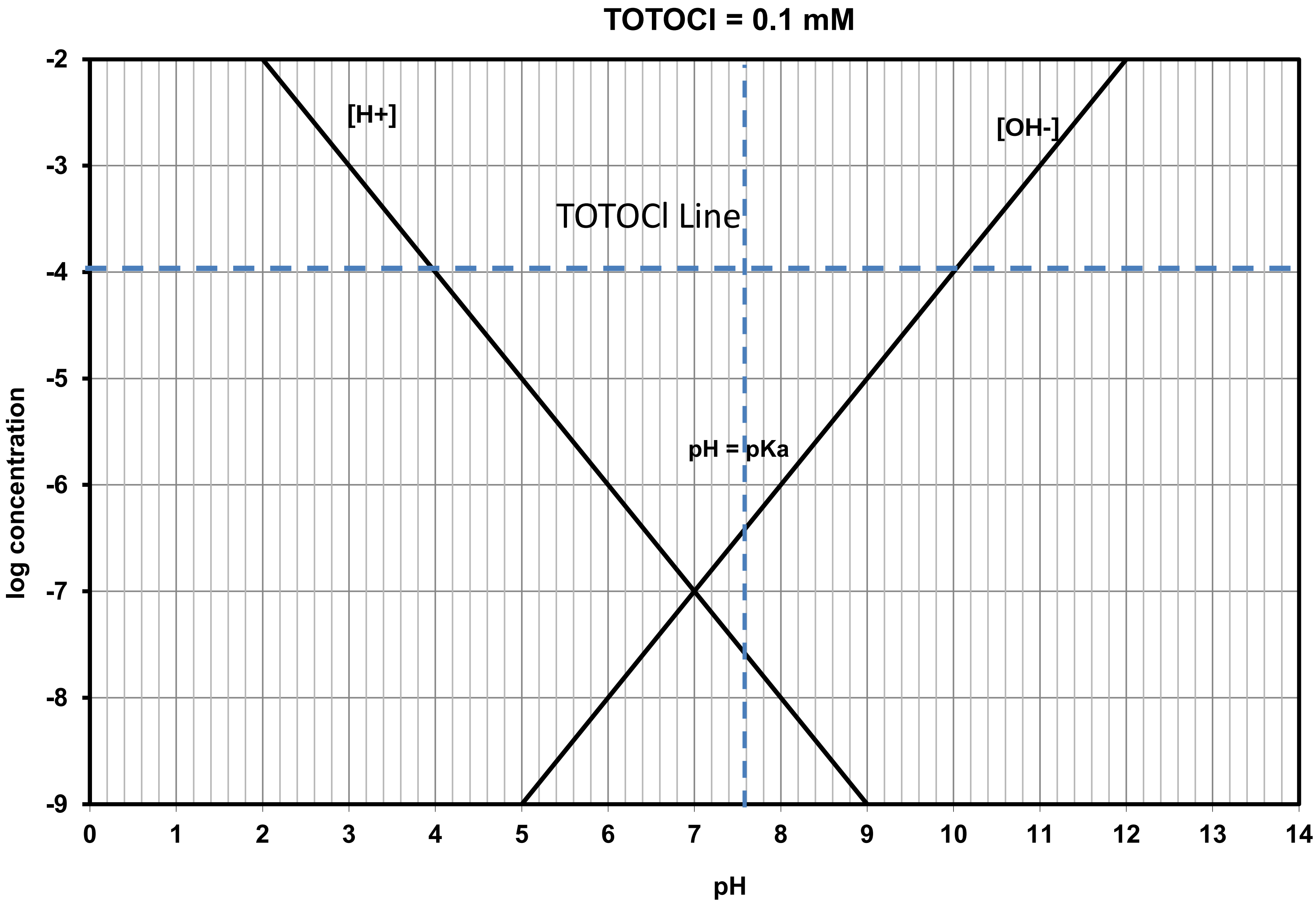
- steps 1 – 4 are always the same
- Make a horizontal line at log C = -4 → this is the MB line
- Make a mark on this line at pH = 7.6 (the pKa) → the HOCl and OCl- lines will intersect there.
- To draw the HOCl line, line up the ruler at the mark on the MB line at 7.6.
- Draw a line exactly parallel to the H+ line, going through the above mark.
- To draw the OCl- line, draw a line parallel to the OH- line, going through the same mark.
- The intersection of the HOCl and OCl- lines occur at pH = 7.6 and at log C = -4.3


TOTOCl = 0.1 mM
[H+]
log concentration
pH
-2
-3
-4
-5
-6
-7
-8
-9
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14



TOTOCl = 0.1 mM
[H+]
[OH-]
log concentration
-2
-3
-4
-5
-6
-7
-8
-9
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH


TOTOCl = 0.1 mM
[H+]
[OH-]
TOTOCl Line
log concentration
pH
-2
-3
-4
-5
-6
-7
-8
-9
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14



TOTOCl = 0.1 mM
[H+]
[OH-]
TOTOCl Line
pH = pKa
log concentration
pH
-2
-3
-4
-5
-6
-7
-8
-9
0
1
2
3
4
5
6
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11
12
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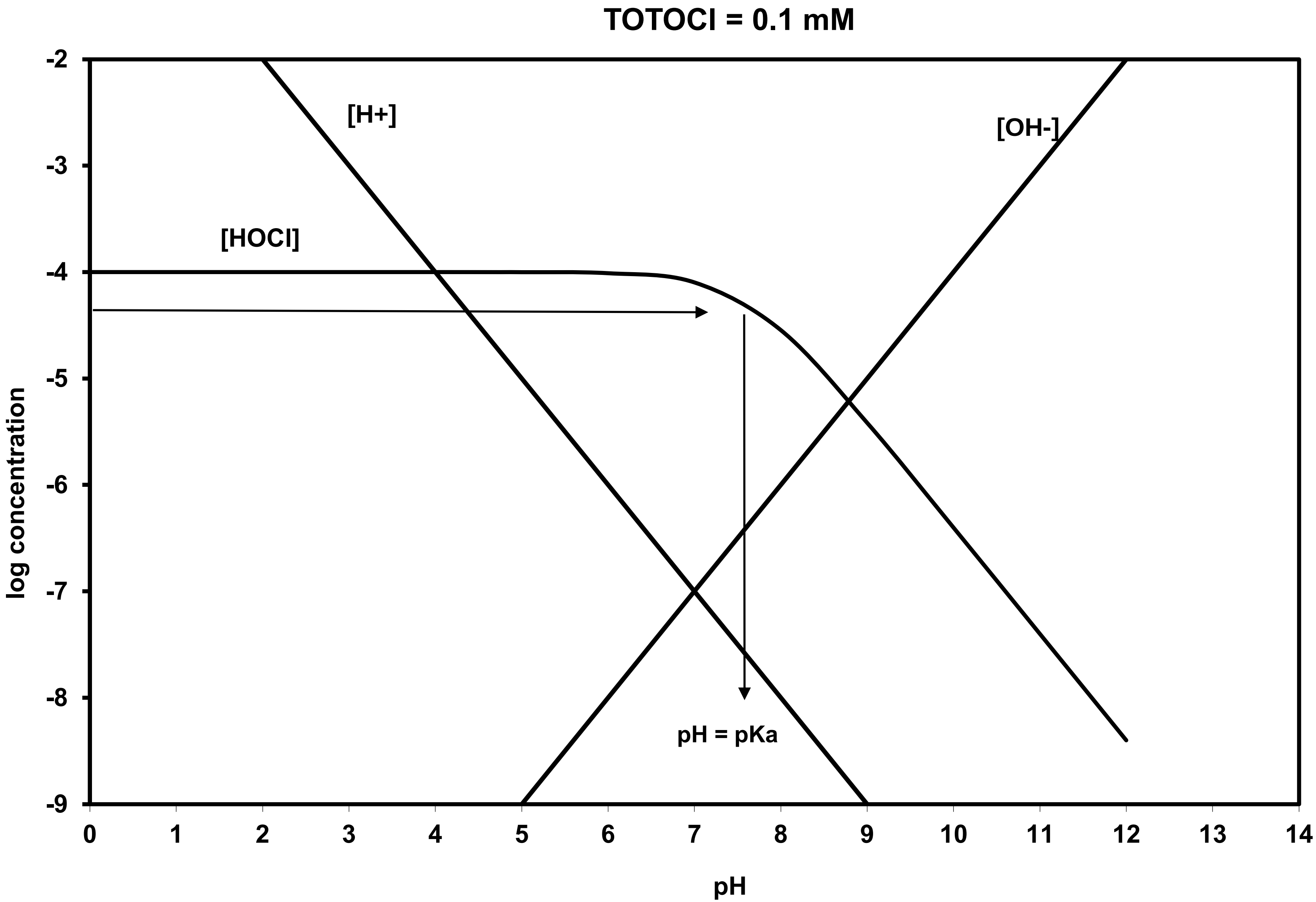
14


TOTOCl = 0.1 mM
[H+]
[OH-]
[HOCl]
pH = pKa
log concentration
pH
-2
-3
-4
-5
-6
-7
-8
-9
0
1
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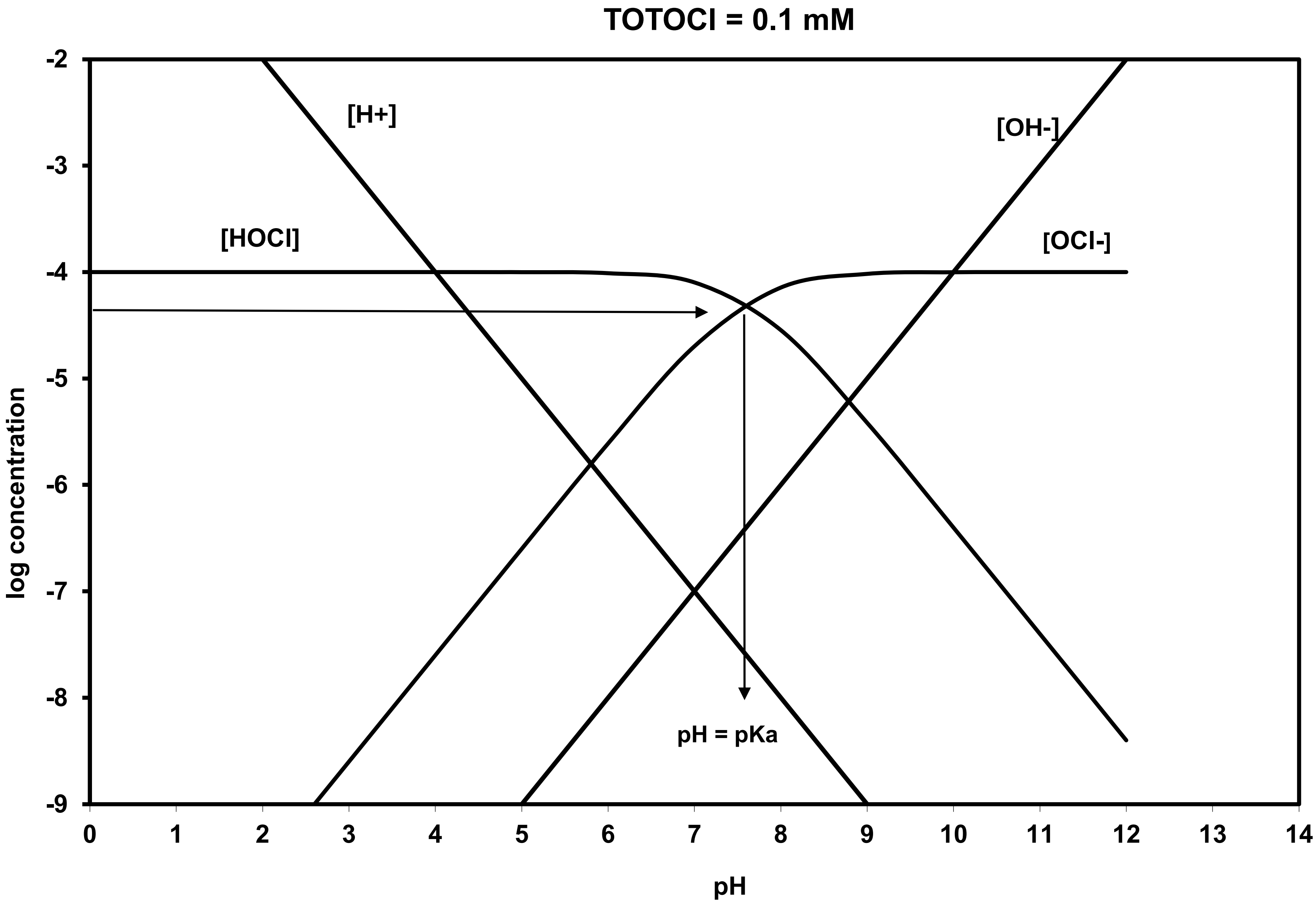
14



TOTOCl = 0.1 mM
[H+]
[OH-]
[HOCl]
[OCl-]
pH = pKa
log concentration
pH
-2
-3
-4
-5
-6
-7
-8
-9
0
1
2
3
4
5
6
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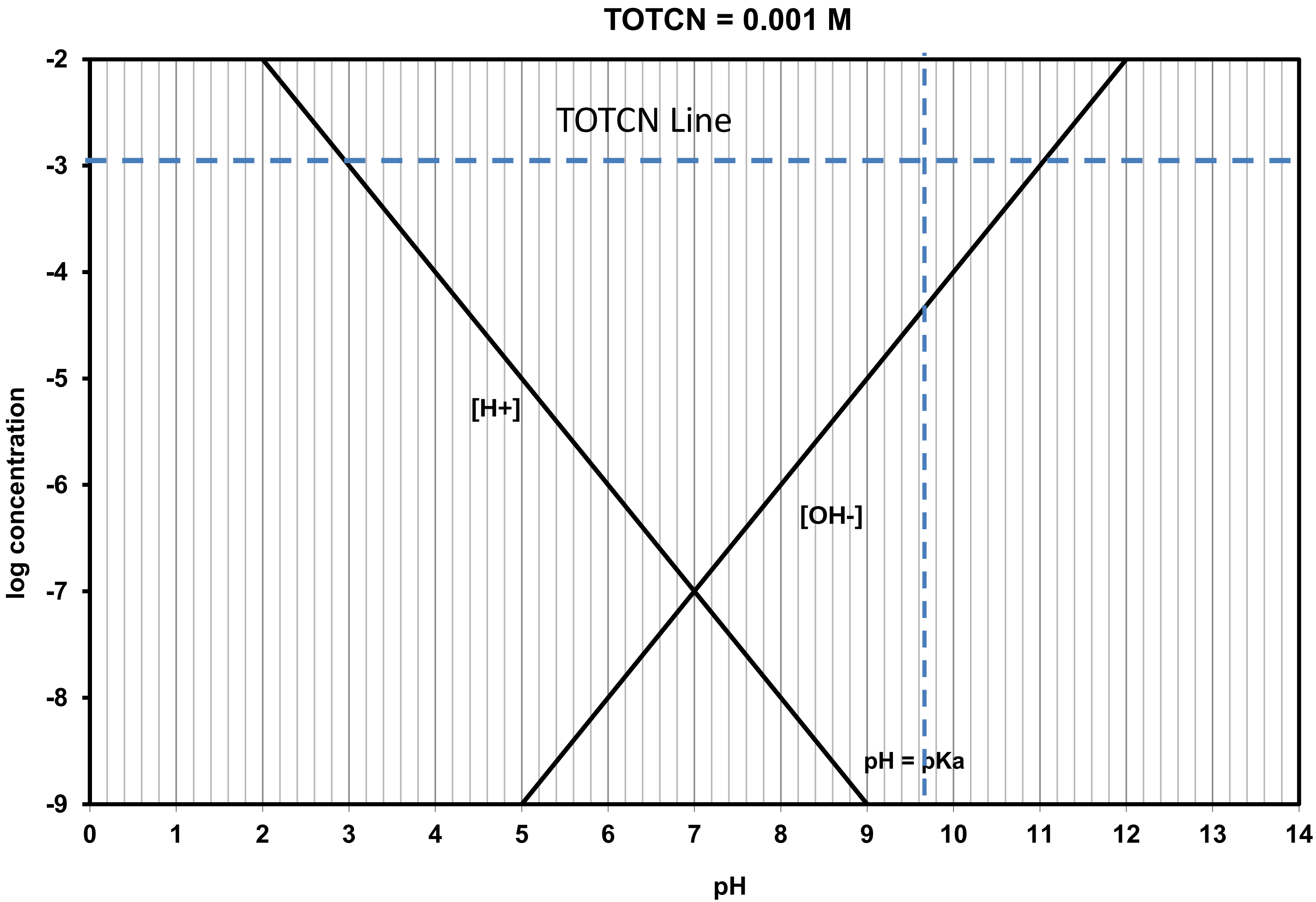
9
10
11
12
13
14

e.g. 10-3 M HCN Solution pKa = 9.3

- steps 1 – 4 are always the same
- Make a horizontal line at log C = -3 $\rightarrow$ this is the MB line
- Make a mark on this line at pH = 9.3 (the pKa) $\rightarrow$ the HCN and CN- lines will intersect there.
- To draw the HCN line, line up the ruler at the mark on the MB line at 9.3
- Draw a line exactly parallel to the H+ line, going through the above mark
- To draw the CN- line, draw a line parallel to the OH- line, going through the same mark
- The intersection of the HCN and CN- lines occur at pH = 9.3 and at log C = -3.3


TOTCN = 0.001 M
TOTCN Line
[H+]
[OH-]
pH = pKa
log concentration
pH
-2
-3
-4
-5
-6
-7
-8
-9
0
1
2
3
4
5
6
7
8
9
10
11
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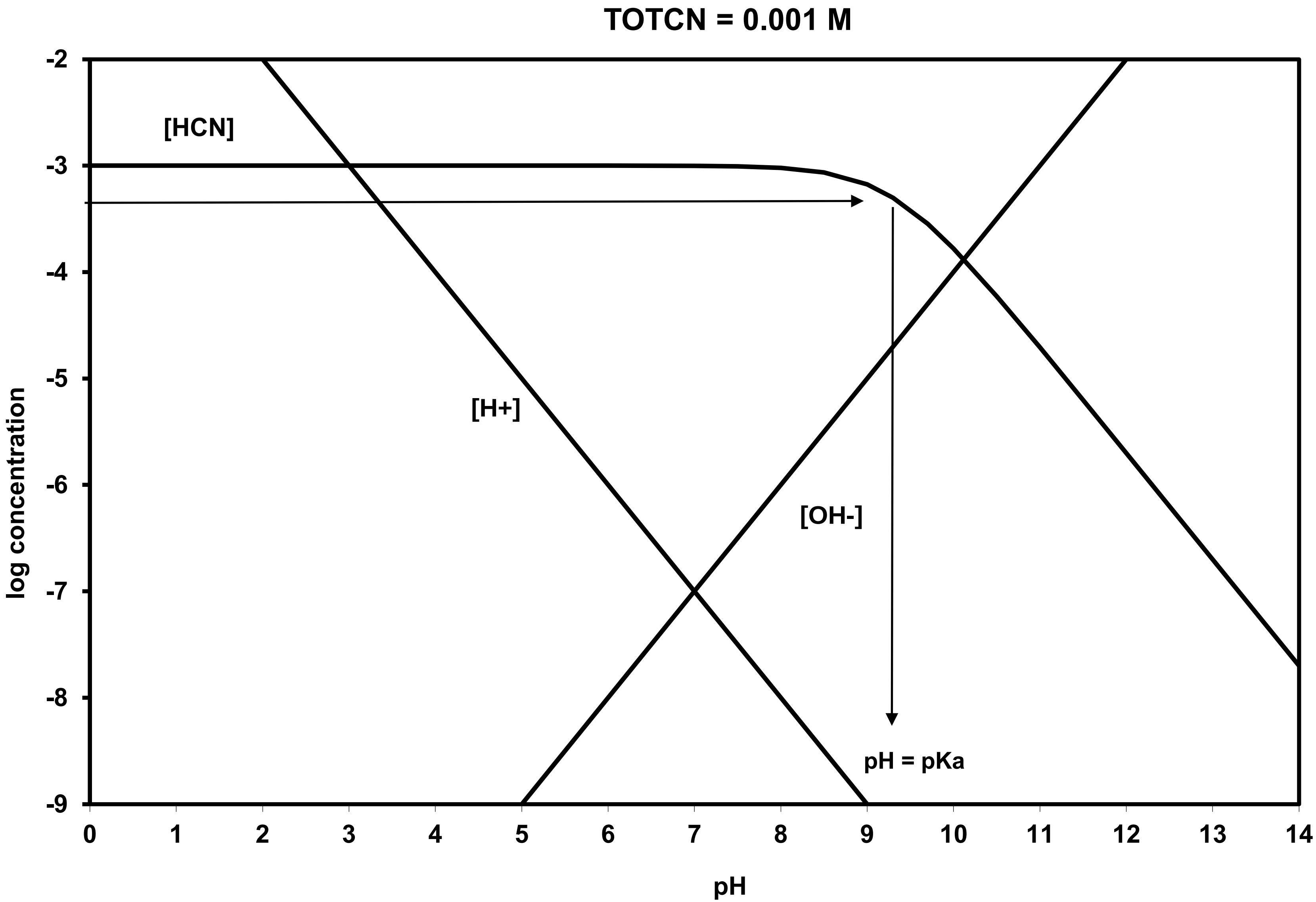
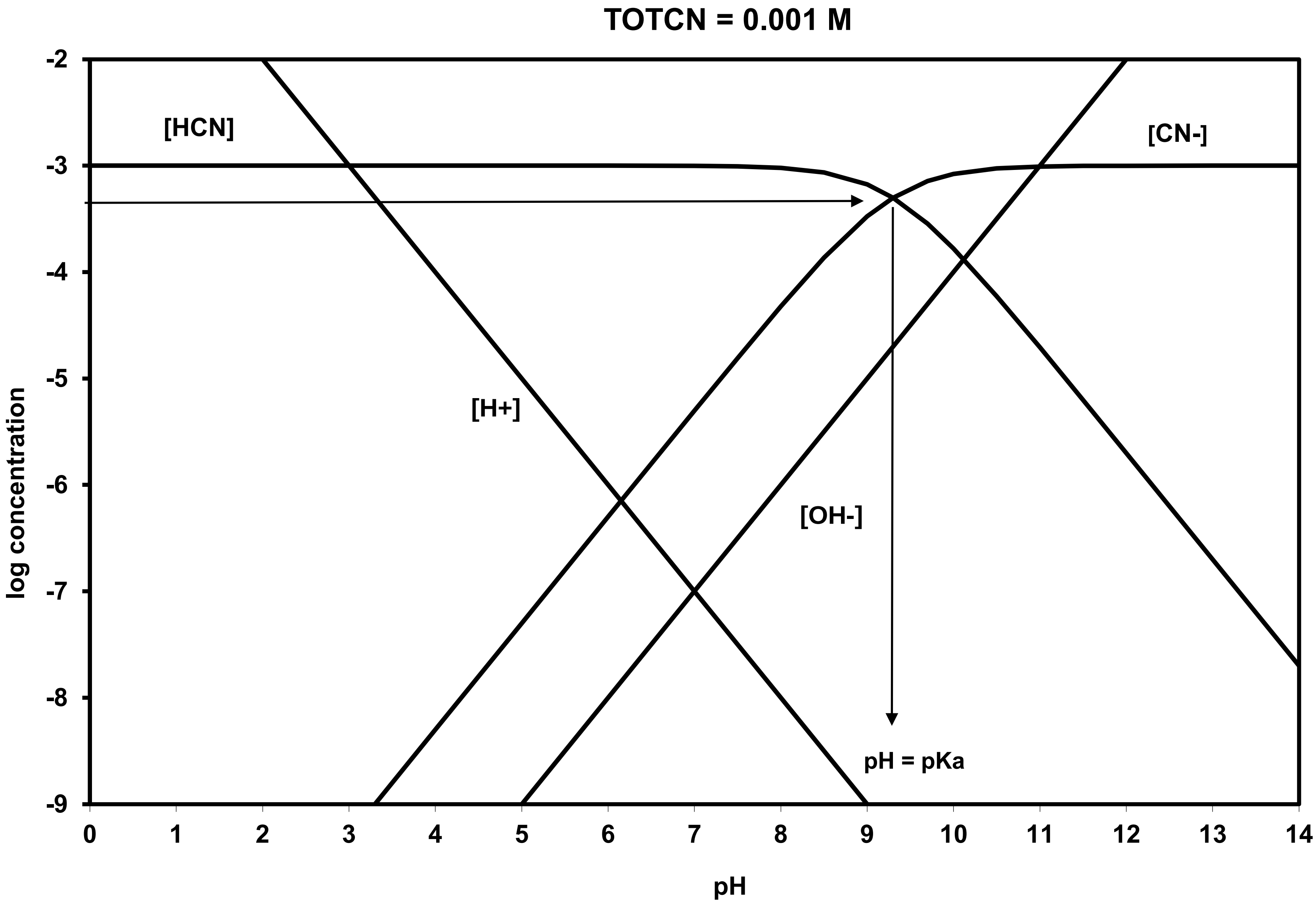
13
14


TOTCN = 0.001 M
[HCN]
[H+]
[OH-]
pH = pKa
log concentration
-2
-3
-4
-5
-6
-7
-8
-9
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH


TOTCN = 0.001 M
[HCN]
[CN-]
[H+]
[OH-]
pH = pKa
log concentration
pH
-2
-3
-4
-5
-6
-7
-8
-9
0
1
2
3
4
5
6
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9
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11
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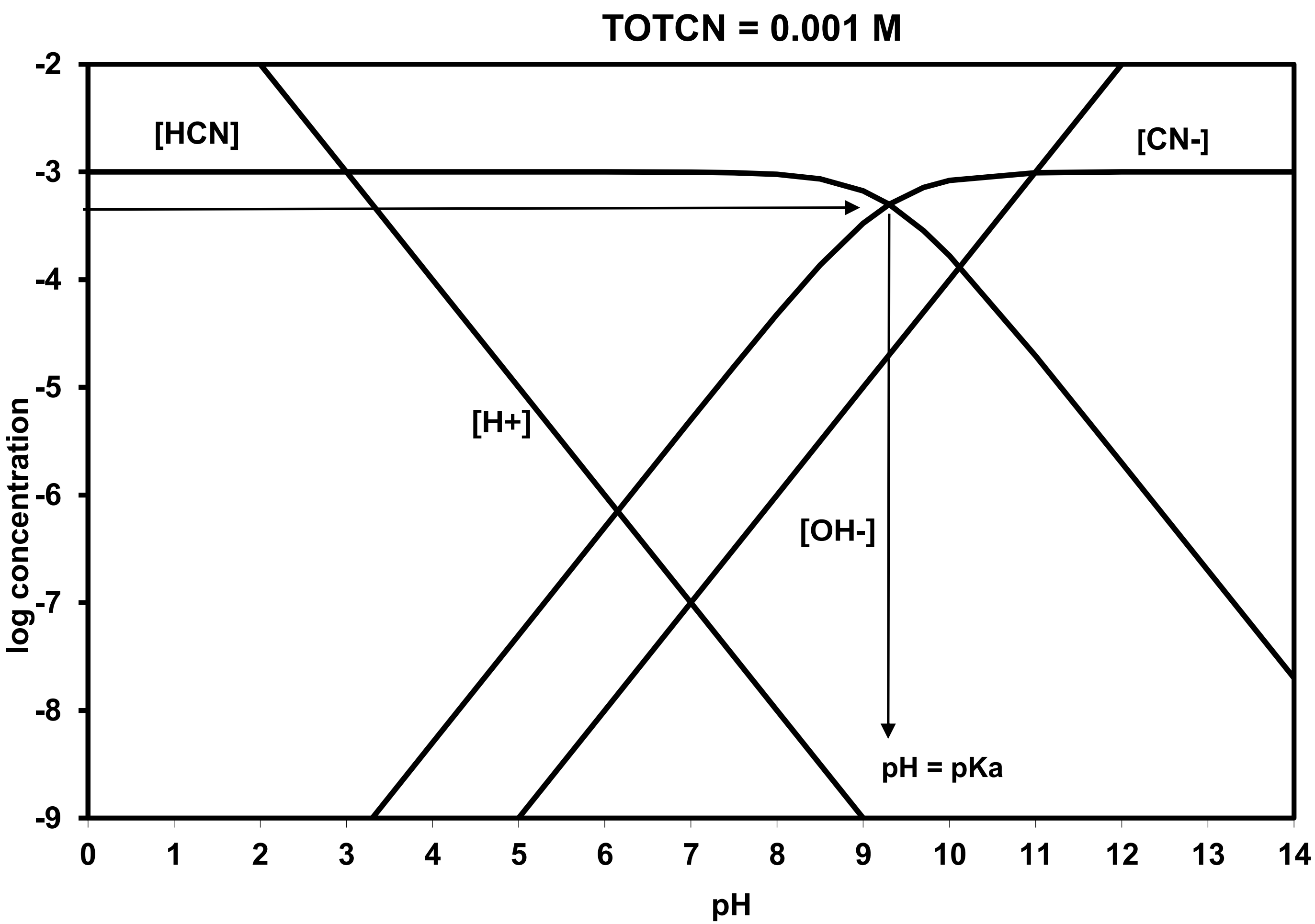
14

Determining pH and concentration of all species from the pC-pH diagram:

- The diagram incorporates all the information required i.e. the Ka's and the MB's
- To determine the pH at equilibrium, we find the pH where the charge balance is satisfied.
- We find the point on the diagram where the RHS of the CB = the LHS.
- Once we know the pH at which the CB is satisfied, we simply determine the concentrations of all the species at this pH from the diagram

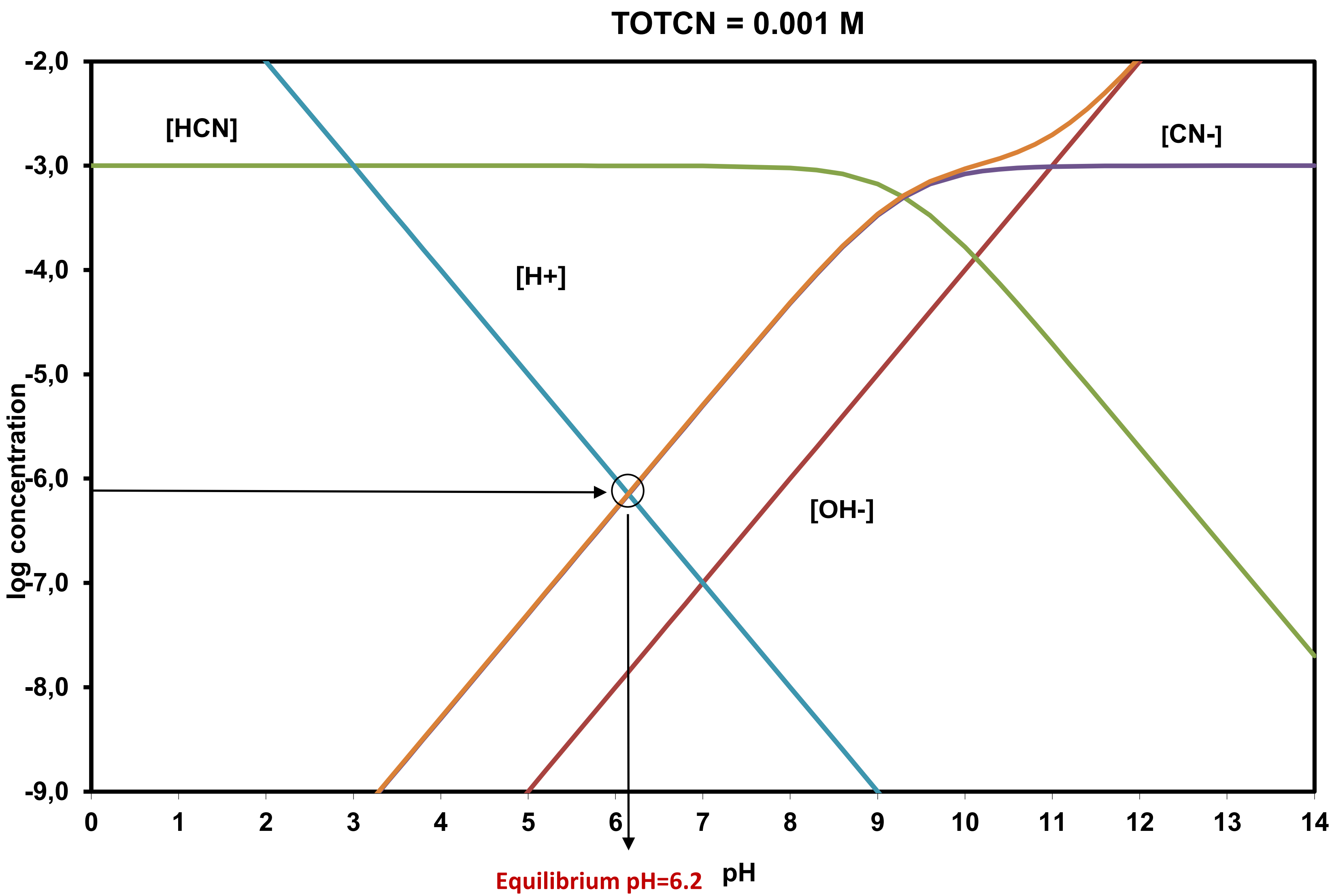
Ex. What are the pH and the concentrations of all species at equilibrium in a 10^{-3} M HCN solution?

- Equilibrium species: H^+ OH^- HCN CN
- K's: K_w $K_a = 10^{-9.3}$
- MB's TOTCN = [HCN] + $[CN^-]$ = 10^{-3} M
- CB: $[H^+] = [OH^-] + [CN^-]$
- Now we find the pH where the charge balance is satisfied, i.e., where the H^+ line is equal to the sum of the OH^- and CN^- lines.



CB : [H+] = [OH-] + [CN-]

LHS RHS



CB : [H+] = [OH-] + [CN-]

LHS RHS

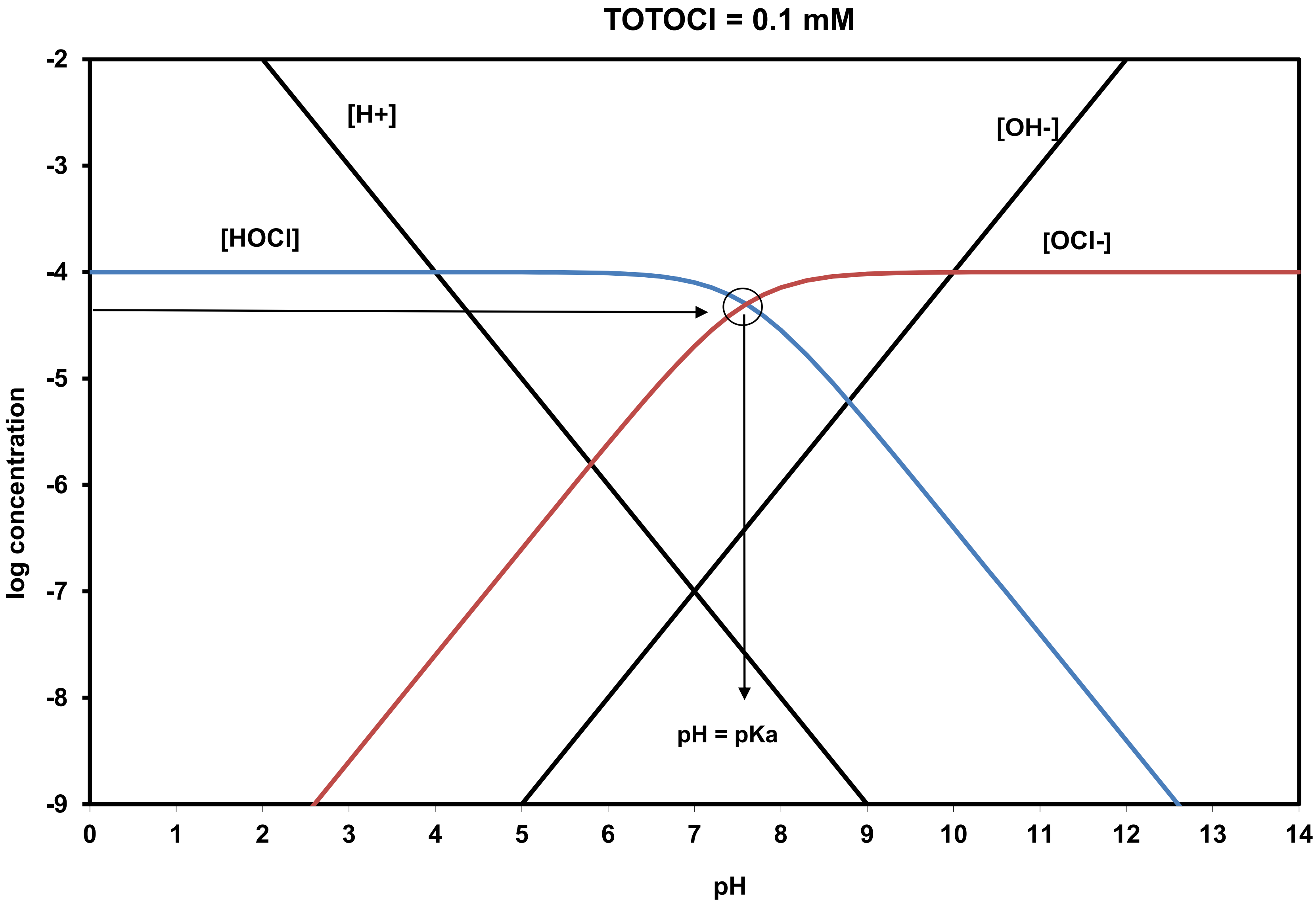
Equilibrium Concentrations of 10^{-3} M HCN

- $[H^+] = 10^{-6.2}$ M = 6.3×10^{-7} M
- $[OH^-] = 10^{-7.8}$ M = 1.59×10^{-8} M
- [HCN] = 10^{-3} M
- $[CN^-]$ $10^{-6.2}$ M
  - Now, the last step is to check the charge balance:

    $10^{-6.2} = 10^{-7.8} + 10^{-6.2}$ ok

Ex. What are the pH and the concentrations of all species at equilibrium in a 0.1 mM HOCl solution?

- Equilibrium species: H^+ OH^- HOCl OCl^-
- K's: K_w $K_a = 10^{-7.60}$
- MB's TOTOCl = [HOCl] + [OCl^-] = 10^{-4} M
- CB: [H^+] = [OH^-] + [OCl^-]
- Now we find the pH where the charge balance is satisfied, i.e., where the H^+ line is equal to the sum of the OH^- and OCl^- lines.


TOTOCl = 0.1 mM
[H+]
[OH-]
[HOCl]
[OCl-]
pH = pKa
log concentration
pH
-2
-3
-4
-5
-6
-7
-8
-9
0
1
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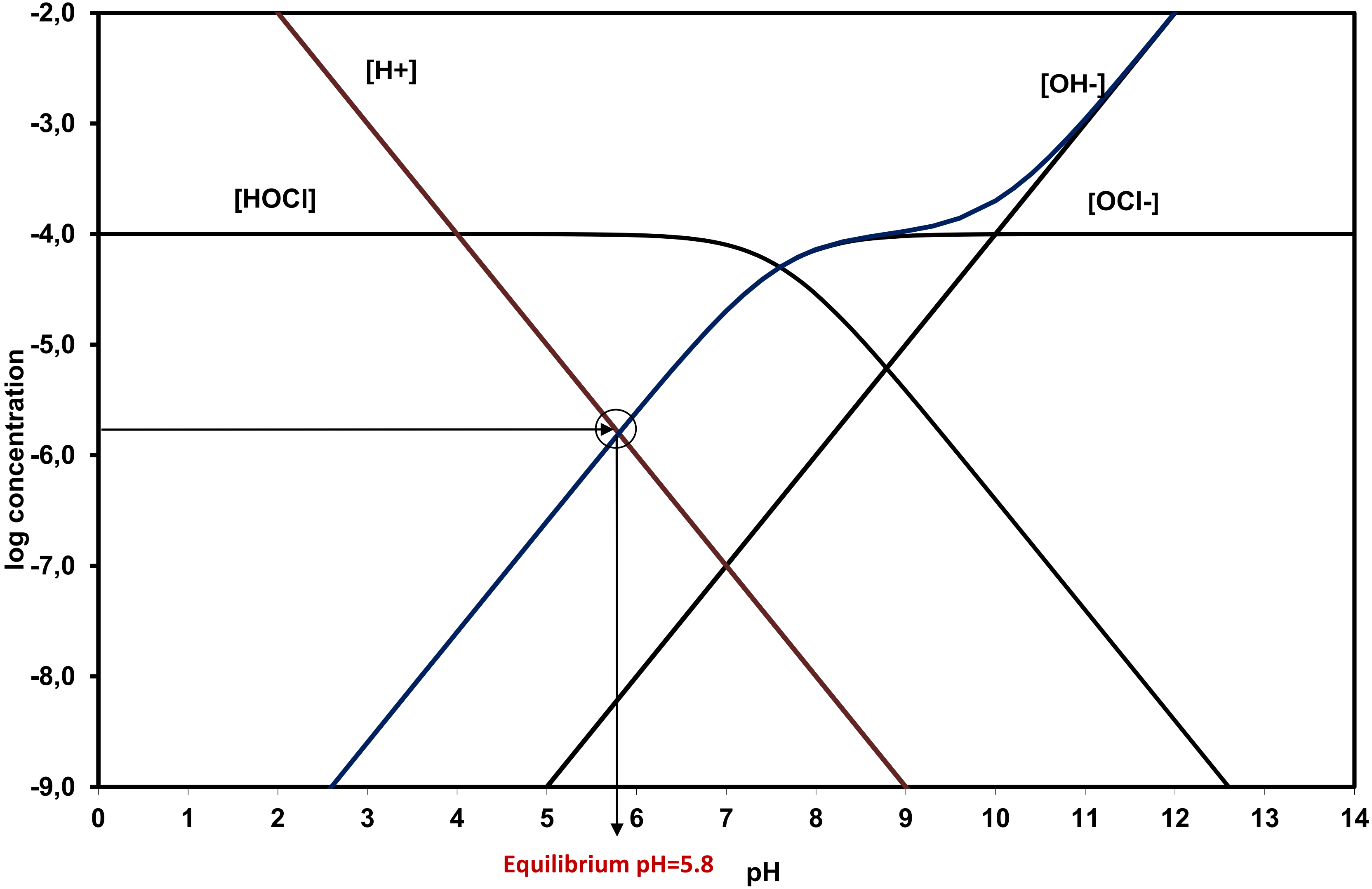
TOTOCl = 0.1 mM



CB : $[H^+]$ = $[OH^-] + [OCl^-]$

LHS RHS

Equilibrium Concentrations of 0.1 mM HOCl

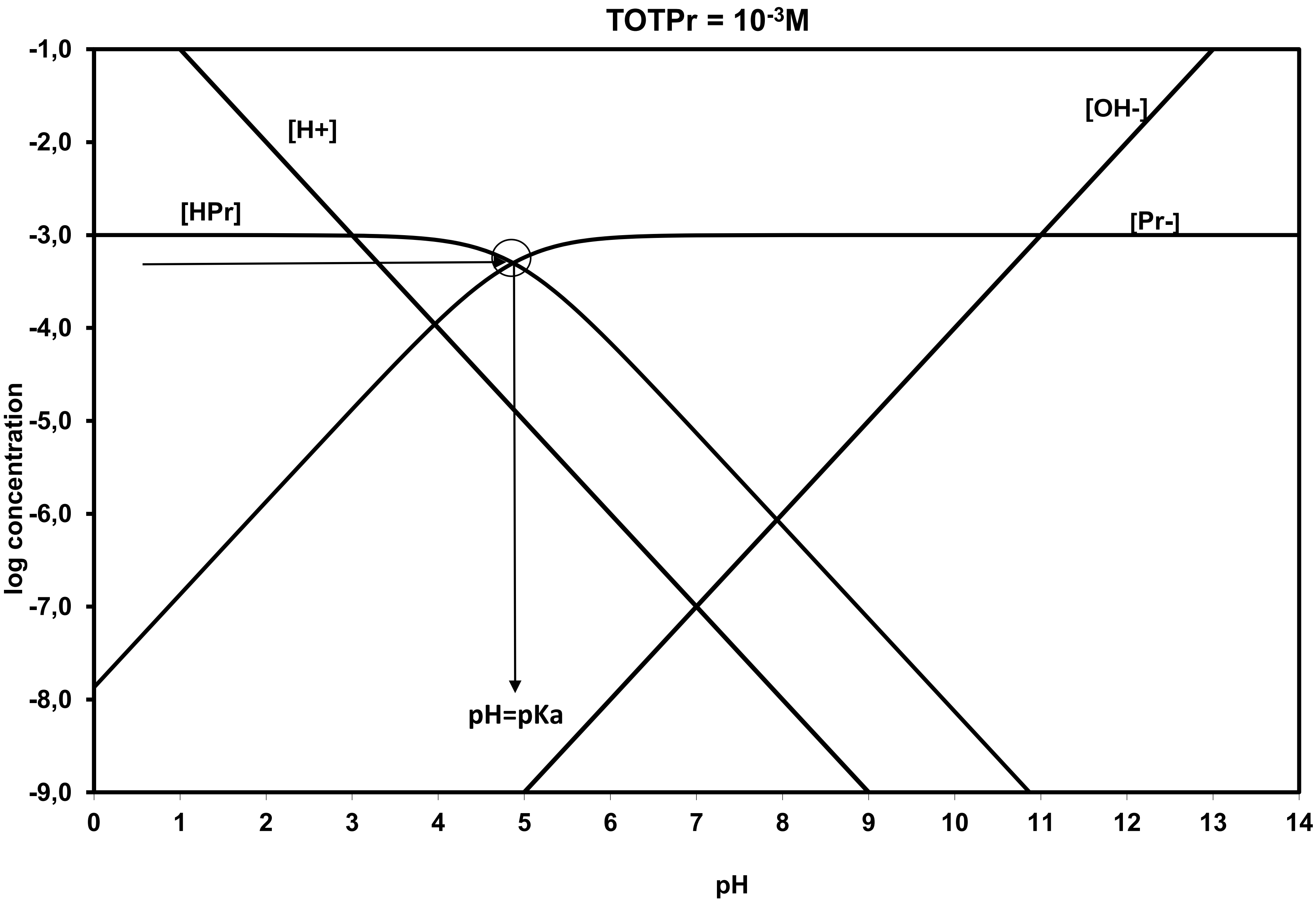
- $[H^+] = 10^{-5.8}$ M = 1.58×10^{-6} M
- $[OH^-] = 10^{-8.2}$ M = 6.3×10^{-9} M
- $[HOCl] = 10^{-4}$ M
- $[OCl^-]$ $10^{-5.8}$ M = 1.58×10^{-6} M

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

    $10^{-5.8} = 10^{-8.2} + 10^{-5.8}$ ok

Ex. What are the pH and the concentrations of all species at equilibrium in a 10^{-3} HPr solution?

- Equilibrium species: H^+ OH^- HPr Pr^-
- K's: K_w $K_a = 10^{-4.87}$
- MB's TOTPr = [HPr] + $[Pr^-]$ = 10^{-3} M
- CB: $[H^+] = [OH^-] + [Pr^-]$
- Now we find the pH where the charge balance is satisfied, i.e., where the H^+ line is equal to the sum of the OH^- and Pr^- lines.



TOTPr = 10-3M
[H+]
[OH-]
[HPr]
[Pr-]
pH=pKa
log concentration
pH
-1,0
-2,0
-3,0
-4,0
-5,0
-6,0
-7,0
-8,0
-9,0
0
1
2
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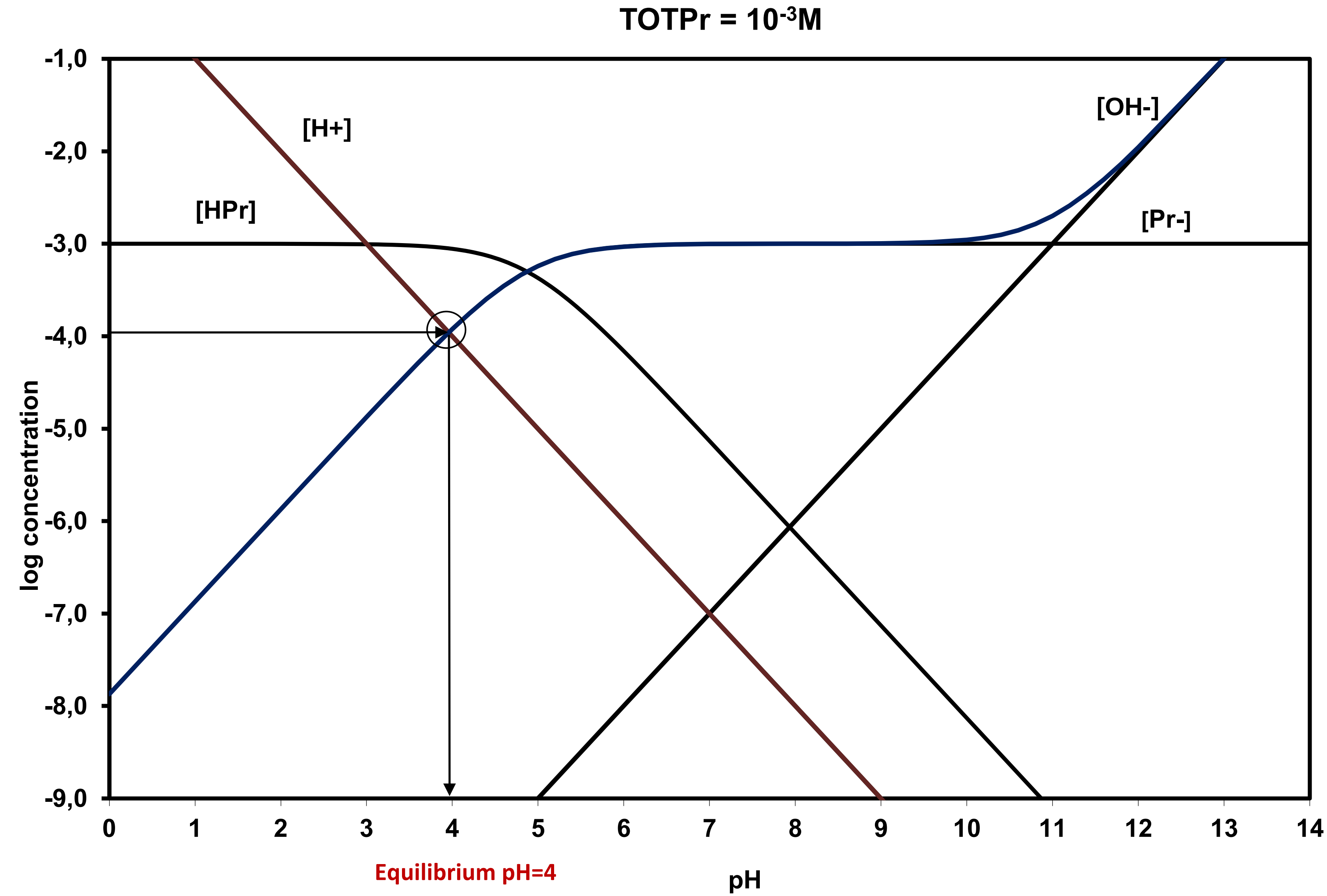


$$\text{CB}: \quad [H^+] = [OH^-] + [Pr^-]$$

LHS RHS

Equilibrium Concentrations of 10^{-3} M HPr

- $[H^+] = 1 \times 10^{-4}$ M
- $[OH^-] = 1 \times 10^{-10}$ M
- $[HPr] = 9 \times 10^{-4}$ M
- $[Pr^-] = 10^{-4}$ M

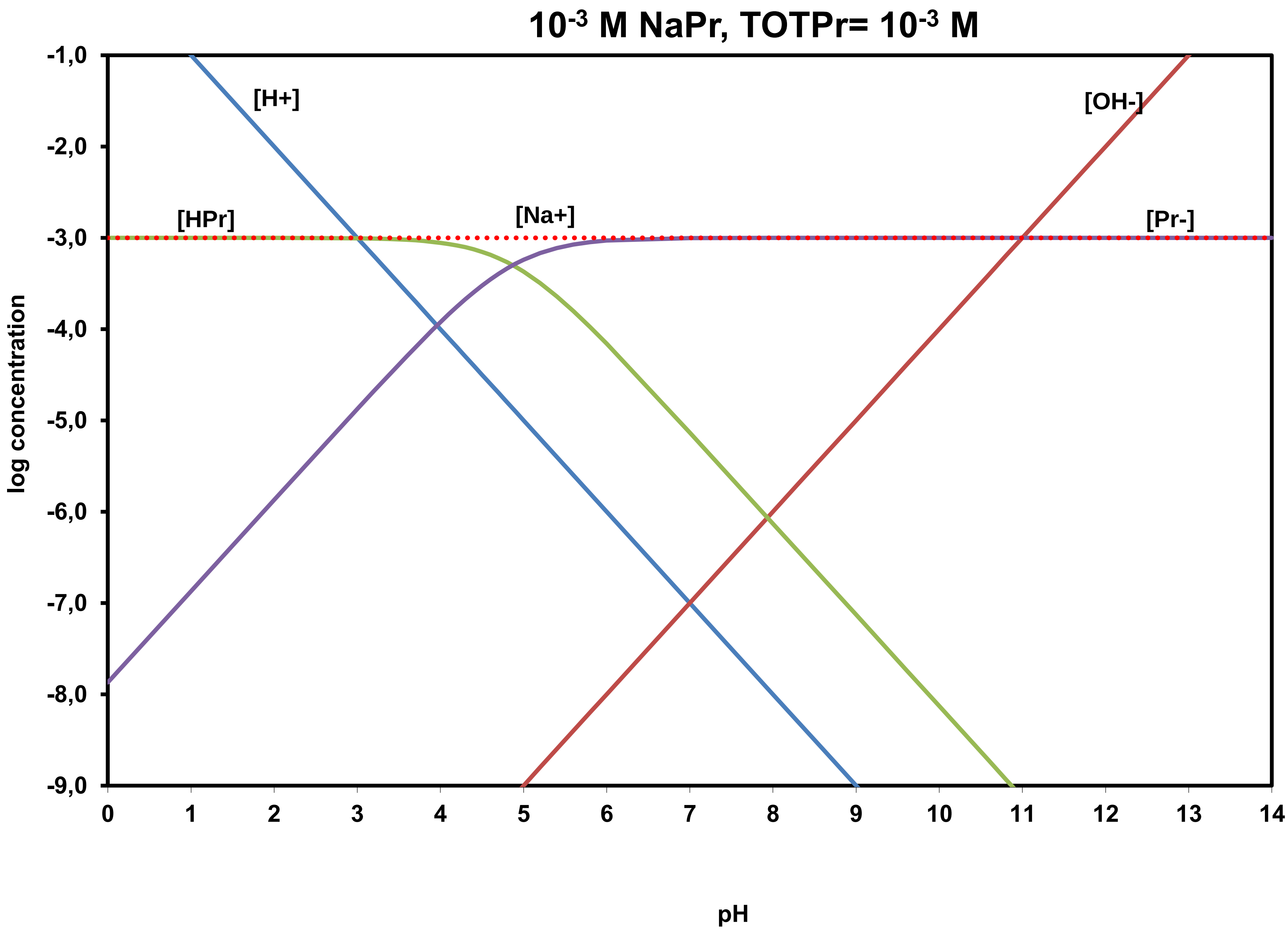
➢ Now, the last step is to check the charge balance:

$$10^{-4} = 10^{-10} + 10^{-4} \qquad \text{ok}$$

Ex. What are the pH and the concentrations of all species at equilibrium in a 10^{-3} M NaPr solution?

- Equilib. species: H^+ OH^- HPr Pr^- Na^+
- K's: K_w $K_a = 10^{-4.87}$
- MB's TOTPr = [HPr] + [Pr^-] = 10^{-3} M
  TOTNa = [Na^+] = 10^{-3} M
- CB: [H^+] + [Na^+] = [OH^-] + [Pr^-]

- Log C-pH diagram is exactly the same as 10^{-3} M HPr, except that there is one additional line for the MB of Na^+. This is simply a horizontal line at log C = -3.
- Now we find the pH where the charge balance is satisfied.
- The sum of the H^+ and Na^+ lines is equal to the sum of the OH^- and Pr^- lines.
- On the LHS→ we need to sum the 2 lines for H^+ and Na^+.
- At pH < 11, Pr^- becomes the dominant species on the RHS. So we follow the Pr^- line until it crosses sum of the LHS lines, in this case, the Na^+ line. But this occurs at a very flat point on the diagram, where both appear to be 10^{-3} M.



10-3 M NaPr, TOTPr= 10-3 M
log concentration
pH
[H+]
[OH-]
[HPr]
[Na+]
[Pr-]
-1,0
-2,0
-3,0
-4,0
-5,0
-6,0
-7,0
-8,0
-9,0
0
1
2
3
4
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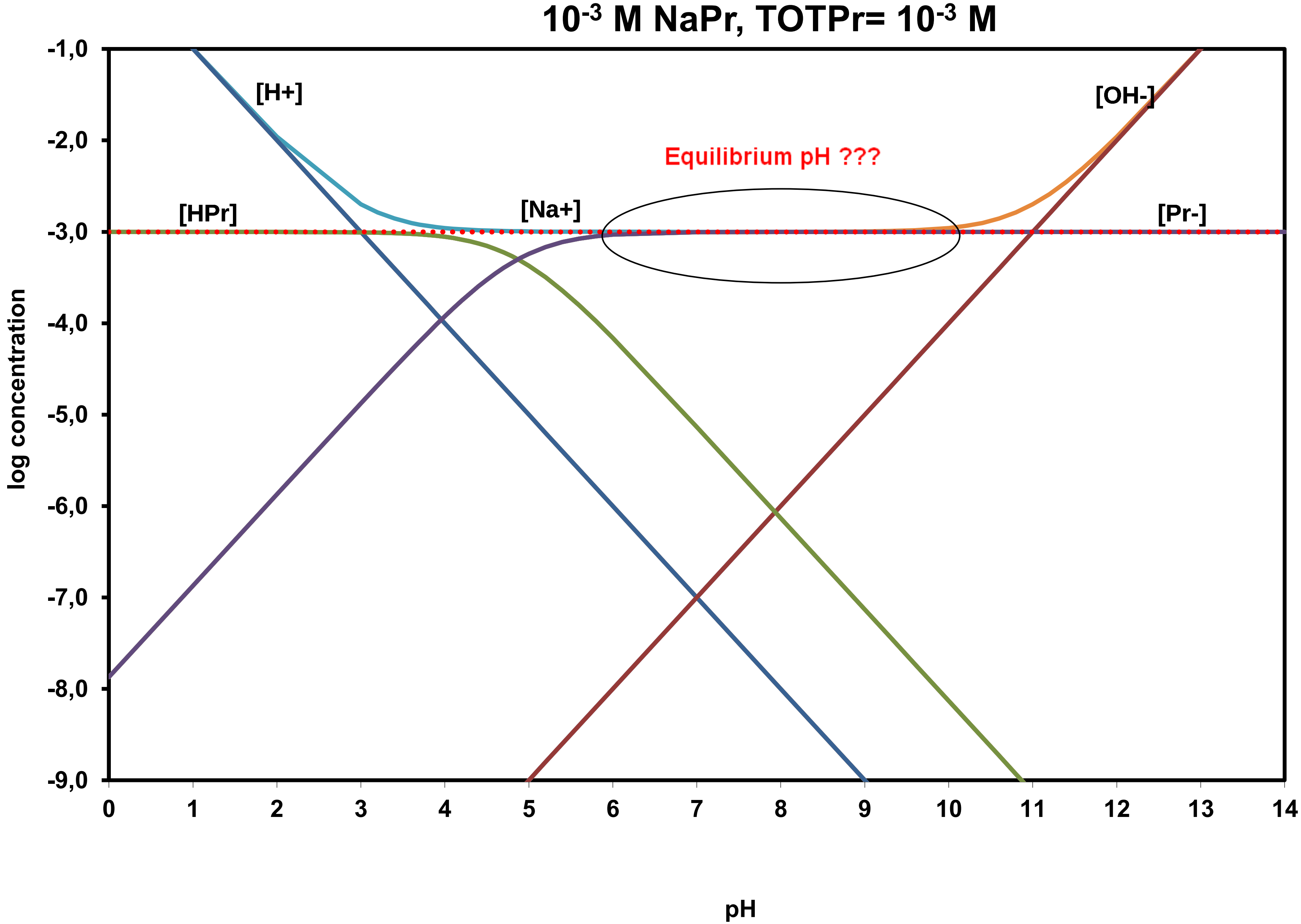


CB : $[Na^+] + [H^+] = [OH^-] + [Pr^-]$

LHS RHS

- We can not distinguish the exact point where the two lines cross. In fact, there is one. But we just can't see it on the diagram.
- Ultimately, this is because we have two very large terms in the CB (relative to the other two), $[Na^+]$ and $[Pr^-]$. This means that the CB is approximately satisfied over a very wide range of pH, where $[Na^+] \sim [CN^-]$.
- We must eliminate one of these large numbers from each side of the CB.
- To get around this, we can combine the CB with the two MB's to get rid of the large terms.

- We know that $TOTNa = TOTPr$

and

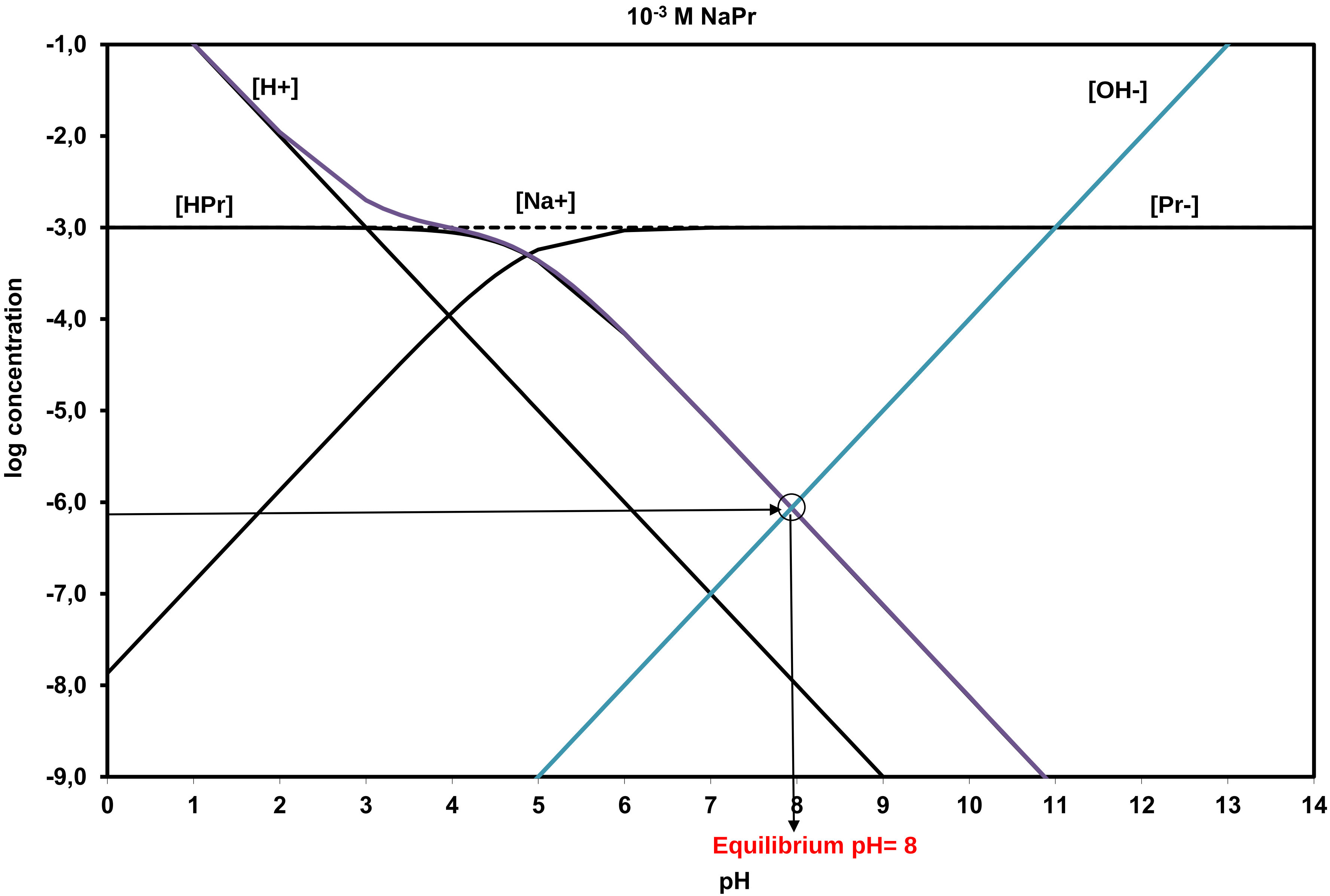
$TOTPr = [HPr] + [Pr^-]$

- Therefore, $[Na^+] = [HPr] + [Pr^-]$
- sub into CB: $[H^+] + [HPr] + \cancel{[Pr^-]} = [OH^-] + \cancel{[Pr^-]}$

or

Modified CB: $[H^+] + [HPr] = [OH^-]$

- Modified CB is a lot easier to solve.



$$CB : [H^+] + [HPr] = [OH^-]$$

LHS RHS

Equilibrium Concentrations of 10^{-3} M NaPr

- $[H^+] = 1x10^{-8}$ M
- $[OH^-] = 1x10^{-6}$ M
- $[Na^+] = 1x10^{-3}$ M
- $[Pr^-] = 1x10^{-3}$ M
- $[HPr] = 1x10^{-6}$ M

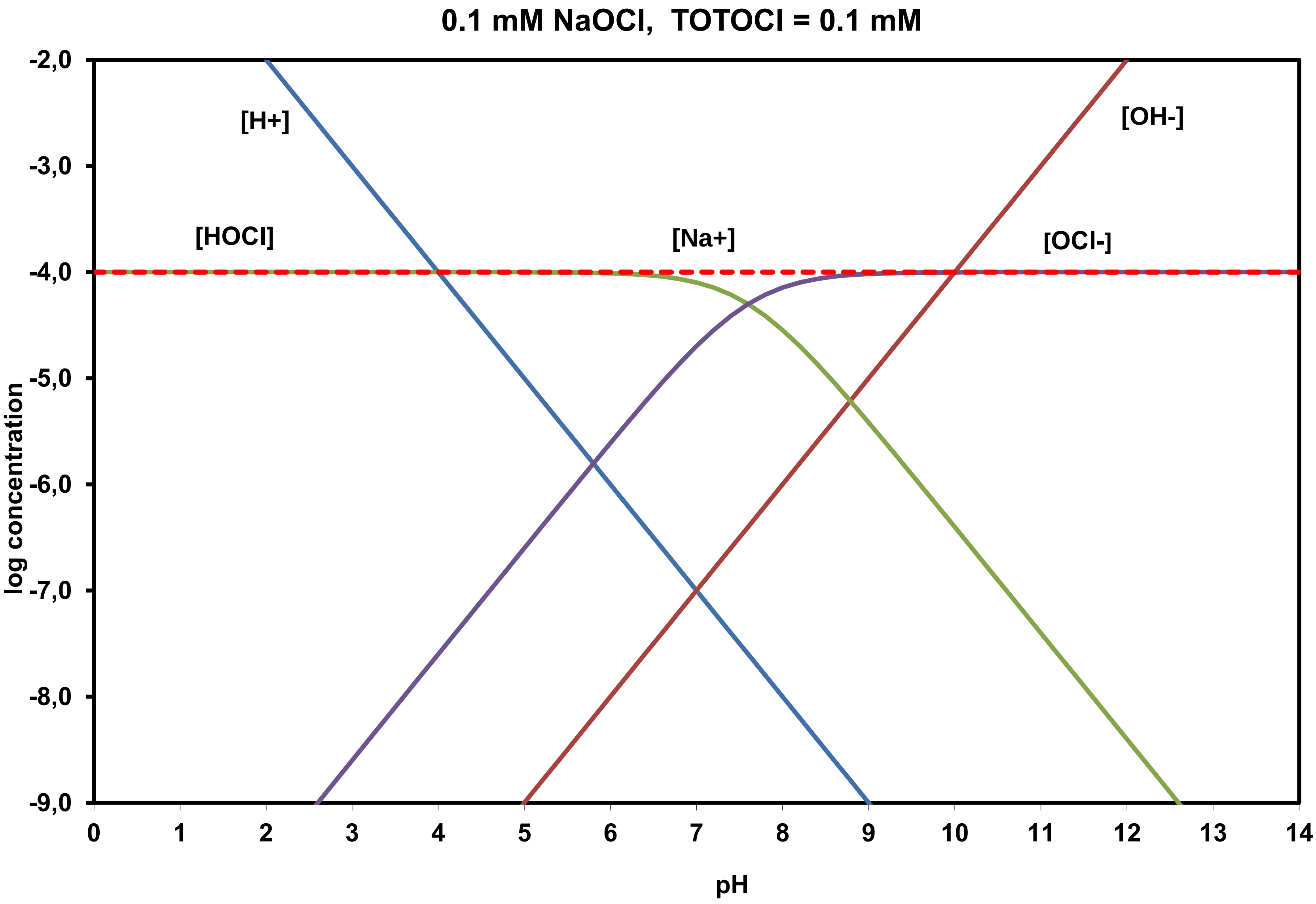
➢ Now, the last step is to check the charge balance:

$$10^{-8} + 10^{-3} = 10^{-6} + 10^{-3} \quad \text{ok}$$

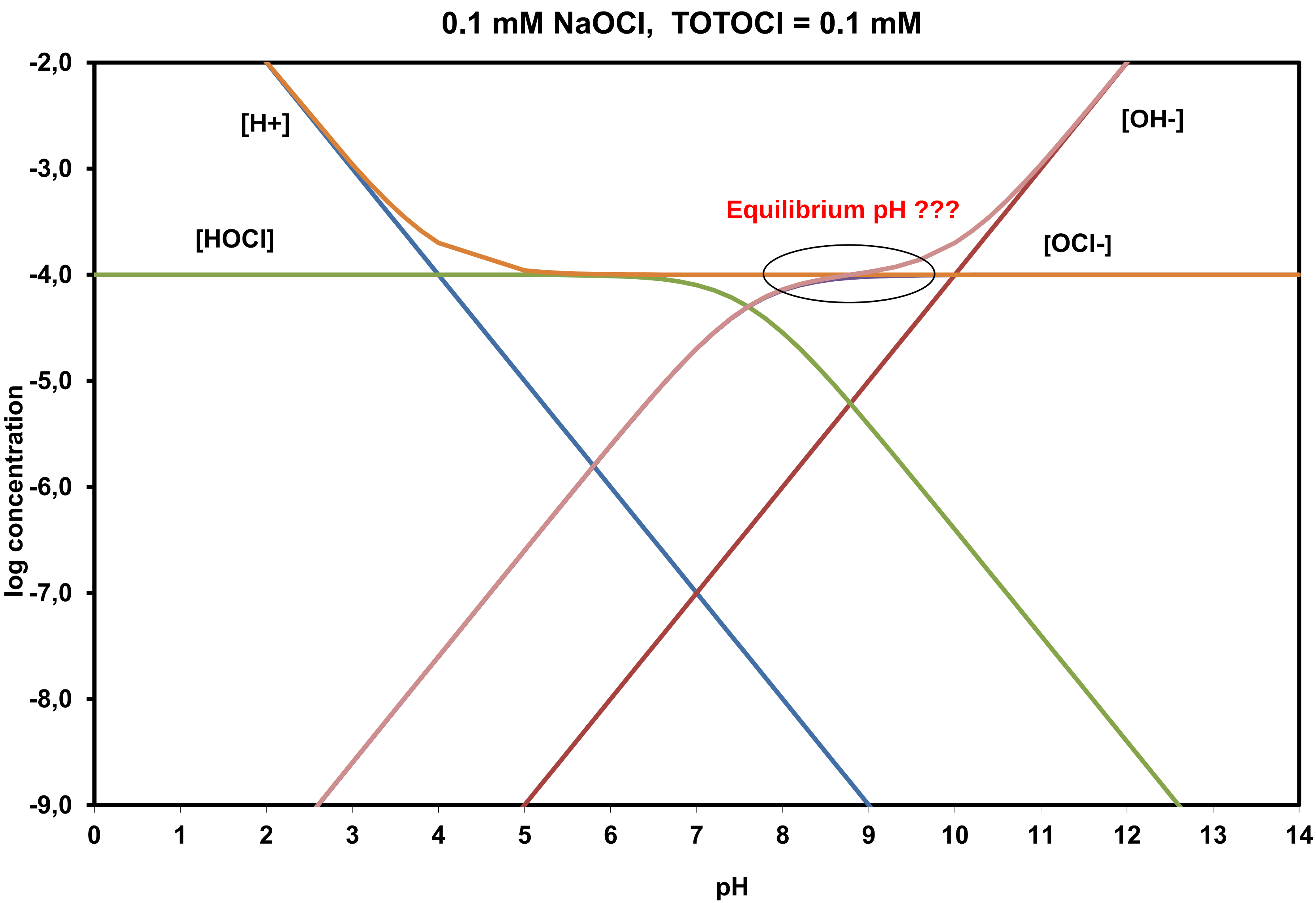
Ex. What are the pH and the concentrations of all species at equilibrium in a 0.1 mM NaOCl solution?

- Equilibrium species: H^+ OH^- HOCl OCl^- Na^+
- K's: K_w $K_a = 10^{-7.60}$
- MB's TOTOCl = [HOCl] + [OCl^-] = 10^{-4} M
  TOTNa = [Na^+] = 10^{-4} M
- CB: [H^+] + [Na^+] = [OH^-] + [OCl^-]

- Log C-pH diagram is exactly the same as 10^{-4} M HOCl, except that there is one additional line for the MB of Na^{+}. This is simply a horizontal line at log C = -4.
- Now we find the pH where the charge balance is satisfied.
- The sum of the H^{+} and Na^{+} lines is equal to the sum of the OH^{-} and OCl^{-} lines.
- The point on the diagram where the RHS of the CB = the LHS occurs at a flat point on the diagram, where both appears to be 10^{-4} M.
- To get around this, we can combine the CB with the two MB's to get rid of the large terms.



0.1 mM NaOCl, TOTOCl = 0.1 mM
[H+]
[OH-]
[HOCl]
[Na+]
[OCl-]
log concentration
-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
pH



$$\text{CB : } [Na^+] + [H^+] \quad = \quad [OH^-] + [OCl^-]$$

LHS RHS

- We know that $TOTNa = TOTOCl$

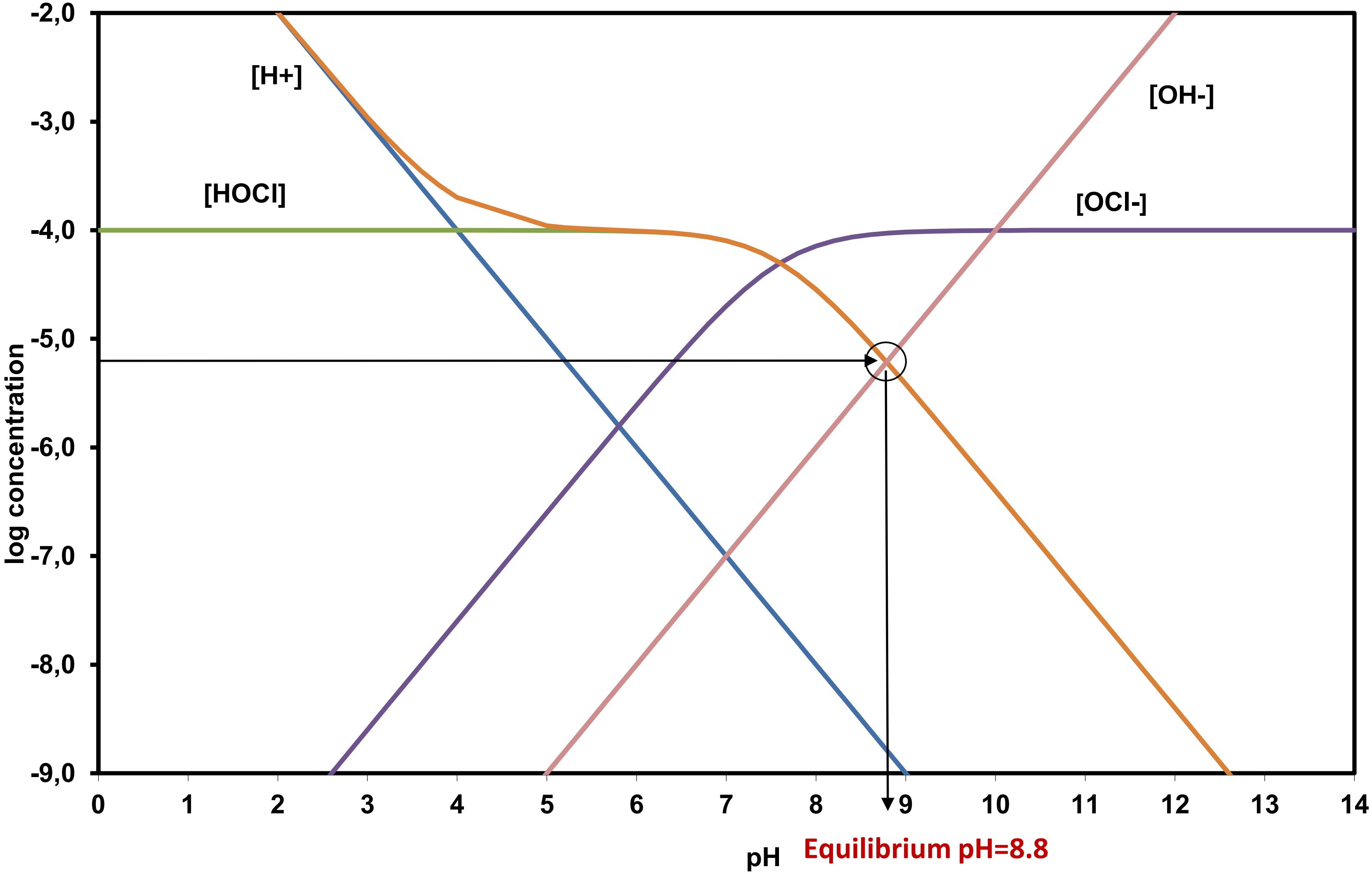
  and

  $TOTOCl = [HOCl] + [OCl^-]$
- Therefore, $[Na^+] = [HOCl] + [OCl^-]$
- sub into CB: $[H^+] + [HOCl] + \cancel{[OCl^-]} = [OH^-] + \cancel{[OCl^-]}$

  or

  Modified CB: $[H^+] + [HOCl] = [OH^-]$
- Modified CB is a lot easier to solve.

0.1 mM NaOCl, TOTOCl = 0.1 mM



CB : $[H^+] + [HOCl] \quad = \quad [OH^-]$

LHS RHS

Equilibrium Concentrations of 10^{-4} M NaOCl

- $[H^+] = 10^{-8.8}$ M = 1.58×10^{-9} M
- $[OH^-] = 1 \times 10^{-5.2}$ M = 6.31×10^{-6} M
- $[Na^+] = 1 \times 10^{-4}$ M
- $[OCl^-] = 1 \times 10^{-4}$ M
- $[HOCl] = 1 \times 10^{-5.2}$ M = 6.31×10^{-6} M

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

$$10^{-8.8} + 10^{-4} = 10^{-5.2} + 10^{-4} \quad \text{ok}$$