EWC 105
Environmental Chemistry

Lecture 6

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Ionization Fractions of Monoprotic Acid

Monoprotic acid-base:

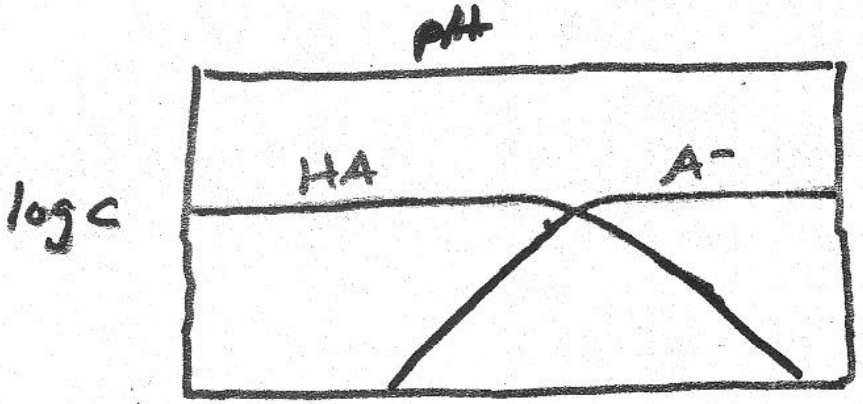
$$HA = A^- + H^+$$

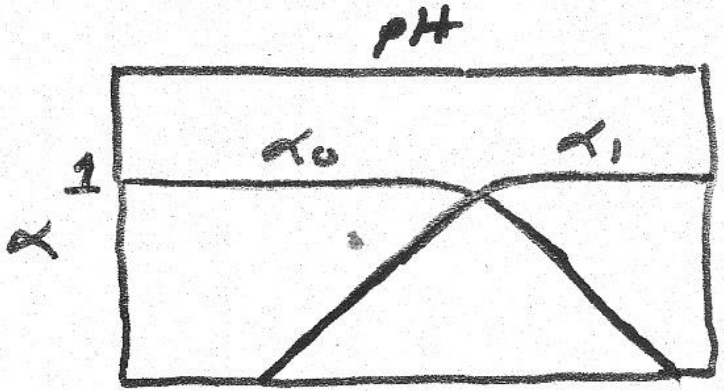
$$C_T = (HA) + (A^-)$$

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

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

α_0, α_1 are called "distribution coefficient"





$(\alpha_0 + \alpha_1) = 1$ at any particular pH

Ionization Fractions of Diprotic Acid

Diprotic acid (e.g., H_2CO_3):

α_0, α_1 and α_2 are called "distribution coefficient"

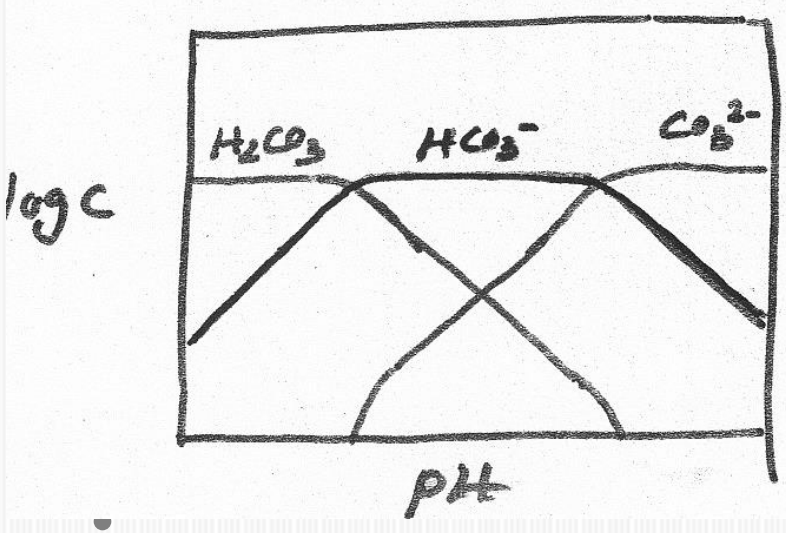
$$C_T = (H_2CO_3) + (HCO_3^-) + (CO_3^{2-})$$

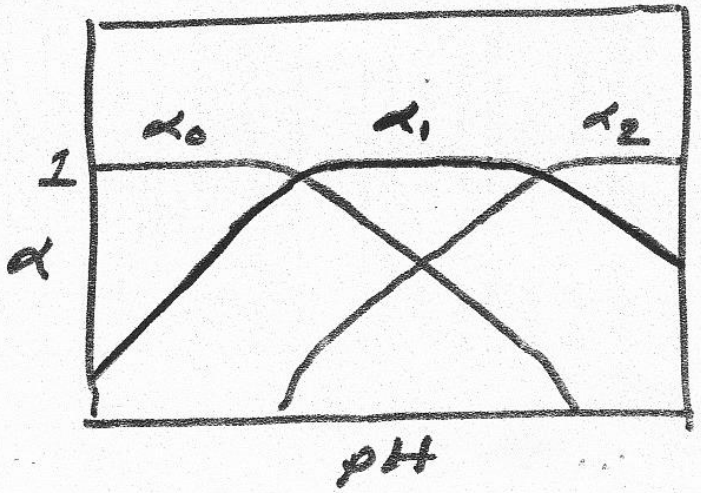
$$(H_2CO_3) = \alpha_0 C_T \quad ; \quad \alpha_0 = \left(1 + \frac{K_1}{H^+} + \frac{K_1 K_2}{(H^+)^2}\right)^{-1}$$

$$(HCO_3^-) = \alpha_1 C_T \quad ; \quad \alpha_1 = \left(\frac{H^+}{K} + 1 + \frac{K_2}{H^+}\right)^{-1}$$

$$(CO_3^{2-}) = \alpha_2 C_T \quad ; \quad \alpha_2 = \left(\frac{(H^+)^2}{K_1 K_2} + \frac{(H^+)}{K_2} + 1\right)^{-1}$$

$$(\alpha_0 + \alpha_1 + \alpha_2) = 1$$





Ionization Fractions of Diprotic Acid

Diprotic acid (e.g., H_2CO_3):

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

$$K_1 = \frac{(H^+)\,(HCO_3^-)}{(H_2CO_3)} \quad \ldots (i)$$

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

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

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

Ionization Fractions of Diprotic Acid

Diprotic acid (e.g., H_2CO_3):

eqn (ii) $\rightarrow$ $(CO_3^{2-}) = \dfrac{K_2 (HCO_3^-)}{(H^+)}$

$= \dfrac{K_2}{(H^+)} \left\{ \dfrac{K_1 (H_2CO_3^-)}{(H^+)} \right\}$ [from eqn (i) $(HCO_3^-) = \dfrac{K_1 (H_2CO_3)}{(H^+)}$ --- (iv)]

$= \dfrac{K_1 K_2 (H_2CO_3^-)}{(H^+)^2}$ --- (v)

Ionization Fractions of Diprotic Acid

Diprotic acid (e.g., H_2CO_3):

eqn (iii) $\longrightarrow (H_2CO_3) + (HCO_3^-) + (CO_3^{2-}) = C_T$

$$\Rightarrow (H_2CO_3) + \frac{K_1 (H_2CO_3)}{(H^+)} + \frac{K_1 K_2 (H_2CO_3)}{(H^+)^2} = C_T \quad \left[\text{using eqns (iv) \& (v)}\right]$$

$$\Rightarrow (H_2CO_3)\left[1 + \frac{K_1}{(H^+)} + \frac{K_1 K_2}{(H^+)^2}\right] = C_T$$

$$\Rightarrow \boxed{(H_2CO_3) = \frac{C_T}{1 + \frac{K_1}{(H^+)} + \frac{K_1 K_2}{(H^+)^2}}}$$

$$\Rightarrow (H_2CO_3) = \alpha_0 C_T \quad , \text{ where } \alpha_0 = \left[1 + \frac{K_1}{(H^+)} + \frac{K_1 K_2}{(H^+)^2}\right]^{-1}$$

$$(H_2CO_3) = \alpha_0 C_T \quad ; \quad \alpha_0 = \left(1 + \frac{K_1}{H^+} + \frac{K_1 K_2}{(H^+)^2}\right)^{-1}$$

Ionization Fractions of Diprotic Acid

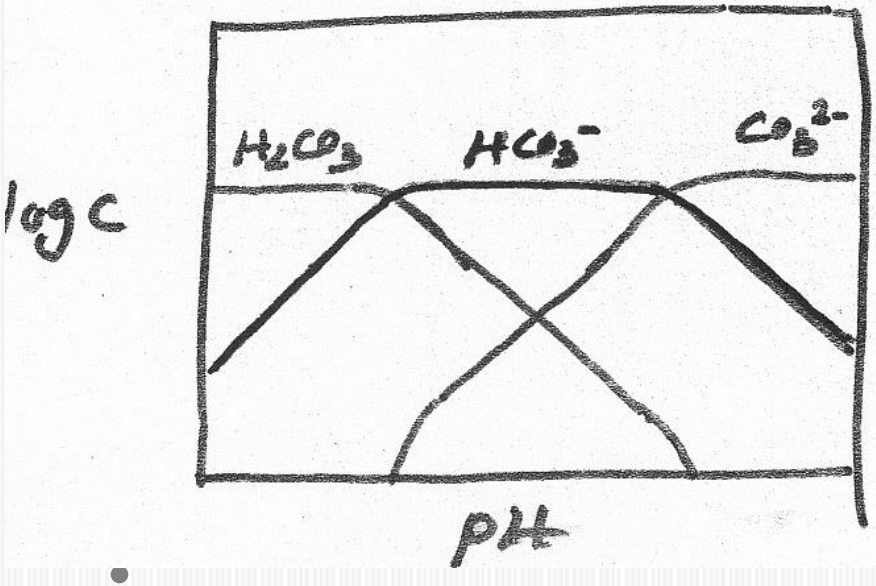
$$C_T = (H_2CO_3) + (HCO_3^-) + (CO_3^{2-})$$

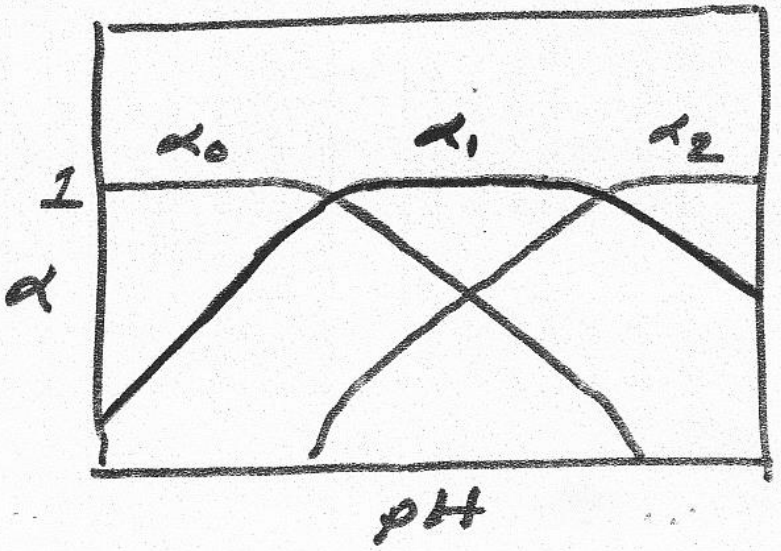
$$(H_2CO_3) = \alpha_0 C_T \quad ; \quad \alpha_0 = \left(1 + \frac{K_1}{H^+} + \frac{K_1 K_2}{(H^+)^2}\right)^{-1}$$

$$(HCO_3^-) = \alpha_1 C_T \quad ; \quad \alpha_1 = \left(\frac{H^+}{K} + 1 + \frac{K_2}{H^+}\right)^{-1}$$

$$(CO_3^{2-}) = \alpha_2 C_T \quad ; \quad \alpha_2 = \left(\frac{(H^+)^2}{K_1 K_2} + \frac{(H^+)}{K_2} + 1\right)^{-1}$$

$$(\alpha_0 + \alpha_1 + \alpha_2) = 1$$





Dissolved CO_2 – Carbonate System

Environmental Significance

- Dissolved constituents in freshwater and seawater comes from minerals or atmosphere.
- Dissolved carbon dioxide (CO_2) plays an important role in regulating pH and composition of natural waters.

Dissolved CO_2 – Carbonate System

Environmental Significance

- Carbonic acid is the most abundant acid in natural water systems and is the acid most responsible for rock weathering.
- Bicarbonate ion (HCO_3^-) is generally the dominant anion in fresh-surface and ground waters.

Dissolved CO_2 – the Carbonate System

Environmental Significance

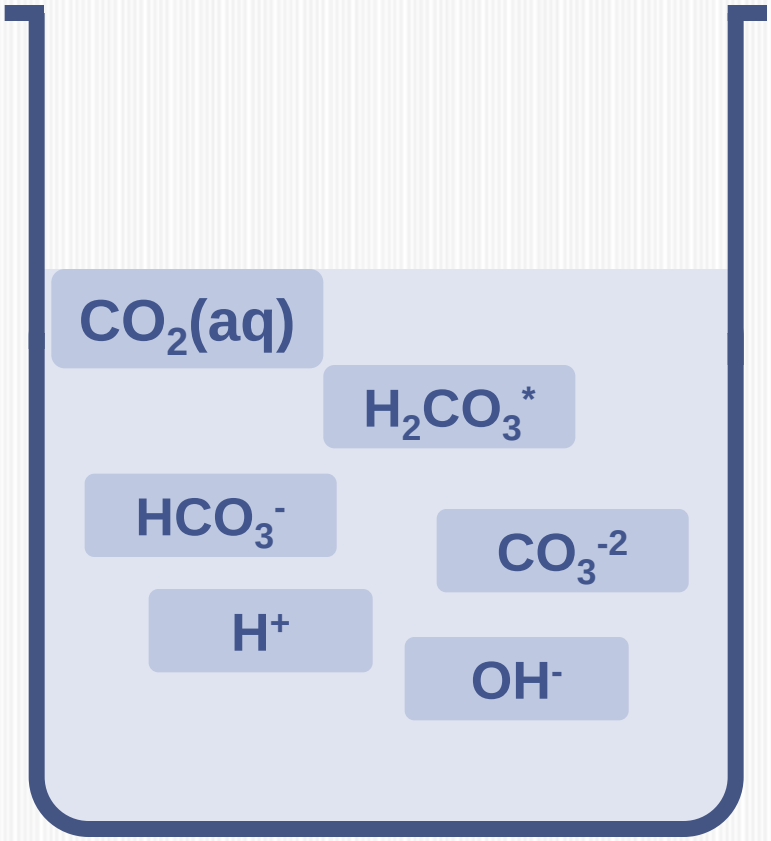
- HCO_3^- and CO_3^{2-} are also the chief contributors to total alkalinity in natural waters.
- In precipitation dissolution reactions, HCO_3^- and CO_3^{2-} are imparted to or withdrawn from water

Dissolved CO_2 – the Carbonate System

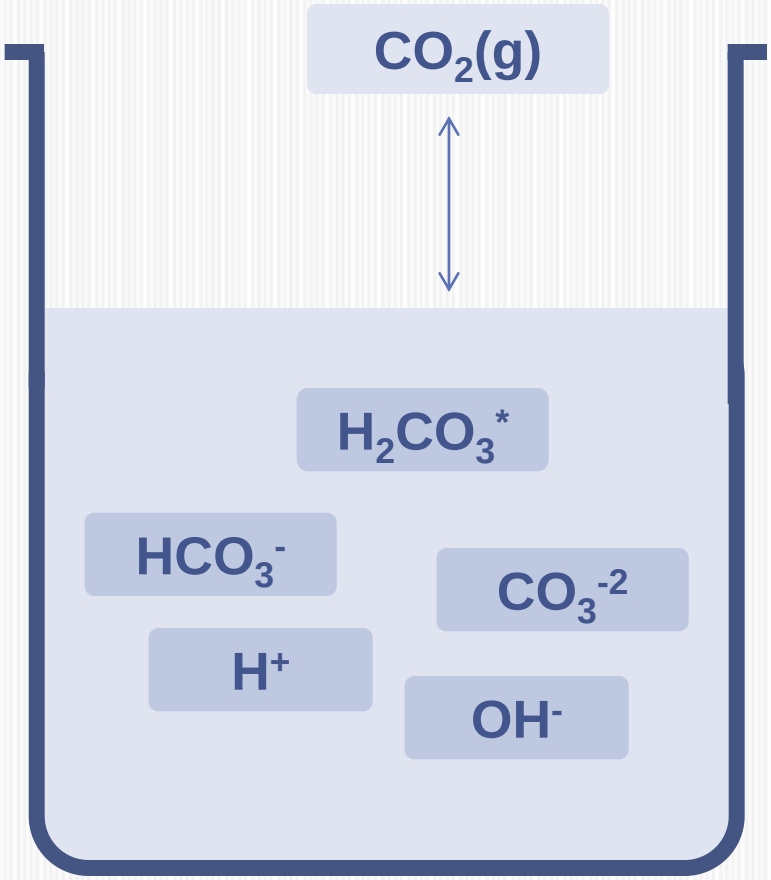
Sources and Sink of CO_2

CO_2 is added to atmosphere by volcanic activity and through combustion of fossil fuel. CO_2 is used up during photosynthesis and set free during respiration and oxidation of organic matter.

Dissolved Carbonate Equilibria – Open & Closed System



Closed system



Open system

Dissolved Carbonate Equilibria – Closed System

Species present in water: Six species:

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

Six equations needed to solve the system:

$$H_2CO_3 = CO_2(aq) + H_2O$$

$$H_2CO_3 = HCO_3^- + H^+$$

$$HCO_3^- = CO_3^{2-} + H^+$$

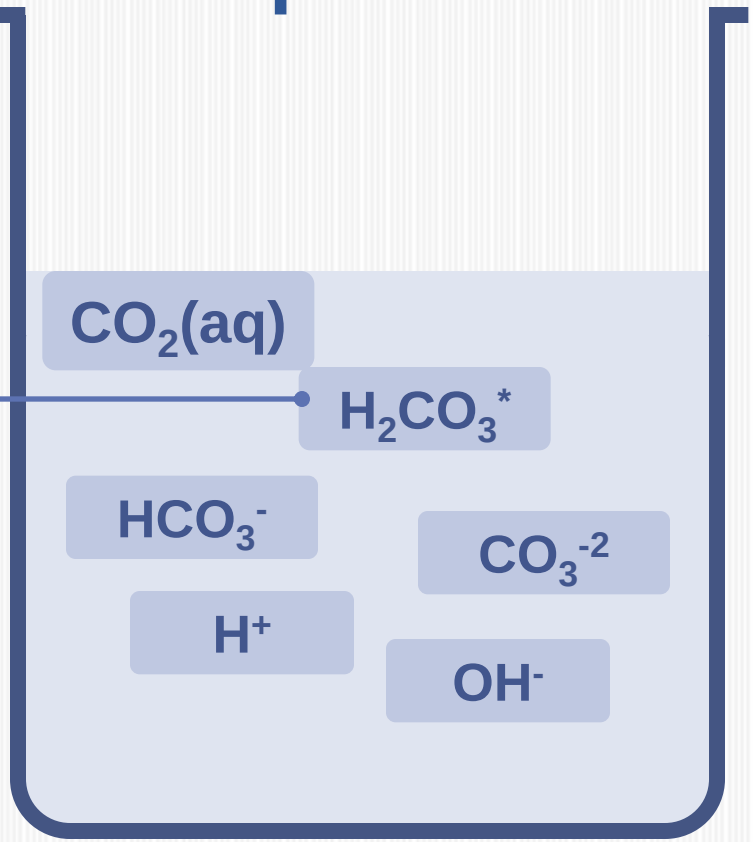
$$H_2O = H^+ + OH^-$$

Mass balance equation

Electroneutrality (or proton condt.)

Dissolved Carbonate Equilibria

Closed System



6 Species

dissolved CO_2

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

Composite Carbonic Acid

True Carbonic Acid

Dissolved Carbonate Equilibria – Closed System

For the reaction: $H_2CO_3 = CO_2(aq) + H_2O$

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

$\therefore CO_2(aq) \gg (H_2CO_3)$

Total analytical concentration of dissolved carbon dioxide,

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

$$\simeq CO_2(aq)$$

Dissolved Carbonate Equilibria – Closed System

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

$$K_1 = \frac{(H^+)\,(HCO_3^-)}{(H_2CO_3)} \quad \ldots (i)$$

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

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

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

Dissolved Carbonate Equilibria – Closed System

∴ Total concentration of dissolved inorganic carbon:

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

(The "*" symbol may be omitted for convenience. in this class. But keep in mind the differences between (H_2CO_3), $CO_2(aq)$ and $(H_2CO_3^*)$).

Dissolved Carbonate Equilibria – Closed System

As shown earlier,

$$(H_2CO_3) = \alpha_0 C_T \quad ; \quad \alpha_0 = \left(1 + \frac{K_1}{(H^+)} + \frac{K_1 K_2}{(H^+)^2}\right)^{-1}$$

$$(HCO_3^-) = \alpha_1 C_T \quad ; \quad \alpha_1 = \left(\frac{(H^+)}{K_1} + 1 + \frac{K_2}{(H^+)}\right)^{-1}$$

$$(CO_3^{2-}) = \alpha_2 C_T \quad ; \quad \alpha_2 = \left(\frac{(H^+)^2}{K_1 K_2} + \frac{(H^+)}{K_2} + 1\right)^{-1}$$

Closed Carbonate System : Log C – pH diagram

CLOSED CARBONATE SYSTEM

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

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

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

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

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

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

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

Closed Carbonate System : Log C – pH diagram

When $pH < pk_1$, i.e. $(H^+) > K_1$, then the acidic (more protonated) species has higher activity, i,e is dominate. Hence, H_2CO_3 is more active than (HCO_3^-) at $pH < pk_1$.

Again, when $pH > pk_1$, i,e: $(H^+) < k_1$, then the comparatively basic (less protonated) species is dominant, hence (HCO_3^-) is more active compared to (H_2CO_3) at $pH > pk_1$.

Closed Carbonate System : Log C – pH diagram

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

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

$$\Rightarrow \log k_2 = \log (H^+) + \log \left(\frac{CO_3^{2-}}{HCO_3^-}\right)$$

$$\Rightarrow -pk_2 = -pH + \log \left(\frac{CO_3^{2-}}{HCO_3^-}\right)$$

$$\Rightarrow pH = pk_2 + \log \left(\frac{CO_3^{2-}}{HCO_3^-}\right) \quad ---(5)$$

When $pH = pk_2$, then $\log (CO_3^{2-}) = \log (HCO_3^-)$

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

Closed Carbonate System : Log C – pH diagram

When $pH < pk_2$, i.e. $(H^+) > K_2$, more acidic (protonated) species i.e (HCO_3^-) is dominant.

When $pH > pk_2$, i.e $(H^+) < K_2$, more basic (less protonated) species, i.e (CO_3^{2-}) is dominant.

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

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

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

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

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

Closed Carbonate System : Log C – pH diagram

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

At $pH < pK_1$, H_2CO_3 dominates among other carbonate species. Hence, from eqn (i), we get,

$$\boxed{H_2CO_3 \approx C_T} \quad \text{---------- [1]}$$

Closed Carbonate System : Log C – pH diagram

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

$$K_1 = \frac{(H^+)\,(HCO_3^-)}{(H_2CO_3)} \qquad \text{---------- (11)}$$

From eqn (ii) $\rightarrow$ $(H_2CO_3) \rightarrow C_T$

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

$$\Rightarrow \log (HCO_3^-) = \log k_1 + \log C_T - \log (H^+)$$

$$= -pk_1 + \log C_T + pH$$

$$\therefore \boxed{\frac{d \log (HCO_3^-)}{dpH} = +1} \qquad \text{--------} \boxed{?}$$

Closed Carbonate System : Log C – pH diagram

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

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

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

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

(H_2CO_3 is replaced by C_T)

$$\Rightarrow \log(CO_3^{2-}) = \log k_2 + \log k_1 - 2\log(H^+) + \log C_T$$

$$= -pk_2 - pk_1 + 2pH + \log C_T$$

$$\therefore \boxed{\frac{d\log(CO_3^{2-})}{dpH} = +2} \quad \text{- - - - - - } \boxed{3}$$

At $pk_1 < pH < pk_2$, (HCO_3^-) is dominant.

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

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

From eqn (ii) $\rightarrow$ $(H_2CO_3) = \frac{(H^+)}{K_1}(HCO_3^-)$, $(HCO_3^-) \rightarrow C_T$

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

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

$$\Rightarrow \log(H_2CO_3) = \log(H^+) - \log k_1 + \log C_T$$

$$= -pH + pk_1 + \log C_T$$

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

From eqn (iii) $\rightarrow$ $(CO_3^{2-}) = \frac{K_2}{(H^+)}(HCO_3^-)$, $(HCO_3^-) \rightarrow C_T$

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

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

$$\Rightarrow \log(CO_3^{2-}) = \log k_2 - \log(H^+) + \log C_T$$

$$= -pk_2 + pH + \log C_T$$

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

At $pH > pk_2$, (CO_3^{2-}) is dominant.

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

$$\therefore \boxed{(CO_3^{2-}) \simeq C_T} \quad \text{---------- 7}$$

From eqn (ii) $\rightarrow$ $(H_2CO_3) = \frac{(H^+)}{K_1}(HCO_3^-)$

$$= \frac{(H^+)}{K_1}\frac{(H^+)}{K_2}(CO_3^{2-}) \quad [\text{from eqn (iii)}] \qquad (CO_3^{2-}) \simeq C_T$$

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

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

$$\log(H_2CO_3) = 2\log(H^+) - \log k_1 - \log k_2 + \log C_T$$

$$= -2pH + pk_1 + pk_2 + \log C_T$$

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

From eqn (iii) $\rightarrow$ $(HCO_3^-) = \frac{(H^+)}{k_2}(CO_3^{2-}) \simeq C_T$

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

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

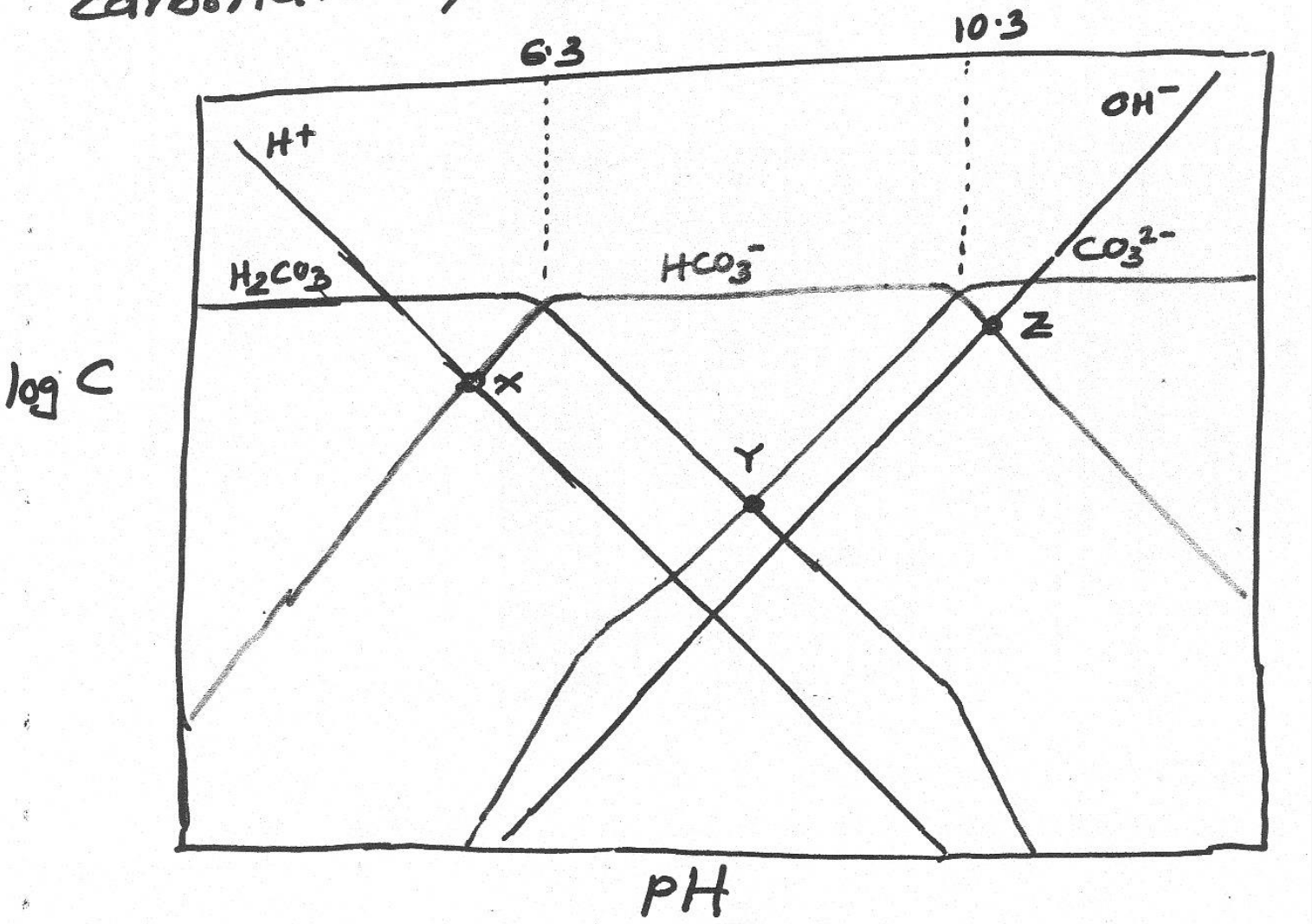
$$\Rightarrow \log(HCO_3^-) = \log(H^+) - \log k_2 + \log C_T$$

$$= -pH + pk_2 + \log C_T$$

$$\therefore \boxed{\frac{d\log(HCO_3^-)}{dpH} = -1} \quad \text{---------- 9}$$

Dissolved Carbonate Equilibria – Closed System

The above expressions may be used to construct log C - pH diagram for the carbonate system (as shown earlier).



Dissolved Carbonate Equilibria – Closed System

- The species in the CO_2-H_2O system: H_2CO_3*, HCO_3^-, CO_3^{2-}, H^+, and OH^-.
- At each p*K* value, conjugate acid-base pairs have equal concentrations.
- At pH < pK_1, H_2CO_3* is predominant, and accounts for nearly 100% of total carbonate.
- At pK_1 < pH < pK_2, HCO_3^- is predominant, and accounts for nearly 100% of total carbonate.
- At pH > pK_2, CO_3^{2-} is predominant.

PRL for Carbonate System

(1) H_2CO_3 added to water.

PRL: H_2O, H_2CO_3

Proton Condition: $(H^+) = (HCO_3^-) + 2(CO_3^{2-}) + (OH^-)$

Solution: At point "x" in log C-pH diagram.

$pH \simeq 4.5$

(2) $NaHCO_3$ added to water.

PRL: H_2O, HCO_3^-

Proton Condition: $(H^+) + (H_2CO_3) = (OH^-) + (CO_3^{2-})$

Solution: At point "y" in log C-pH diagram

$pH = 8.3$

(3) Na_2CO_3 added to water.

PRL: H_2O, $\# CO_3^{2-}$

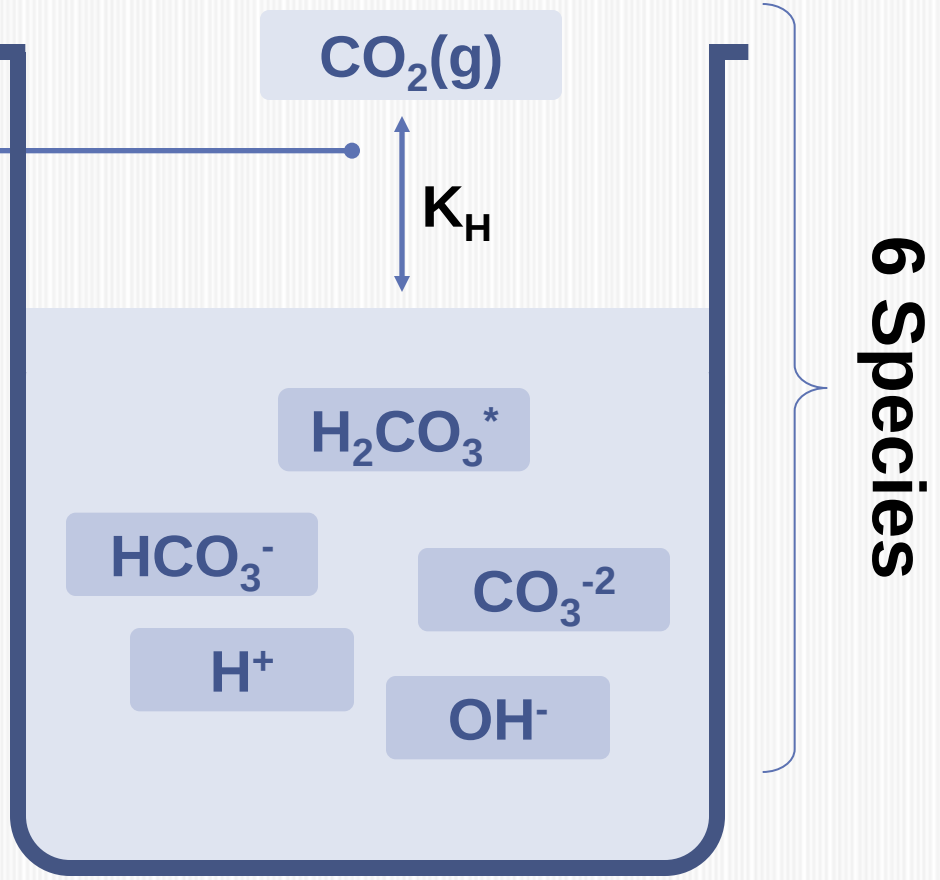
Proton condition: $2(H_2CO_3) + (HCO_3^-) + (H^+) = (OH^-)$

Solution: At point "z" in log C-pH diagram

$pH \simeq 10.5$

Dissolved Carbonate Equilibria

Open System



Henry's Law

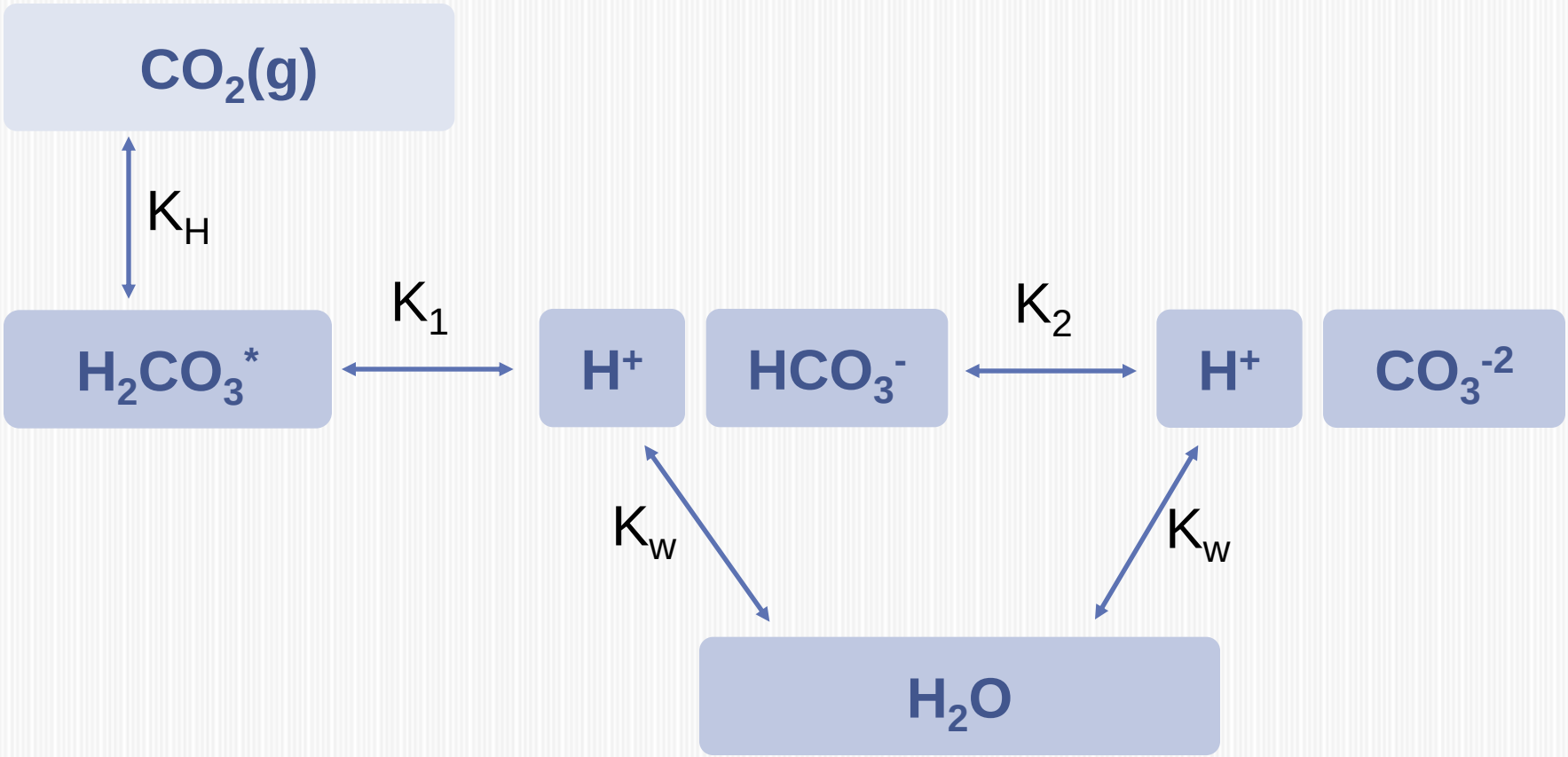
$$\{ H_2CO_3^* \} = K_H \cdot P_{CO2}$$

Composite Carbonic Acid

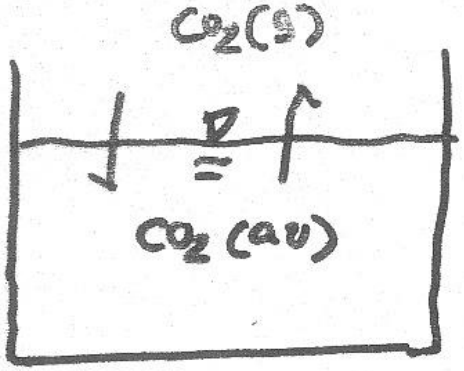
CO_2 Partial Pressure

$K_H = 10^{-1.47}$ M atm^{-1} (at 25 °C)

Dissolution of CO_2 – Open System



Dissolution of CO_2 – Open System



$$CO_2(g) \rightleftharpoons CO_2(aq)$$

$$K_D = \frac{CO_2(aq)}{CO_2(g)}$$ ($\simeq 1.2$ when both expressed in moles/L).

now, $CO_2(g)$ (m/L) $= \frac{n \text{ moles}}{V \text{ (vol.)}} = \frac{P_{CO_2}}{RT}$ ($\because PV = nRT$)

where, $R = 0.082$ atm/m-°K.

T = Temp. in °K.

$\therefore$ $CO_2(aq) = \frac{K_D}{RT} P_{CO_2}$.

$\therefore$ $\boxed{(H_2CO_3^*) = k_H \cdot P_{CO_2}}$

k_H = Henrys law consth (m/L-atm).

Dissolution of CO_2– Open System

For atmosphere. $P_{CO_2} = 10^{-3.5}$ atm.

$k_H = 10^{-1.5}$ m/L-atm.

$\therefore (H_2CO_3) = k_H \cdot P_{CO_2} = 10^{-5}$ M. (const. as long as P_{CO_2} is const.).

Therefore, $$\frac{d \log(H_2CO_3)}{dpH} = 0$$ for entire pH range

Hence, (H_2CO_3) is independent of pH.

Draw a horizontal line through the value of log(k_H. P_{CO2}) in Log C scale of the Log C vs pH graph.
The line indicates the plot for concentration of H_2CO_3.

Dissolution of CO_2– Open System

- The concentration of HCO_3^- as a function of pH is next calculated from K_1:

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

but we have already calculated $(H_2CO_3^*)$

$$(H_2CO_3^*) = p_{CO_2} K_H$$

so

$$(HCO_3^-) = \frac{K_1 K_H p_{CO_2}}{(H^+)}$$

$$\log(HCO_3^-) = \log(K_1 K_H p_{CO_2}) + pH$$

$$\frac{d\log(HCO_3^-)}{dpH} = +1$$

for entire pH range

Dissolution of CO_2– Open System

- The concentration of CO_3^{2-} as a function of pH is next calculated from K_2:

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

but we have already calculated HCO_3^- so:

$$(HCO_3^-) = \frac{K_1 K_H p_{CO_2}}{(H^+)} \quad \text{and} \quad (CO_3^{2-}) = \frac{K_2 K_1 K_H p_{CO_2}}{(H^+)^2}$$

$$\log(CO_3^{2-}) = \log\left(K_2 K_1 K_H p_{CO_2}\right) + 2\,pH$$

$$\frac{d\log(CO_3^{2-})}{dpH} = +2$$

for entire pH range

Dissolution of CO_2– Open System

- The total concentration of carbonate C_T is obtained by summing:

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

$$C_T = p_{CO_2} K_H + \frac{K_1 p_{CO_2} K_H}{(H^+)} + \frac{K_1 K_2 p_{CO_2} K_H}{(H^+)^2}$$

$$\log C_T = \log\left[p_{CO_2} K_H \left(1 + \frac{K_1}{(H^+)} + \frac{K_1 K_2}{(H^+)^2} \right) \right]$$

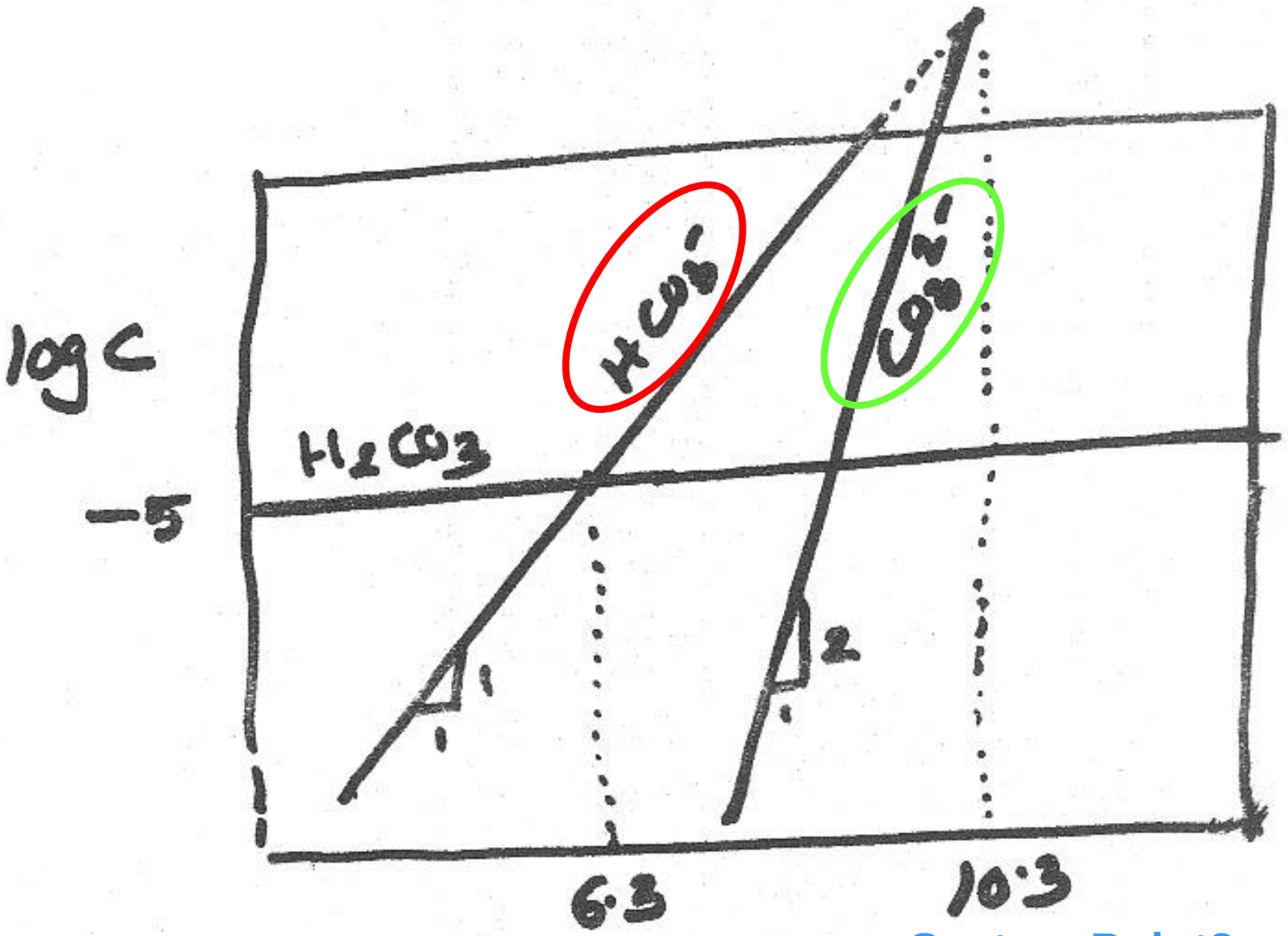
Plotting Log C vs pH for Open carbonate System

- Take a normal graph paper. Mark abscissa (pH) from 0 to 14. Mark ordinate (Log C) from 0 to -10.
- Draw a horizontal line representing the value of $\log(k_H . P_{CO2})$.
- Locate a point on this horizontal line at pH = pK_1(6.3). This point is called system point1.
- Draw a 45° line sloping left (positive slope) of the system point1.

Plotting Log C vs pH for Open carbonate System

- Locate a point on this 45° line at pH = pK_2(10.3). This point is called system point2.
- Draw a line with +2 slope regarding the system point2.

Log C vs pH Diagram for Open Carbonate System



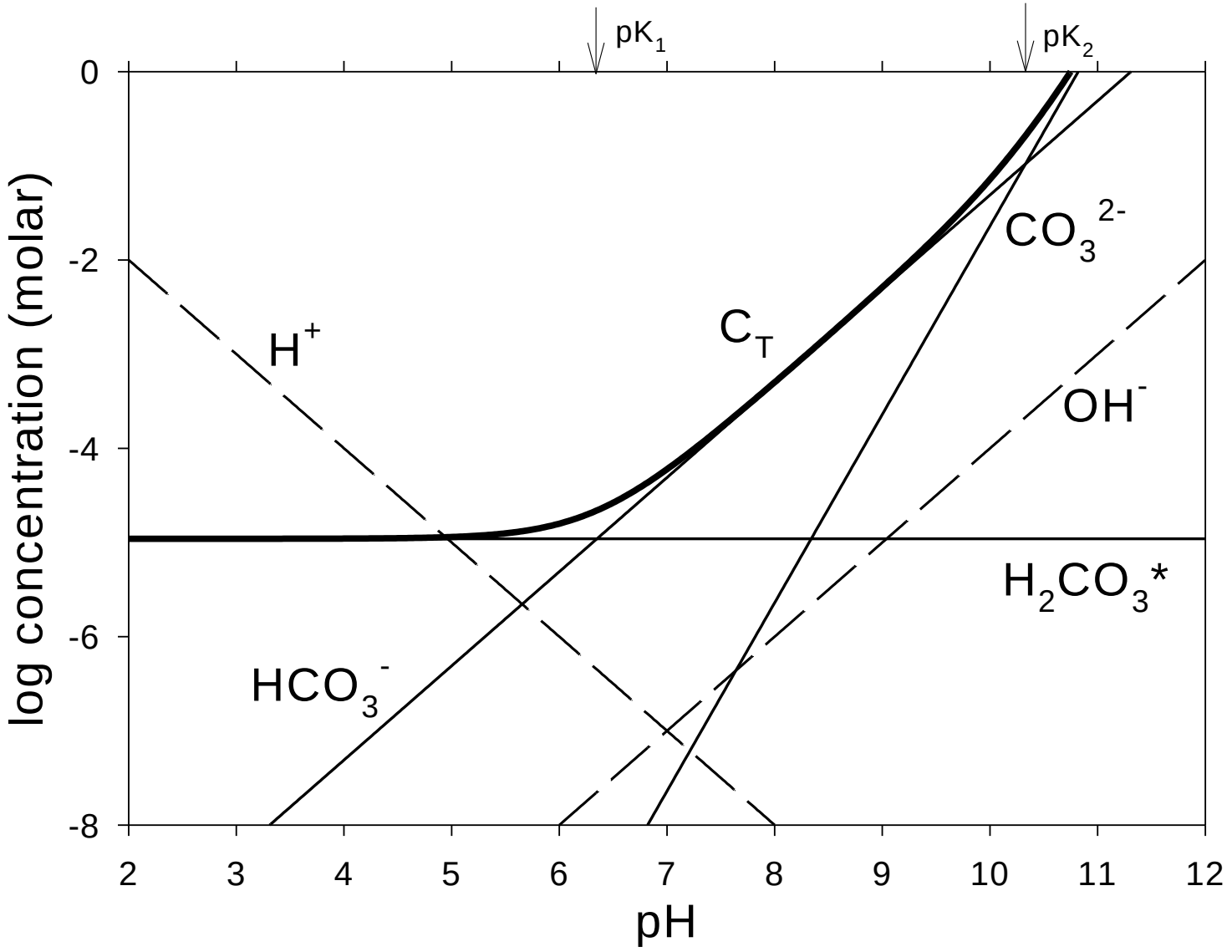
System Point1

pH = pK1

System Point2

pH = pK2

Log C – pH diagram of open-system conditions for carbonate system with a fixed $p_{CO_2} = 10^{-3.5}$ atm.



Log C – pH diagram of open-system conditions for carbonate system with a fixed $p_{CO_2} = 10^{-2.0}$ atm.

