SA 25/09/23

Book refs: 1, 4 most recommended

Aquatic Chemistry

Definition

Application

Arsenic contamination of ground water

As (III) - Arsenite - dissolved - higher mobility - more toxic

As(V) - Arsenate - presepitative - concentrated/solid

Ocean-atmosphere interaction

প্রবাল দ্বীপ - formated CO_3 - requires more surface water to atmosphere ~~interaction~~ contact point

Industrial waste and ground water contamination

** Physical properties of water [1/2 ques from here]

* Why water has exceptional boiling & freezing point compared to molecules w/ similar atom

memorize boiling/freezing point of other molecules.

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Solid phase / Physical props of water

- ice float on water: aquatic species survives in frozen lake.

Heat capacity:

- extremely high capacity w/o significant increase in temperature: used as coolant

Universal solvent

- polar nature → solvent for other polar compounds.

Surface tension

- polar — hence higher surface tension
- H·B — " " one of the highest " "

Medium of life

- photosynthesis.

Effects of solutes on physical props of water

** Increased conct. of solute

lowering of freezing point

increasing of boiling point [additional energy is required to seperate solute]

decrease of vapor pressure

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Hydrogen bond

attraction between one molecule's hydrogen atom and another molecule's atom (electronegative).

Polarity of water molecule

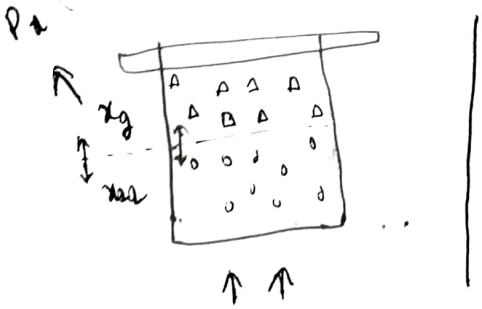
dipole

Dissolution in water

Major Aquatic Chemical Processes

Solubility of gases in water

Henry's law



$x_{aq} \propto P_x$

$\therefore = KP_x$

☆☆☆ Sources of aquatic O_2

- mostly from dry atmosphere
-

☆☆☆ Sinks of aquatic O_2

- Biodegradation of organics, pollutants
- Metabolic activity of algae (during night)

Diurnal variation

Daily fluctuations of dissolved oxygen

Solubility of O_2 in water depends

- water temp → increase, decreases solubility
- Partial pressure of O_2 in atmosphere ↑
- Salts in water ↓

Oxygen in water

O_2 solubility

Dissolved O_2 conc.

actual < max

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Aquos CO_2

Graph & calc → next class
2 piece each

CO_2 → acid → acid → basic
weak acid HCO_3^- CO_3^{2-}

Sources of CO_2 in water

-

-

Sinks of CO_2 in water

Importance of CO_2 in --

- dramatically change pH of water
- lower pH → dissolves heavy matter in water

Equilibrium of chemical Reactions

Le Chatelier's Principle of equilibrium

$$A + B \rightleftharpoons C + D$$

$$\frac{[C][D]}{[A][B]} = K;$$ K = equilibrium const at a given temp

$$aA + bB + \cdots \rightleftharpoons cC + dD + \cdots$$

$$\frac{[C]^c[D]^d \cdots}{[A]^a[B]^b \cdots} = K$$ ... mass law equation / law of mass action

Activity & Activity Coefficient

$$K = \frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}$$; $\{\}$ → activity conc.

$$\{A\} = \gamma[A], \quad \gamma \leq 1$$

for very dilute soln, $\gamma = 1$

for pure water, pure solid, pure liquid → $\gamma = 1$

Ion product of water

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

$$\frac{(H^+)(OH^-)}{(H_2O) \approx 1} = K_w = \text{Ion product of water}$$

$K_w = (H^+)(OH^-) = 10^{-14}$ at 25°c

$\log K_w = -4470.99/T + 6.0875 - 0.01706T$;

where, T = absolute temp (°c)

At, 0°c, $K_w = 0.12 \times 10^{-14}$

50°c, $K_w = 0.12 \times 10^{-14}$ X

Ion product of water

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

$pk = -\log(K)$

Thus at 25°c : $K_w = 10^{-14}$

$pK_w = 14$

Ionization of Acids & Bases

Acid, Base

- Strong Acid / Base

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★★★ Dissociation equations

Strong acid/base

almost completely dissociates

K_a is higher (10^{+x})

$K_a = \frac{(prod)}{(react)} \longrightarrow$ lower

weak acid/base

K_a is lower (10^{-x})

Solubility of solids in water

$CaCO_3(s) = Ca^{2+} + CO_3^{2-}$

activities of pure phase solids = 1

$K_{sp} = (Ca^{2+})(CO_3^{2-}) \longrightarrow K_{sp}$ = solubility prod

$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$

$K_{sp} = (Ca^{2+})(SO_4^{2-})$

$Ca_3(PO_4)_2(s) = 3Ca^{2+} + 2PO_4^{3-}$

$K_{sp} = (Ca^{2+})^3 (PO_4^{3-})^2$

Solubility Product

$K_{sp} = (A^+)^a (B^-)^b$

$(A^+)^a (B^-)^b < K_{sp}$ ...

...

...

অবক্ষেপ → sludge

★★★ Colloids in water

Characteristics

★★ Tyndall Effect

Importance of colloids

Types of colloids in water

★★ Electrostatic props of colloidal particles

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Equilibrium eqn.

1, 2 → equi. eqn

(i, ii → system

monoprotic acid

$HA \longrightarrow H^+ + A^-$ —— (1)

$K_a = \frac{(H^+)(A^-)}{(HA)}$ —— (i) (mass law eqn)

$H_2O \rightarrow H^+ + OH^-$ —— (2)

$K_w = (H^+)(OH^-)$ —— (ii)

Ionic species

HA, H^+, A^-

H_2O, H^+, OH^-

for Electro neutrality

Charge balance eqn,

$(H^+) = (OH^-) + (A^-)$ —— (iii)

Mass balance eqn

$C_T = (HA) + (A^-)$ —— (iv)

Proton condition

PRL (Proton Reference Level)

Σ Species ~~gaining~~ losing (H^+) compared to PRL = Σ Species gaining (H^+) Compared to PRL

RRL: H_2O, Acid added, Base added, Part of salt that participates in Acid-Base Reaction

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$NaHCO_3 \rightarrow Na^+ + \underbrace{HCO_3^-}_{PRL}$; $Na_2CO_3 \rightarrow 2Na^+ + \underbrace{CO_3}_{PRL}$

Proton condition:

HA, H^+, A^-

H_2O, H^+, OH^-

PRL: H_2O, HA

$$(OH^-) + (A^-) = (H^+) \quad \longrightarrow (v)$$

For monoprotic acid, charge balance eqn and proton condition will be identical.

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Dissociation eq^n

Table 4.1, red, HBr, next

Acetic acid → $CH_3COOH \leftrightarrow H^+ + CH_3COO^-$ —— (1)

$H_2O \leftrightarrow H^+ + OH^-$ —— (2)

Species in equilibrium: CH_3COOH, H^+, CH_3COO^-

H_2O, OH^- —— (3)

$$K_a = \frac{(H^+)(CH_3COO^-)}{(CH_3COOH)} = 1.8 \times 10^{-5} \text{ (at 25 °C)}$$

$$K_w = (H^+)(OH^-) = 10^{-14} \text{ (at 25°C)}$$ —— (4)

PRL:

H^+ excess & H^+ deficiency w/ respect to PRL

case: PRL → CH_3COOH

excess: H^+

deficiency: CH_3COO^-

Mass balance eq^n: $C_T = (CH_3COOH) + (CH_3COO^-)$ —— (5)

(C_T → total concentration of acid 10^{-2})

Charge balance eq^n: $(CH_3COO^-) + (OH^-) = (H^+)$ —— (6)

Proton condition : PRL: CH_3COOH, H_2O

$(H^+) = (CH_3COO^-) + (OH^-)$ —— (7)

(4) =>

solve for next class

solve page 24 (Lec 5)

Dissolution of Acetic Acid,

$$CH_3COOH \longleftrightarrow CH_3COO^- + H^+ \quad \text{—— (i)}$$

and water,

$$H_2O \longleftrightarrow H^+ + OH^- \quad \text{—— (ii)}$$

Species at equilibrium; CH_3COOH, CH_3COO^-, H^+
H_2O, OH^-

Now, $$K_a = \frac{(CH_3COO^-)(H^+)}{(CH_3COOH)} = 1.8 \times 10^{-5} \quad \text{—— (iii)}$$

$$K_w = (H^+)(OH^-) = 10^{-14} \quad \text{—— (iv)}$$

Charge balance eqn: $(CH_3COO^-) + (OH)^- = (H^+)$ —(v)

Mass balance eqn: $C_T = (CH_3COOH) + (CH_3COO^-)$ — (vi)

Proton conditions: PRL: H_2O, CH_3COOH

$$(H^+) = (OH^-) + (CH_3COO^-) \quad \text{— (vii)}$$

4.15e-4

From (iv), $(OH^-) = \frac{10^{-14}}{(H^+)}$ —— (viii)

Using (viii) on (v),

$$(CH_3COO^-) = (H^+) - \frac{10^{-14}}{(H^+)} \quad \text{—— (ix)}$$

From (vi), $(CH_3COOH) = C_T - (CH_3COO^-)$ —— (x)

Using (x) on (iii),

$$(CH_3COO^-)(H^+) = 1.8\times10^{-5} \times \{C_T - (CH_3COO^-)\}$$

$$\text{or, } (H^+)\left\{(H^+) - \frac{10^{-14}}{(H^+)}\right\} = 1.8\times10^{-5}\left[C_T - \left\{(H^+) - \frac{10^{-14}}{(H^+)}\right\}\right]$$

$$\text{or, } (H^+)\left[\frac{(H^+)^2 - 10^{-14}}{(H^+)}\right] = 1.8\times10^{-5}\left[\frac{(H^+)C_T - (H^+)^2 + 10^{-14}}{(H^+)}\right]$$

$$\text{or, } (H^+)^3 - 10^{-14}(H^+) = 1.8\times10^{-8}(H^+) - 1.8\times10^{-5}(H^+)^2 + 1.8\times10^{-19}$$

$$\text{or, } (H^+)^3 + 1.8\times10^{-5}(H^+)^2 - (1.8\times10^{-8} + 10^{-14})(H^+) - 1.8\times10^{-19} = 0$$

$\therefore (H^+) = 1.25\times10^{-4}$, $(OH^-) = 8\times10^{-11}$, $(CH_3COO^-) = 1.25\times10^{-4}$

$(CH_3COOH) = 9.875\times10^{-3}$, $(H_2O) = 10^{-7}$

Approximate soln

In exam, use this method only when specified

HCN dissolution: $HCN \longleftrightarrow H^+ + CN^-$ —— (1)

and water: $H_2O \longleftrightarrow H^+ + OH^-$ —— (2)

Species at equilibrium: $HCN, H^+, CN^-, H_2O, OH^-$

Mass action eqⁿ,

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

$$K_w = (H^+)(OH^-) = 10^{-14} \quad \text{—— (ii)}$$

Mass balance eqⁿ: $C_T = (HCN) + (CN^-)$ —— (iii)

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

Proton condition:

$$(H^+) = (CN^-) + (OH^-) \quad \text{—— (v)}$$

for weak acids, $(HCN) >> (CN^-)$; (CN^-) is negligible for additive eqⁿ.

now in eqⁿ (iii) $C_T = 10^{-4} = (HCN)$

(i) $\Rightarrow K_A = \dfrac{(H^+)\,[(H^+) - (OH^-)]}{(HCN)}$

$\Rightarrow [H^+] = K_w + K_A \cdot C_+$

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

$\therefore pH = 6.57$

Check assumption:

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

$\therefore (CN^-) = 10^{-6.63} \ll 10^{-4}$

$C_T = 10^{-4} + 10^{-6.63} \simeq 10^{-4}$

Assumption OK.

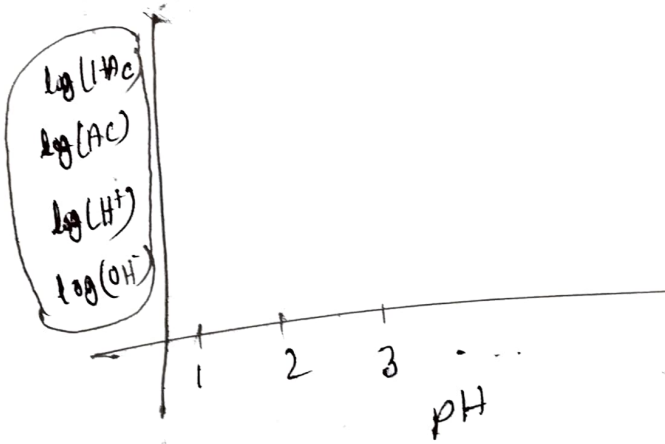
Graphical Approach

draw graph for next class H^+ & OH^- and derive both

$HAc \rightleftharpoons H^+ + Ac^-$

$$K_a = \frac{(H^+)(Ac^-)}{(HAc)} \quad \text{—— (I)}$$

$$C_T = (HAc) + (Ac^-) \quad \text{—— (II)}$$



Graphical Approach

pH diagram for weak monoprotic acid:

$$C_t = (HAc) + (Ac^-)$$

$$\therefore (HAc) + K_a \frac{(HAc)}{(H^+)}$$

$$\therefore C_t = \frac{(H^+)(HAc) + K_a (HAc)}{(H^+)}$$

$$\therefore (HAc) = C_t \frac{(H^+)}{(H^+) + K_a}$$

$$C_t = \frac{(H^+)(Ac^-)}{K_a} + (Ac^-)$$

$$= \frac{(H^+)(Ac^-) + K_a (Ac^-)}{K_a}$$

$$\therefore (Ac^-) = C_t \frac{K_a}{(H^+) + K_a}$$

Graphical approach

log C – pH diagram for (H^+) & (OH^-)

Mass law eqⁿ for water:

$$(H^+)(OH^-) = K_w \quad \text{(i)}$$

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

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

From (i),

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

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

$$HAC \longrightarrow H^+ + AC^-$$

$$K_A = \frac{(H^+)(AC^-)}{(HAC)} \; ; \; pK_A = 4.74$$

$$C_T = (HAc) + (Ac^-) = 10^{-3} \quad \text{(a)}$$

$$(HAc) = C_T \frac{(H^+)}{(H^+) + K_A} \quad \text{and,} \quad (Ac^-) = C_T \frac{K_A}{(H^+) + K_A} \quad \text{(b)}$$

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$pH < pK_A \longrightarrow H^+ >>> K_A$ Case 1

$(H^+) + K_A \simeq (H^+)$

$Eq^n(a) \rightarrow (HAc) = \dfrac{C_T (H^+)}{(H^+)} = C_T$

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

$= \dfrac{d \log(HAc)}{d pH} = 0$

$Eq^n(b) \rightarrow (Ac^-) = \dfrac{C_T K_A}{(H^+)}$

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

$= \log C_T + \log K_A + pH$

$\Rightarrow \dfrac{d \log(Ac^-)}{d pH} = 0 + 0 + 1$

case 2: $pH > pK_A \rightarrow K_A >>> H^+$

$$Eq^n (a) \rightarrow \frac{C_T (H^+)}{K_A} = (HAc)$$

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

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

$$\Rightarrow \frac{d \log (HAc)}{d pH} = -1 + 0 + 0$$

$$Eq^n (b) \rightarrow (Ac^-) = \frac{C_T K_A}{K_A}$$

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

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

potato
tomato

Case 3: $pH = pK_A$; $H^+ = K_A$

from (a) → $K_A = \frac{(H^+)(Ac^-)}{(HAc)}$

$\Rightarrow (HA) = (Ac^-)$

from (b) → $(HAc) = (Ac^-) = \frac{C_T}{2}$

$\log(HAc) = \log(Ac^-) = \log\frac{C_T}{2}$

$= \log C_T - \log 2$

$\Rightarrow \log(HAc) = \log(Ac^-) = \log C_T - \log 2$

Assignment next class

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Cont...

Proton condition

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

→ explain on graph which point is valid for this eqn

Lec - 6

$$\alpha_0 = \alpha_{HA} = \frac{(HA)}{C_T} = \frac{H^+}{K + H^+}$$

$$\alpha_1 = \alpha_{A^-} = \frac{(A^-)}{C_T} = \frac{K}{K + H^+}$$

$$\alpha_0 + \alpha_1 = 1$$

6.37 10.33

Diprotic acid (eg. H_2CO_3): → memorize pK_1 & pK_2

$$C_T = (H_2CO_3) + (HCO_3^-) + (CO_3^{2-})$$

$$(H_2CO_3) = \alpha_0 C_T$$

---

derive, α_1, α_2 | α_0

The carbonate system

★★★ Dissolved carbonate equilibria - open & closed system

SA

06/11/23

Closed system (closed from atmosphere)

Species present in water: six species

$CO_2(aq)$, H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, OH^-

Six eqⁿ needed to solve

mass action law:

For the reaction: $H_2CO_3 = CO_{2(aq)} + H_2$

$$K = \frac{(CO_2)(aq)}{(H_2CO_3)} \simeq 650$$

$\therefore CO_2(aq) \gg H_2CO_3$

$$(H_2CO_3^*) = (H_2CO_3) + CO_2(aq)$$

$$\simeq CO_2(aq)$$

$H_2CO_3 \longrightarrow H^+ + HCO_3^-$, $K_1 = 4.3 \times 10^{-7}$, $pK_1 = 6.37$

$$K_1 = \frac{(H^+)(HCO_3^-)}{(H_2CO_3)} \quad \text{——— (1)}$$

~~Hco~~

$HCO_3^- \longrightarrow H^+ + CO_3^{2-}$; $K_2 = 4.7 \times 10^{-11}$, $pK_2 = 10.33$

$$K_2 = \frac{(H^+)(CO_3^{2-})}{(HCO_3^-)} \quad \text{—— (ii)}$$

$$(H_2CO_3) + (HCO_3^-) + (CO_3^{2-}) = C_T \quad \text{—— (iii)}$$

—

$$C_T = (H_2CO_3^*) + (HCO_3^-) + (CO_3^{2-})$$

—

Closed carbonate system

$$H_2CO_3 \rightarrow H^+ + (HCO_3^-)$$

$$K_1 = \frac{(H^+)(HCO_3^-)}{(H_2CO_3)}$$

$$\Rightarrow \log K_1 = \log (H^+) + \log \left(\frac{HCO_3^-}{H_2CO_3}\right)$$

$$\Rightarrow -pK_1 = -pH + \log \left(\frac{HCO_3^-}{H_2CO_3}\right)$$

$$\Rightarrow pH = pK_1 + \log \left(\frac{HCO_3^-}{H_2CO_3}\right) \quad \text{---} \quad (a)$$

when, $pH = pK_1$, $\log (HCO_3^-) = \log (H_2CO_3)$

$$\therefore (HCO_3^-) = (H_2CO_3) \quad \text{---} \quad (i)$$

when $pH < pK_2$ i.e., $(H^+) > K_2 \rightarrow (H_2CO_3^*)$ is dominant

" $pH > pK_2$ i.e, $(H^+) < K_2 \rightarrow (HCO_3^{2-})$ " "

$HCO_3^- \longrightarrow H^+ + CO_3^{2-}$

$$K_2 = \frac{(H^+)\,(CO_3^{2-})}{(HCO_3^-)}$$

$$\Rightarrow \log K_2 = \log (H^+) + \log\left(\frac{CO_3^{2-}}{HCO_3^-}\right)$$

$$\Rightarrow -pK_2 = -pH + \log\left(\frac{CO_3^{2-}}{HCO_3^-}\right)$$

$$\Rightarrow pH = pK_2 + \log\left(\frac{CO_3^{2-}}{HCO_3^-}\right) \quad \text{—— (b)}$$

when $pH = pK_2$ then $\log(CO_3^{2-}) = \log(HCO_3^-)$

$$\therefore CO_3^{2-} = HCO_3^-$$

when $pH < pK_2$ i.e., $(H^+) > K_2 \longrightarrow HCO_3^-$ dominant

$pH > pK_2$ i.e., $(H^+) < K_2 \longrightarrow CO_3^{2-}$ "

$$C_T = (H_2CO_3) + (HCO_3^-) + (CO_3^{2-}) \quad \text{—— (i)}$$

At $pH < pK_1$

$$H_2CO_3 \approx C_T$$

$pK_1 = 6.3$

$pK_2 = 10.3$

$$C_T = (H_2CO_3) + (HCO_3^-) + (CO_3^{2-}) \quad \text{—— (i)}$$

At $pH < pK_1 \rightarrow (H_2CO_3) \simeq C_T$ —— (1)

$$\Rightarrow \log(H_2CO_3) = \log C_T$$

$$\Rightarrow \frac{d \log (H_2CO_3)}{dpH} = 0$$

—

$$H_2CO_3 \rightarrow H^+ + HCO_3^-$$

$$K_1 = \frac{(H^+)(HCO_3^-)}{(H_2CO_3)} \quad \text{—— (ii)}$$

From eq^n (ii),

$$(HCO_3^-) = \frac{K_1}{(H^+)} (H_2CO_3) \rightarrow C_T = 10^{-3}$$

$$\Rightarrow \log (HCO_3) \equiv \text{---}$$

$$\Rightarrow \frac{d \log (HCO_3)}{dpH} = +1 \quad \text{—— (2)}$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-}$$

$$K_2 = \frac{(H^+)(CO_3^{2-})}{(HCO_3^-)} \quad \text{---} \quad (iii)$$

From eq^n (iii), →

$$(CO_3^{2-}) = \frac{K_2}{(H^+)} (HCO_3^-)$$

$$= \frac{K_2}{(H^+)} \frac{K_1}{(H^+)} (H_2CO_3) \quad \xrightarrow{C_T} \quad [\text{from eq}^n (ii)]$$

$\Rightarrow$ - - - - - -

$$\rightarrow \frac{d \log (CO_3^{2-})}{d pH} = +2 \quad \text{- - -} \quad (3)$$

At $pK_1 < pH < pK_2$, (HCO_3^-) is dominant

$$\therefore (HCO_3^-) = C_T \quad \text{—— (4)}$$

$\rightarrow \log \rightarrow d\log$

From eqn (ii),

$$\frac{d\log(H_2CO_3)}{dpH} = -1 \quad \text{—— (5)}$$

From eqn (iii),

$$\frac{d\log(CO_3^{2-})}{dpH} = +1 \quad \text{—— (6)}$$

At $pH > pK_2$, (CO_3^{2-}) dominant

$$\therefore (CO_3^{2-}) = C_T \Rightarrow \log(CO_3^{2-}) = \log C_T \Rightarrow \frac{d\log(CO_3^{2-})}{dpH} = 0 \quad \text{— (7)}$$

From eqn (ii),

$$\frac{d\log(H_2CO_3)}{dpH} = -2 \quad \text{— (8)}$$

From eqn (iii),

$$\frac{d\log(HCO_3^-)}{dpH} = \quad \text{— (9)}$$

SA | Rough / Midterm

HAc dissociation: $HAc \rightleftharpoons H^+ + Ac^-$

and H_2O: $H_2O \rightleftharpoons H^+ + OH^-$

Species at equilibrium: $HAc, H^+, Ac^-, H_2O, OH^-$

Mass action eqn:

$$K_A = \frac{(H^+)(Ac^-)}{(HAc)} = 1.8 \times 10^{-5} \quad \text{— (i)}$$

$$K_W = (H^+)(OH^-) = 10^{-14} \quad \text{— (ii)}$$

Mass balance eqn: $C_T = (HAc) + (Ac^-) = 10^{-3}$ — (iii)

Charge " " : $(H^+) = (Ac^-) + (OH^-)$ — (iv)

Proton cond. eqn : References; H_2O, HAc

$$(H^+) = (Ac^-) + (OH^-) \quad \text{— (v)}$$

From (ii), $(OH^-) = \frac{10^{-14}}{(H^+)}$

From (iv), $(Ac^-) = (H^+) - \frac{10^{-14}}{(H^+)}$

From (iii), $(HAc) = 10^{-3} - (H^+) + \frac{10^{-14}}{(H^+)}$

From (i),

$$1.8 \times 10^{-5} = \frac{(H^+)\left[(H^+) - \frac{10^{-14}}{(H^+)}\right]}{10^{-3} - \left[(H^+) - \frac{10^{-14}}{(H^+)}\right]}$$

$$\Rightarrow K_A C_T - K_A\left[(H^+) - \frac{10^{-14}}{(H^+)}\right] = (H^+)^2 - 10^{-14}$$

$$\Rightarrow K_A C_T - K_A\left[\frac{(H^+)^2 - 10^{-14}}{(H^+)}\right] = (H^+)^2 - 10^{-14}$$

$$\Rightarrow K_A C_T - (H^+)^2 + 10^{-14} = K_A\left[\frac{(H^+)^2 - 10^{-14}}{(H^+)}\right]$$

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

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

$$\therefore (H^+) = 1.25 \times 10^{-4}$$

Approximate

For weak acids, $(HAc) \gg (Ac^-)$

From (iii), $(HAc) = 10^{-3}$

From (ii), $(OH^-) = \frac{10^{-14}}{(H^+)}$

From (iv), $(Ac^-) = (H^+) - \frac{10^{-14}}{(H^+)}$

From (i),

$$1.8 \times 10^{-5} = \frac{(H^+)\left[(H^+) - \frac{10^{-14}}{(H^+)}\right]}{10^{-3}}$$

$$\Rightarrow K_A C_T = (H^+)^2 - K_w$$

$$\therefore (H^+) = 1.34 \times 10^{-4},$$

Check

$$(Ac^-) = 1.34 \times 10^{-4}$$

$HCN \rightleftharpoons H^+ + CN^-$

$H_2O \rightleftharpoons H^+ + OH^-$

$\Big\}$ $H^+, CN^-, OH^-, HCN, H_2O$

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

$$K_w = (H^+)(OH^-) = 10^{-14}$$

$$C_t = (CN^-) + (HCN) = 10^{-4}$$

$$(H^+) = (OH^-) + (CN^-)$$

—

$$(OH^-) = \frac{10^{-14}}{(H^+)}$$

$$(CN^-) = (H^+) - \left[\frac{10^{-14}}{(H^+)}\right]$$

$$(HCN) = 10^{-4} - \left[(H^+) - \frac{10^{-14}}{(H^+)}\right]$$

—

$$10^{-9.2} = \frac{(H^+)\left[(H^+) - \frac{10^{-14}}{(H^+)}\right]}{10^{-4} - \left[(H^+) - \frac{10^{-14}}{(H^+)}\right]}$$

$$\Rightarrow 10^{-9.2} \times 10^{-4} - 10^{-9.2}\left[(H^+) - \frac{10^{-14}}{(H^+)}\right] = (H^+)^2 - 10^{-14}$$

$$\Rightarrow 10^{-13.2} - (H^+)^2 + 10^{-14} = 10^{-9.2}\left[\frac{(H^+)^2 - 10^{-14}}{(H^+)}\right]$$

$$\Rightarrow 10^{-13.2}(H^+) - (H^+)^3 + 10^{-14}(H^+) - 10^{-9.2}(H^+)^2 + 10^{-23.2} = 0$$

$$\Rightarrow (H^+)^3 + 10^{-9.2}(H^+)^2 + (-10^{-14} - 10^{-13.2})(H^+) - 10^{-23.2} = 0$$

$$\therefore (H^+) = 2.7 \times 10^{-7}, \quad (CN^-) = 2.33 \times 10^{-7}, \quad (HCN) = 9.98 \times 10^{-5}$$

Assumption:

$$(HCN) = 10^{-4}$$

$$10^{-9.2} = \frac{(H^+)\left[(H^+) - \frac{10^{-14}}{(H^+)}\right]}{10^{-4}}$$

$$\Rightarrow 10^{-13.2} = (H^+)^2 - 10^{-14}$$

$$\therefore (H^+) = 2.7 \times 10^{-7}$$

Graphical

Dissociation of water: $H_2O \rightleftharpoons H^+ + OH^-$

Mass action eqn:

$$K_w = (H^+)(OH^-) \quad \text{— (1)}$$

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

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

From (1), $\log(OH^-) = \log(10^{-14}) - \log(H^+)$

$$= -14 + pH$$

At $pH = 1$, $\log(H^+) = -1$; $\log(OH^-) = -13$

$pH = 14$, " $= -14$; " $= 0$

Dissociation of HAc: $HAc \rightleftharpoons H^+ + Ac^-$

Mass action eqn:

$$K_a = \frac{(H^+)(Ac^-)}{(HAc)}; \quad pK_a = 4.74$$

Mass balance eqn:

$$C_T = (Ac^-) + (HAc) = 10^{-3}$$

Now

$$C_T = \frac{K_a(HAc)}{(H^+)} + (HAc)$$

$$\Rightarrow C_T = HAc\left[\frac{K_a + (H^+)}{(H^+)}\right]$$

$$\therefore (HAc) = C_T \frac{(H^+)}{K_a + (H^+)} \quad -(1)$$

$$C_T = (Ac^-) + \frac{(H^+)(Ac^-)}{K_a}$$

$$\Rightarrow C_T = (Ac^-)\left[\frac{K_a + (H^+)}{K_a}\right]$$

$$\therefore (Ac^-) = C_T \frac{K_a}{(H^+) + K_a} \quad -(1)$$

Case (I): $pH << pK_a$; $(H^+) >> K_a$

$\therefore (H^+) + K_a \simeq (H^+)$

From eqn (I): $(HAc) = C_T \frac{(H^+)}{(H^+)}$

$= C_T$

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

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

eqn (II): $(Ac^-) = C_T \frac{K_a}{(H^+)}$

$\Rightarrow \log(Ac^-) = \log C_T + \log K_a - \log(H^+)$

$= \log C_T + \log K_a + pH$

$\Rightarrow \frac{d \log(Ac^-)}{dpH} = 1$

Case (2): $pH > pK_a$; $(H^+) \ll K_a$

$\therefore (H^+) + K_a \simeq K_a$

From eqn (1): $(HAc) = C_T \frac{H^+}{K_a}$

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

$= \log C_T - pH - \log K_a$

$\Rightarrow \frac{d \log(HAc)}{dpH} = -1$

eqn (IP): $(Ac^-) = C_T \frac{K_a}{K_a}$

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

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

Case (3): $pH = pK_a$; $(H^+) = K_a$

From eqn (i): $(HAc) = \frac{C_T}{2}$

eqn (ii): $(Ac^-) = \frac{C_T}{2}$

$\therefore \log(HAc) = \log(Ac^-) = \log C_T - \log 2$

$= -3 - 0.3$

$= -3.3$

Check: $(H^+) = (Ac^-) + (OH^-)$

(i) At pH : 7; $10^{-7} = x + 10^{-7}$ ($x = 10^{-3}$) is not true

(ii) Ap pH : 4.74; $\sim 10^{-4.8} = 10^{-3.3} + 10^{-9.3}$ is possible

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Buffer

Composite of weak acid and its conjugate base and
weak base " acid

pH of natural water is controlled by bi-carbonate & carbonate

★★ Significance of pH

★ pH control

Controls of pH on natural ~~yeah~~ water

★★★ Lec7 P24 graph

Math/Lec 7 P 25 Capacity diagram

water 1, pH = 6.1

(alk) = 1×10^{-3} M = 1.0 mM

water 2, pH = 9

(alk) = 2 mM

C_{T_1} = 2.8 mM

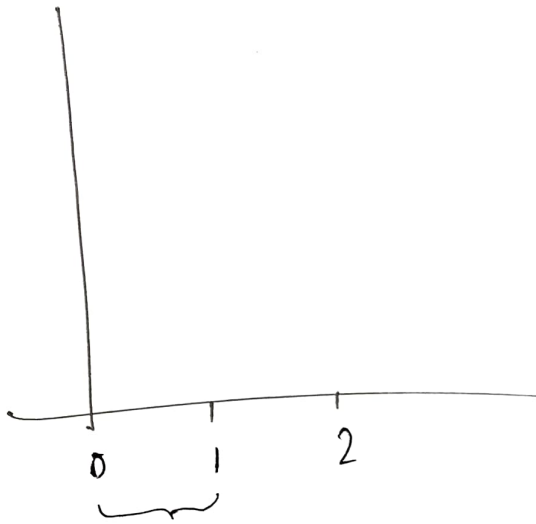
C_{T_2} = 1.9 mM

For the mixture,

$C_T = \frac{2.8 + 1.9}{2}$ mM

= 2.35 mM

* pH is not a conservative prop & can't be averaged



Using compass

2 → 3

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Example 2

Surface waters, pH = 6.5

(alk) = 1.0 mM

From capacity diagram, C_T = 1.7 mM

bring compass,
2 scales (smaller, longer)
pencil, rubber

With Na_2CO_3,

slope: 2:1 for CO_3
as valence is 2

Redox equilibria

sewage – waste water; not solid, liquid

waste treatment plant – at pagla; nearby buriganga

Electron activity and pE

Concept of pH & pE

detritous -> leftover

Water Pollution Manggement

Water Pollution Sources

Point sources

Nonpoint source

Organic compounds

- Bio-degradable
- Non-biodegradable

Water Pollution by Organic compounds

Water source in home for next class incl. modzone

d

*** Degradation of Organic Matter

Aerobic decomposition or oxidation

Anaerobic " " "

1. Organic matter

↓

2. Bacterial oxi- ..

---

1. Acid Forming Bacteria

2. Mathanogenic Bacteria

---

bacteria

Aerobic — O_2

Anaerobic — ~~NO_3~~ NO_2 / ~~SO_4~~ O_2

Facultative → w/ w/o O_2

*** Major Effects of Organic Pollution in water

write down all 3 points in exam

nutrient here nitrogen phosphorus

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Params for measuring organic Pollution

BOD (Biochemical Oxygen Demand)

COD (chemical Oxygen Demand)

Both biodegradable & non biodegradable

~~COD = BOD~~

COD = greater than or equal to BOD

BOD never greater than COD

1 ppm = 1 mg L^{-1}

Metal organic Interaction

Metal - organic complex ⟶ reversible

Organometallic ~~compound~~ complex ⟶ irreversible

---

unidentate ligand

~~Chelator~~

Chelation process

Chelat

Organometallic compounds

Explain w/ examples

←

POPs (Persistent organ Pollutants)

01/01/24

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Water Quality Params — Stringent (कठोर)

Src & impacts of each param

Color → apparent, true color

—Water Quality Standards

Source – ECR

⭐⭐⭐ Acid-Base Reactions in Soil

Acidity / basicity formation & removal

memorize reactions

⭐⭐⭐ CEC



Ion Exchange Equilibria in Soil

Nutrients in Soil

Nitrogen

Phosphorus

Pollutants

Fate

~~Soil-water partition~~

Soil-water partition coefficient

$K_d = C_s / C_w$

Organic pollutant affinity to soil is ~~higher~~ high

For orgic portion,

$K_d = f_{oc} K$

Application of Dissolution

Solubility of salts

Silver chromate

☆☆ Page 8, Lec 13

$$K_{so} = (Ca^{2+})(SO_4^{2-})$$