EWC 105
Environmental Chemistry

Lecture 5

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Solving Equilibrium Problems

Techniques:

- Numerical solution (manual)
  (Simultaneous solution of equations)

- Graphical approach using Log-concentration diagrams (esp. for acid-base problems)

- Tableau method

- Computer softwares
  (MINEQL+, PHREEQC)

Numerical Solution to Equilibrium Problems

An equilibrium system can be defined by a system of equations, which include:

(i) Mole/ Mass Balance Equation

(ii) Mass Law/Mass Action Equation

(iii) Electroneutrality or Charge Balance Equation

(iv) Proton Condition

Numerical Solution to Equilibrium Problems

(i) Mole/ Mass Balance Equation

Example:

10^{-3} M acetic acid (HAc) added to water

$$HAc = H^+ + Ac^-$$

Therefore, total concentration of acetic ion,

$$\mathbf{C_T = (HAc) + (Ac^-)}$$

Numerical Solution to Equilibrium Problems

(ii) Mass Law/Mass Action Equation

Example: 10^{-3} M acetic acid (HAc) added to water

$$HAc = H^+ + Ac^-$$

$$\mathbf{K_A = \{H^+\}\{Ac^-\} / \{HAc\}}$$

$$\mathbf{= 1.8 \times 10^{-5}} \text{ (at 25° C)}$$

For water, $\mathbf{\{H^+\}\{OH^-\} = K_w = 10^{-14}}$ (at 25° C)

(This Mass Law equation for water must always be considered)

Table 4.1 | Typical ionization constants for weak acids at 25°C

Acid	Equilibrium equation	K_A	pK_A	Environmental significance
Acetic	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.8×10^{-5}	4.74	Organic wastes
Ammonium	$NH_4^+ \rightleftharpoons H^+ + NH_3$	5.56×10^{-10}	9.26	Nitrification
Boric	$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^-$	$5.8 \times 10^{-10} (K_{A1})$	9.24	Nitrogen analysis
Carbonic†	$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$	$4.3 \times 10^{-7} (K_{A1})$	6.37	Many applications
	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	$4.7 \times 10^{-11} (K_{A2})$	10.33	
Hypobromous	$HOBr \rightleftharpoons H^+ + OBr^-$	2.3×10^{-9}	8.64	Disinfection
Hydrofluoric	$HF \rightleftharpoons H^+ + F^-$	7.1×10^{-4}	3.15	Fluoridation
Hydrocyanic	$HCN \rightleftharpoons H^+ + CN^-$	4.8×10^{-10}	9.32	Toxicity
Hydrogen	$H_2S \rightleftharpoons H^+ + HS^-$	$9.1 \times 10^{-8} (K_{A1})$	7.04	Odors, corrosion
sulfide	$HS^- \rightleftharpoons H^+ + S^{2-}$	$1.3 \times 10^{-13} (K_{A2})$	12.89	
Hypochlorous	$HOCl \rightleftharpoons H^+ + OCl^-$	2.9×10^{-8}	7.54	Disinfection
Phenol	$C_6H_5OH \rightleftharpoons H^+ + C_6H_5O^-$	1.2×10^{-10}	9.92	Tastes, industrial waste
Phosphoric	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	$7.5 \times 10^{-3} (K_{A1})$	2.12	Analytical buffer, plant
	$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$	$6.2 \times 10^{-8} (K_{A2})$	7.21	nutrient
	$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	$4.8 \times 10^{-13} (K_{A3})$	12.32	
Propionic	$CH_3CH_2COOH \rightleftharpoons H^+ + CH_3CH_2COO^-$	1.3×10^{-5}	4.89	Organic wastes, anaerobic digestion

†By convention, $[H_2CO_3^*]$ is taken to equal the sum of the actual carbonic acid concentration $[H_2CO_3]$ plus the dissolved carbon dioxide concentration $[CO_2(aq)]$.

Numerical Solution to Equilibrium Problems

(iii) Electroneutrality or Charge Balance Equation - All positively charged species in a solution must be balanced by equivalent numbers of negatively charged species.

Example 1: HAc added to water

At equilibrium -

Species present : H_2O, H^+, OH^-, Hac, Ac^-

Therefore, the charge balance equation:

$$\mathbf{(H^+) = (OH^-) + (Ac^-)}$$

Numerical Solution to Equilibrium Problems

(iii) Electroneutrality or Charge Balance Equation

Example 2: NaCl added to water

At equilibrium -

Species present: H_2O, H^+, OH^-, Na^+, Cl^-

Therefore, $(H^+) + (Na^+) = (OH^-) + (Cl^-)$

Numerical Solution to Equilibrium Problems

(iii) Electroneutrality or Charge Balance Equation

Example 3: $Ca(OH)_2$ added to water

At equilibrium -

Species present: H_2O, H^+, OH^-, Ca^{2+}

Therefore, **$(H^+) + 2\,(Ca^{2+}) = (OH^-)$**

[Note:1 mol of Ca^{2+} is equivalent to 2 mol of positive charge, thus the divalent calcium concentration is multiplied by 2]

Numerical Solution to Equilibrium Problems

(iv) Proton Condition

- Used to solve acid-base equilibrium problems

- Is the mass balance of protons relative to appropriate reference species (PRL- Proton Reference Level).

- The species with an excess of protons must be balanced by the species with a deficiency in proton.

- It can be written as :

Σ(moles/L (M) of species having excess H^+ relative to PRL= Σ(moles/L (M) of species having deficiency of H^+ relative to PRL

Numerical Solution to Equilibrium Problems

Reference Species (PRL)

- Water is always used as a PRL for H^+ and OH^-.

- Relative to H_2O, H^+ has an excess of one proton, whereas OH^- has a deficiency of one proton.

- For other acid-base species in the solution, PRL is usually assumed to be the species added.

- For example, if acetic acid (CH_3COOH) is added to water, CH_3COOH would be the PRL and CH_3COO^- has a deficiency of one proton relative to CH_3COOH.

Numerical Solution to Equilibrium Problems

Some basic rules on PRL:

-1) H_2O is always a "PRL"

-2) Weak acids/bases are "PRL" (when added to water)
(Ex. H_2CO_3, HCN, HAc, NH_3)

-3) For salts: part that enters into acid/base reaction is the "PRL".

Ex. $NaHCO_3$ added to water.

$NaHCO_3 = Na^+ + HCO_3^-$

$\therefore$ HCO_3^- is the PRL.

Ex. Na_2CO_3 added to water.

$Na_2CO_3 = 2Na^+ + CO_3^{2-}$

$\therefore$ CO_3^{2-} is the PRL.

Numerical Solution to **Equilibrium** Problems

Thus, for equilibrium problem, system of equations are-

(i) Mole/ Mass Balance Equation

(ii) Mass Law/Mass Action Equation

(iii) Electroneutrality or Charge Balance Equation

(iv) Proton Condition

For a given system, a simultaneous solution of the above equations [(i) – (iv)] will give concentrations of species at equilibrium.

Numerical Solution to Equilibrium Problems

Steps:

1. Define the equilibrium equations involved.

2. List all chemical species present initially and at the equilibrium condition

3. Identify the concentrations of each species for each element or entity under initial conditions so that appropriate mass and charge balances can be made.

4. List all appropriate equilibrium relationships between the species of concern, together with associated equilibrium constants.

Numerical Solution to Equilibrium Problems

Steps:

5. List all mass and charge balance relationships for the system.

6. For acid-base problems, list the appropriate proton condition.

7. Relationships from steps 4 to 6, must result in as many independent equations as there are unknown species present.

8. A simultaneous solution of the equations from steps 4 to 6 will give the concentration of each species at equilibrium.

Numerical Equilibrium Calculations

A mass equal to 10^{-2} mol of acetic acid is added to sufficient water to make 1 liter of solution at 25°C. What is the equilibrium concentration of all species involved? Ignore activity corrections.

1. The problem is one of ionization of a single weak monoprotic acetic in water. When acetic acid is added to water, it ionizes as follows: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$.
2. Elements or chemical entities originally present are CH_3COOH, H_2O, H^+, and OH^-.
3. Chemical species likely to be present after equilibrium is attained are

Acetic acid: CH_3COOH (HAc) and CH_3COO^- (Ac^-)

Water: H_2O, H^+, OH^-

Numerical Equilibrium Calculations

4. Initial conditions are

$[HAc] = 10^{-2}$ mol/L $= C_T$

$[H_2O]$ = 1 liter of solution (mass change will be negligible during ionization), and

$[H^+] = [OH^-] = 10^{-7}$ mol/L

5. Equilibrium relationships of interest are (noting that molar concentration equals activity for this problem)

$$[H^+][OH^-] = K_W = 10^{-14} \quad \text{at } 25°C \qquad (4.4)$$

$$\frac{[H^+][Ac^-]}{[HAc]} = K_A = 1.8 \times 10^{-5} \quad \text{at } 25°C \qquad (4.5)$$

Numerical Equilibrium Calculations

6. Mass and charge balance realtionships. The acetic acid entity is conserved during ionization such that

$$[HAc] + [Ac^-] = C_T \tag{4.6}$$

The charge balance between all cations and anions is

$$[H^+] = [OH^-] + [Ac^-] \tag{4.7}$$

The proton condition, with H_2O and HAc being the reference species, is

$$[H^+] = [OH^-] + [Ac^-]$$

In this case the charge balance and proton condition are identical.

Numerical Equilibrium Calculations

$$[H^+][OH^-] = K_W = 10^{-14} \quad \text{at } 25^\circ C \qquad (4.4)$$

$$\frac{[H^+][Ac^-]}{[HAc]} = K_A = 1.8 \times 10^{-5} \quad \text{at } 25^\circ C \qquad (4.5)$$

$$[HAc] + [Ac^-] = C_T \qquad (4.6)$$

$$[H^+] = [OH^-] + [Ac^-] \qquad (4.7)$$

Numerical Equilibrium Calculations

$$[H^+][OH^-] = K_W = 10^{-14} \quad \text{at } 25^\circ C \qquad (4.4)$$

$$[H^+] = [OH^-] + [Ac^-] \qquad (4.7)$$

Now replacing $[OH^-]$ in equation 4.7 with the help of equation 4.4

From eqn 4.4, $[OH^-] = K_w / [H^+]$

Now from eqn 4.7, $[Ac^-] = [H^+] - [OH^-]$

$$= \mathbf{[H^+] - K_w / [H^+]} \quad \textbf{…… (4.8)}$$

Numerical Equilibrium Calculations

$$\frac{[H^+][Ac^-]}{[HAc]} = K_A = 1.8 \times 10^{-5} \quad \text{at } 25°C \qquad (4.5)$$

$$[HAc] + [Ac^-] = C_T \qquad (4.6)$$

From eqn 4.5, $[H^+]\,[Ac^-] = K_A\,[HAc]$

$= \mathbf{K_A\ (C_T - [Ac^-])}$ (from eqn 4.6)

…….. (4.9)

Numerical Equilibrium Calculations

$$[Ac^-] = [H^+] - K_w / [H^+] \quad \ldots\ldots\ldots\ldots (4.8)$$

And $[H^+]\,[Ac^-] = K_A\,(C_T - [Ac^-])$ ……. (4.9)

Now, replacing $[Ac^-]$ from eqn 4.8 to eqn 4.9,

$$[H^+]\,[Ac^-] = K_A\,(C_T - [Ac^-])$$

Or, $[H^+]\,\{[H^+] - K_w / [H^+]\} = K_A\,\{C_T - ([H^+] - K_w / [H^+])\}$

……

……

……

$$[H^+]^3 + K_A[H^+]^2 - (K_A C_T + K_w)[H^+] - K_A K_w = 0 \qquad (4.10)$$

Numerical Equilibrium Calculations

$$[H^+]^3 + K_A[H^+]^2 - (K_A C_T + K_W)[H^+] - K_A K_W = 0 \qquad (4.10)$$

Equation (4.10) can be solved for $[H^+]$, which can then be substituted into Eqs. (4.4) through (4.7) to determine the concentrations of the other species at equilibrium. The results are

$$[H^+] = 4.15 \times 10^{-4}$$
$$[OH^-] = 2.41 \times 10^{-11}$$
$$[HAc] = 9.59 \times 10^{-3}$$
$$[Ac^-] = 4.15 \times 10^{-4}$$

Numerical Equilibrium Calculations

Ex. 1. Calculate pH of a 10^{-4} M HCN solution (Given $pK_A = 9.2$).

Soln. Steps:

(1) Identify species present in water:

Reactions: $H_2O = H^+ + OH^-$

$HCN = H^+ + CN^-$

∴ Species: (H_2O), H^+, OH^-, HCN, CN^-

Numerical Equilibrium Calculations

(2) $K_W = (H^+)(OH^-) = 10^{-14}$ ——— (i)

(3) $K_A = \dfrac{(H^+)(CN^-)}{(HCN)} = 10^{-9.2}$ ——— (ii)

(4) Mass balance: $C_T = (HCN) + (CN^-) = 10^{-4}$ ——— (iii)

(5) Charge balance: $(H^+) = (OH^-) + (CN^-)$ ——— (iv)

Numerical Equilibrium Calculations

$K_W = (H^+)(OH^-) = 10^{-14}$ ——— (i)

Charge balance : $(H^+) = (OH^-) + (CN^-)$ ——— (iv)

From eqn (i), $(OH^-) = K_w / (H^+)$

Now from eqn (iv), $(CN^-) = (H^+) – (OH^-)$

$= \mathbf{(H^+) - K_w / (H^+)}$ **…… (v)**

Numerical Equilibrium Calculations

$$K_A = \frac{(H^+)(CN^-)}{(HCN)} = 10^{-9.2} \quad \text{---------- (ii)}$$

Mass balance: $C_T = (HCN) + (CN^-) = 10^{-4}$ ---- (iii)

From eqn (ii)

$(H^+)(CN^-) = K_A (HCN)$

or, $(H^+)(CN^-) = K_A \{C_T - (CN^-)\}$

or, $(H^+)\{(H^+) - K_w/(H^+)\} = K_A [C_T - \{(H^+) - K_w/(H^+)\}]$

Replacing (CN-) from eqn (v)

$(CN^-) = \mathbf{(H^+) - K_w / (H^+)}$ **…… (v)**

.....

.....

$$(H^+)^3 + K_A (H^+)^2 - (K_A C_T + K_w)(H^+) - K_A . K_w = 0$$

This equation is valid for all monoprotic acids

Numerical Equilibrium Calculations

$$(H^+)^3 + K_A(H^+)^2 - (K_A C_T + K_w)(H^+) - K_A \cdot K_w = 0$$

This equation is valid for all monoprotic acids

For this problem,

$$(H^+)^3 + 10^{-9.2}(H^+)^2 - 7.31\times10^{-14}(H^+) - 6.31\times10^{-24} = 0$$

solving by trial and error. $(H^+) \simeq 2.75\times10^{-7}\ M$

$= 10^{-6.56}\ M.$

$\therefore pH = 6.56$

Numerical Equilibrium Calculations

Species concentrations:

$(H^+) = 10^{-6.56}\ M$

$(OH^-) = 3.64 \times 10^{-8}\ M$

$(CN^-) = (H^+) - K_w/(H^+) = 2.39 \times 10^{-7}\ M$

$(HCN) = 9.98 \times 10^{-4}\ M$

Numerical Equilibrium Calculations

Ex. 1 (cont'd) manual numerical solution often tedious. "Approximate Solution" method often gives reasonable results:

Steps (1) — (5): Same as before

Numerical Equilibrium Calculations

(6) Look for terms in additive equations that are negligible. Neglect these terms and proceed with the solution.

For this problem, (HCN) is a weak acid. ∴ Poor dissociation. Hence we can assume, $(HCN) \gg (CN^-)$.

now, in Eq. (iii), $(H^+) + (CN^-) = 10^{-4} = C_T$

$\therefore (H^+) \simeq 10^{-4} = C_T$.

Numerical Equilibrium Calculations

From (ii) $(H^+)(CN^-) = K_A \cdot (HCN)$

$\Rightarrow (H^+)\left[(H^+) - \frac{K_w}{(H^+)}\right] = K_A \cdot C_T$.

$\Rightarrow \boxed{(H^+)^2 = K_w + K_A \cdot C_T}$

This is valid for all weak acids.

$\therefore$ For this problem, $(H^+) = \sqrt{10^{-14} + 10^{-9.2} \cdot 10^{-4}}$

$\therefore (H^+) = 10^{-6.57}$.

$\therefore pH = 6.57$.

Numerical Equilibrium Calculations

Check assumption:

$$\frac{(H^+)(CN^-)}{(HCN)} = 10^{-9.2}.$$

$$\therefore (CN^-) = \frac{10^{-9.2} \times 10^{-4}}{10^{-6.57}}.$$

$$\Rightarrow (CN^-) = 10^{-6.63} << 10^{-4}$$

$$(10^{-4} + 10^{-6.63} \simeq 10^{-4}).$$

Assumption OK.

Graphical Approach

In graphical procedure pH is used as a 'master variable' and is plotted as abscissa. The logarithm of concentration (log c) of each species of importance is plotted as ~~as~~ on the ordinate. This diagram is then ~~solved~~ used ~~on the~~ to solve equilibrium problem.

Graphical Approach

Log C- pH diagram for (H^+) and (OH^-)

$(H^+)(OH^-) = K_w$.

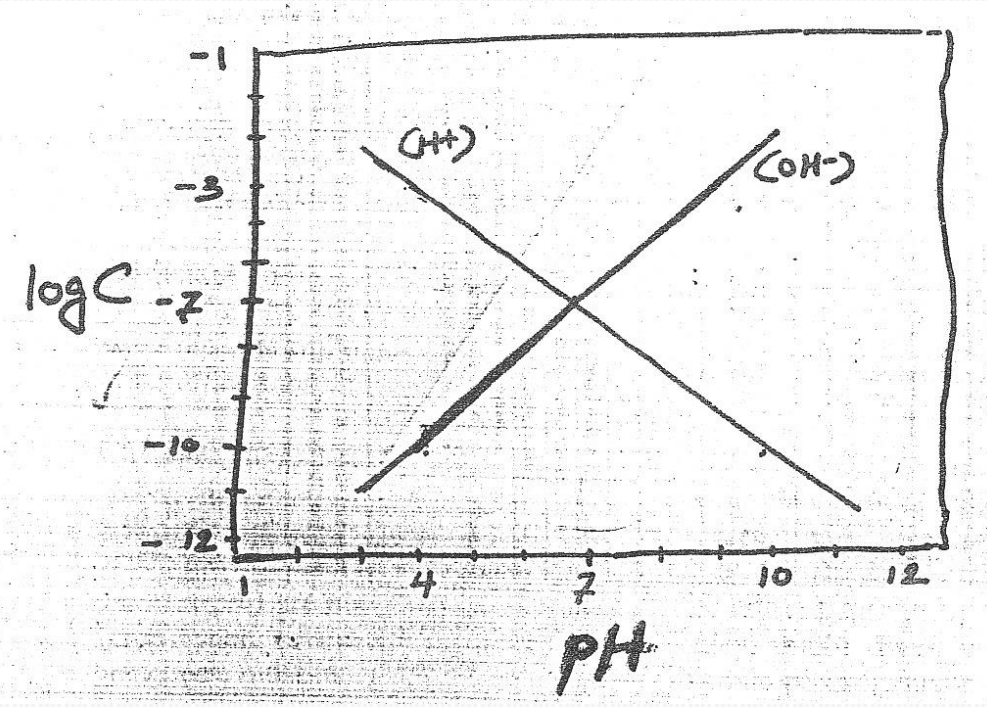
$pH = -\log (H^+)$

$\therefore \boxed{\log (H^+) = -pH}$

$\log (OH^-) = \log K_w - \log (H^+)$

$\Rightarrow \boxed{\log (OH^-) = -14 + pH}$

pH	log (H+)	log (OH-)
0	0	-14
1	-1	-13
2	-2	-12
3	-3	-11
4	-4	-10
5	-5	-9
6	-6	-8
⋮		
12	-12	-2
13	-13	-1
14	-14	0



Plot on a "Normal Graph Paper"

Graphical Approach

Log C- pH diagram for weak monoprotic acid

Consider an acid: $HAc = H^+ + Ac^-$

$$K_A = \frac{(H^+)(Ac^-)}{(HAc)} \quad \text{---- (1)}$$

$$C_T = (HAc) + (Ac^-) \quad \text{---- (2).}$$

From eqn (2) $\rightarrow$ $(HAc) = C_T - (Ac^-)$

$$= C_T - \frac{K_A (HAc)}{(H^+)} \quad \text{[From eqn (1)]}$$

$$\Rightarrow (H^+)(HAc) = C_T(H^+) - K_A(HAc)$$

$$\Rightarrow (HAc)\{(H^+) + K_A\} = C_T(H^+)$$

$$\Rightarrow (HAc) = \frac{C_T(H^+)}{(H^+) + K_A} = f(pH) \quad \text{---(A)}$$

$\alpha_o = (H^+) / \{ (H^+) + K_A \}$ = Distribution Coefficient

$(HAc) = \alpha_o C_T$

Log C- pH diagram for weak monoprotic acid

Consider an acid: $HAc = H^+ + Ac^-$

$$K_A = \frac{(H^+)(Ac^-)}{(HAc)} \quad \text{---- (1)}$$

$$C_T = (HAc) + (Ac^-) \quad \text{---- (2).}$$

Can derive:

$$(HAc) = \frac{C_T(H^+)}{(H^+) + K_A} = f(pH) \quad \text{---(A)}$$

$$(Ac^-) = \frac{C_T K_A}{(H^+) + K_A} = f(pH) \quad \text{---(B)}$$

α_0 , α_1 are distribution coefficients.

From (A) --- $(HAc) = \alpha_0 C_T$
From (B) --- $(Ac^-) = \alpha_1 C_T$

Now plot (A) and (B)

Consider two cases:

(i) $(H^+) \gg K_A$; i.e., $pH < pK_A$ and

(ii) $(H^+) \ll K_A$; i.e., $pH > pK_A$

Log C- pH diagram for weak monoprotic acid

Case (i): $(H^+) \gg K_A$ or $pH < pK_A$.

Here, $[(H^+) + K_A] \simeq (H^+)$

$$(HAc) = \frac{C_T(H^+)}{(H^+) + K_A} = f(pH) \quad ---(A)$$

$\therefore$ From (A), $(HAc) = \frac{C_T(H^+)}{(H^+)} = C_T$.

$$\Rightarrow \log(HAc) = \log C_T$$

$$\frac{d\log(HAc)}{dpH} = 0$$

Log C- pH diagram for weak monoprotic acid

Case (i): $(H^+) \gg K_A$ or $pH < pK_A$.

Here, $[(H^+) + K_A] \simeq (H^+)$

$$(Ac^-) = \frac{C_T K_A}{(H^+) + K_A} = f(pH) \quad \cdots (B)$$

From (B), $(Ac^-) = \frac{C_T \cdot K_A}{(H^+)}$

$$\Rightarrow \log (Ac^-) = \log C_T + \log K_A - \log pH$$

$$\Rightarrow \log Ac = \log C_T - pK_A + pH$$

$$\therefore \frac{d \log (Ac)}{dpH} = +1$$

Log C- pH diagram for weak monoprotic acid

Case (ii): $(H^+) \ll K_A$ or $pH > pK_A$

Here, $[(H^+) + K_A] \simeq K_A$.

$$(HA^-) = \frac{C_T(H^+)}{(H^+) + K_A} = f(pH) \quad \text{---(A)}$$

$\therefore$ From (A), $(HA^-) = \frac{C_T(H^+)}{K_A}$.

$\Rightarrow \log(HA^-) = \log C_T + \log(H^+) - \log K_A$

$\Rightarrow \boxed{\log(HA^-) = \log C_T - pH + pK_a}$

$$\therefore \frac{d\log(HA^-)}{dpH} = -1$$

Log C- pH diagram for weak monoprotic acid

Case (II): $(H^+) \ll K_A$ or $pH > pK_A$

Here, $[(H^+) + K_A] \simeq K_A$.

$$(Ac^-) = \frac{C_T K_A}{(H^+) + K_A} = f(pH) \quad \cdots (B)$$

From (B), $(Ac^-) = C_T$

$$\log (Ac^-) = \log C_T$$

$$\frac{d \log (Ac^-)}{dpH} = 0$$

Log C- pH diagram for weak monoprotic acid

Consider the case when $(H^+) = K_A$ or $pH = pK_A$

$$\frac{(H^+)(Ac^-)}{(HAc)} = K_A .$$

$\therefore$ when $pH = pK_A$ (or $(H^+) = K_A$),

$$(Ac^-) = (HAc) .$$

now, $C_T = (HAc) + (Ac^-) .$

$\therefore$ when, $pH = pK_A$, $(HAc) = (Ac^-) = \frac{C_T}{2} .$

$$\Rightarrow \boxed{\log (HAc) = \log (Ac^-) = \log C_T - \log 2 = \log C_T - 0.3}$$

→ Now the above equations can be used to plot log C - pH diagram for (HAc) and (Ac^-) (or for any monoprotic acid).

Graphical Approach

Steps to be followed in constructing Log C- pH diagrams for weak monoprotic acids:

(1) Take a normal graph paper. Mark abscissa (pH) from 0 to 14. (or 0 to 12). Mark ordinate (lg C) from 0 to -10.

(2) Draw a horizontal line representing C_T.

(3) Locate a point on this line at $pH = pK_A$. This point is called the system point

Graphical Approach

Steps to be followed in constructing Log C- pH diagrams for weak monoprotic acids:

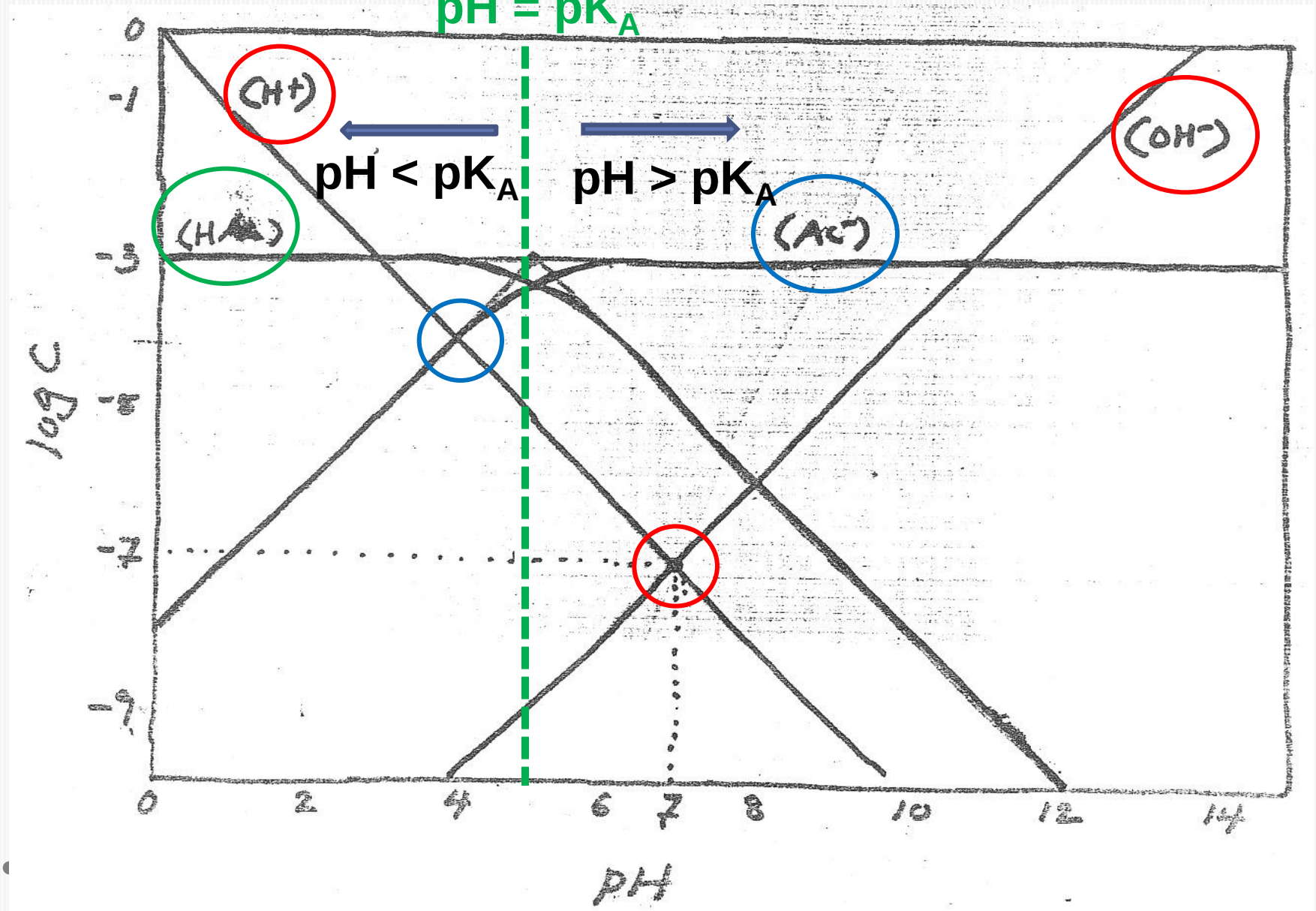
④ Draw 45° lines sloping left and right of the system point.

⑤ Locate a point, 0.3 log units below the system point. Connect the horizontal and 45° lines with short curves passing through this point

⑥ Also draw lines for (H^+) and (OH^-) at 45° which intersect at pH = 7 & log C = -7.

Graphical Approach

Construction of Log C- pH diagram for 10^{-3} M HAc solution:



Graphical Approach

Solution for species concentration

The method of solution is to –

- locate a point of the Log C – pH diagram, where the proton condition is solved and
- check this solution using the charge balance equation.

Graphical Approach

Solution for species concentration

- Here, the charge balance and proton condition (H_2O and HAc are the reference species) are identical as follows:

$$[H^+] = [OH^-] + [Ac^-] \ldots\ldots\ldots (1)$$

- Locate a point on the Log C – pH diagram, where eqn 1 is solved.

- Look at intersections of lines in the diagram involving the species in the charge balance eqn.

Graphical Approach

- Intersection of $[H^+]$ and $[OH^-]$ lines at pH= 7 (in the diagram), cannot the solve the charge balance, as $[Ac^-]$ is much higher than 1×10^{-7}.
- Hence, the solution lies at the intersection of $[H^+]$ and $[Ac^-]$, at pH ≈3.2 (diagram).
- Note, mass balance between [HAc] and $[Ac^-]$ is solved at any pH on the diagram.