

Lecture 6: Carbonate Geochemistry (Acid-Base Reactions)

I. Review: Activity-concentration relationships

- a. Equilibrium constants (K_{eq}) change as a function of temperature, resulting in increases or decreases in the ratio of products to reactants:

$$\ln(K_{T2}) - \ln(K_{T1}) = \frac{\Delta H_{rxn}^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

- b. The saturation index (SI) describes whether a solution is undersaturated ($Q < K_{eq}$ and $SI < 0$) or oversaturated ($Q > K_{eq}$ and $SI > 0$) with respect to mineral:

$$SI = \log(Q/K_{eq})$$

If the solution is undersaturated, mineral dissolution occurs; if the solution is oversaturated, mineral precipitation occurs.

- c. The activity of a species in solution (a_i) is equal to the product of its concentration (m_i) and an activity coefficient (γ_i):

$$a_i = \gamma_i \times m_i$$

- d. Activity coefficients generally decrease with increasing ionic strength and can be calculated from Debye-Huckel theory equations.
e. For condensed phases (liquids and solids), $a_i = 1$.

II. Acid-base reactions in the environment

Rainwater, particularly acid rain, is acidic (pH < 6). Stream water is near neutral (pH 6-8), while ocean water is slightly basic (pH 8). The change in pH as rain moves through watersheds to the oceans is due to acid-base reactions. These changes vary across landscapes, e.g. stream pH has shown heterogeneous response to acid rain inputs. We're going to examine the chemical reactions that impact these trends.

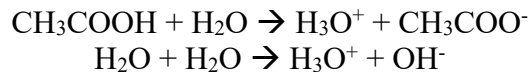
A. Acid-Base reactions – Brønsted-Lowry Definition

acid – anything that donates a proton

base – anything that accepts a proton

conjugate base – base formed from the deprotonation of an acid

conjugate acid – acid formed from the protonation of a base



All acid-base questions can be solved with equilibrium constants and mass and charge balance:

- (1) ratio of products to reactants at equilibrium:

$$K_{eq} = \frac{\prod a_{products}}{\prod a_{reactants}}$$

- (2) charge balance of a solution:

$$0 = \sum m_{cations} z_{cations} - \sum m_{anions} z_{anions}$$

- (3) mass balance of a solution:

$$0 = \sum mass_{products} - \sum mass_{reactants}$$

Normality (N): describe the concentration of H⁺ or OH⁻ in a solution

B. Buffer solutions

Buffer solution – a solution that resists changes in pH and consists of either:

i) weak acid + its conjugate base

ii) weak base + its conjugate acid

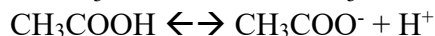
weak acids – only partially dissociate (small K_{eq})



$$K_{eq} = K_a = \frac{a_{\text{CH}_3\text{COO}^-} a_{\text{H}^+}}{a_{\text{CH}_3\text{COOH}}} = 1.76 \times 10^{-5}$$

** K_a = acid dissociation equilibrium constant

Example 1: The conjugate base sodium acetate (NaCH_3COO) is added to acetic acid to form a buffer solution. What is the pH of a solution at equilibrium to which 1 M acetic acid and 1 M sodium acetate are added?



NaCH_3COO (a salt) completely dissociates, while CH_3COOH partially dissociates to yield H^+ :

$$K_a = \frac{a_{\text{CH}_3\text{COO}^-} a_{\text{H}^+}}{a_{\text{CH}_3\text{COOH}}}$$

Use a RICE table to predict the pH of the buffer solution:

R – reaction

I – initial concentration

C – change in concentration

E – end concentration

RICE table: all concentrations are M (= mol/L)

R	CH_3COOH	\rightarrow	CH_3COO^-	+	H^+
I	1		1		0
C	- x		+ x		+ x
E	1 - x		1 + x		x

$$K_a = \frac{a_{\text{CH}_3\text{COO}^-} a_{\text{H}^+}}{a_{\text{CH}_3\text{COOH}}} = \frac{x(1+x)}{1-x} = 1.76 \times 10^{-5}$$

$$x^2 + 1.0000176x - (1.76 \times 10^{-5}) = 0$$

We can solve this quadratic equation and derive $x \approx 0.0000176$, so $\text{pH} = 4.754$

However, we can assume that since **buffers** contain **weak** acids, $x \ll 1$ and $(1+x) \sim 1$ and $(1-x) \sim 1$:

$$x = 1.76 \times 10^{-5} = a_{\text{H}^+}$$
$$\text{pH} = -\log(a_{\text{H}^+}) = -\log(1.76 \times 10^{-5}) = 4.754$$

The pH of a buffer solution containing 1 M acetic acid + 1 M sodium acetate is 4.75.

Example 2: What happens to the pH of the above mix solution when a strong acid (0.01 M HCl) is further added?

R	CH ₃ COOH	→	CH ₃ COO ⁻	+	H ⁺
I	1		1		0.01
C	+ x		- x		- x
E	1 + x		1 - x		0.01 - x

$$K_a = \frac{a_{\text{CH}_3\text{COO}^-} a_{\text{H}^+}}{a_{\text{CH}_3\text{COOH}}} = \frac{(1-x)(0.01-x)}{1+x} = 1.76 \times 10^{-5}$$

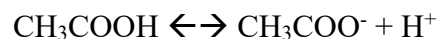
$$x^2 - 1.0100176x + 0.0099824 = 0$$

We can solve this quadratic equation and derive $x=0.009982045$

So $a_{\text{H}^+} = 0.01 - 0.009982 = 0.000018$ and $\text{pH} = 4.745$

Alternatively,

Add a strong acid to the buffer solution:



CH₃COOH increases by 0.01 M (1.01 M) and CH₃COO⁻ decreases by 0.01 M (= 0.99 M)

$$K_a = \frac{a_{\text{CH}_3\text{COO}^-} a_{\text{H}^+}}{a_{\text{CH}_3\text{COOH}}} = \frac{0.99 a_{\text{H}^+}}{1.01}$$

$$a_{\text{H}^+} = 1.80 \times 10^{-5} \text{ and } \text{pH} = 4.746$$

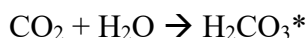
Conclusion: Adding H⁺ to the reaction CH₃COOH ↔ CH₃COO⁻ + H⁺ will drive it to the left to form acetic acid. Thus, the protons are “sequestered” and pH doesn’t change significantly. Adding OH⁻ drives the reaction to the right, and protons are released.

Alert: Add enough H⁺ or OH⁻ to the solution and the pH *will* change

C. The Bicarbonate Buffering System

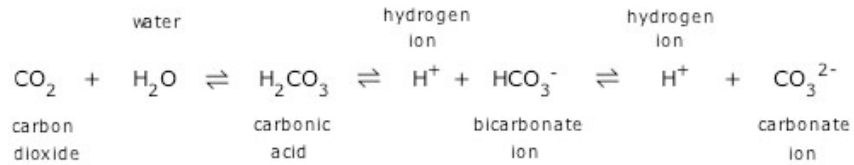
We can explore bicarbonate buffering in the environment as an example of acid-base reactions.

CO₂ gas dissolves in water until equilibrium is reached (or vice versa... e.g. when a soda can degasses open opening):



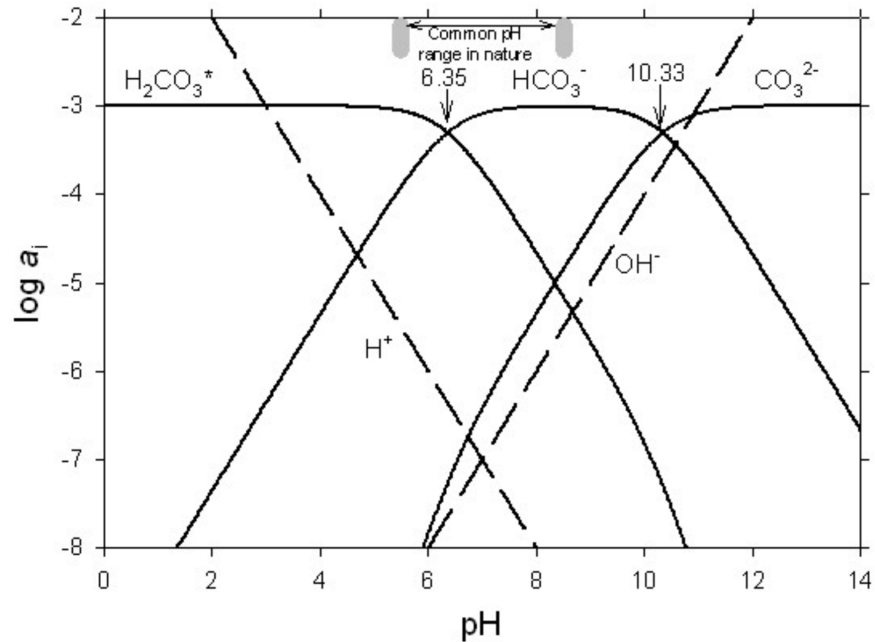
H₂CO₃* represents all forms of CO₂ dissolved in water (H₂CO₃* = H₂CO₃ + HCO₃⁻ + CO₃²⁻)

We can use a series of equations to determine the concentration of H⁺ as carbonic acid deprotonates.



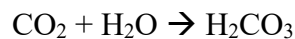
The species that form depend on the pH of the solution.

Bjerrum plot:



Question: how do we determine the pH of a carbonate-bicarbonate buffering system?

1. Write a balanced reaction for the dissolution of CO₂ in water:



2. Determine the concentration of H₂CO₃ in water at equilibrium and standard conditions (25°C, 1 atm). We assume that f_{CO₂} = P_{CO₂}.

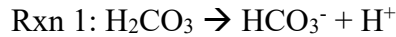
$$K_{\text{CO}_2} = \frac{a_{\text{H}_2\text{CO}_3}}{a_{\text{H}_2\text{O}}P_{\text{CO}_2}}$$

Rearrange to find a_{H₂CO₃}:

$$a_{\text{H}_2\text{CO}_3} = K_{\text{CO}_2}P_{\text{CO}_2}$$

**Henry's Law – the concentration of a dissolved gas is proportional to its pressure in the gas phase at equilibrium. In air, P_{CO₂} = 10^{-3.5} atm.

For most gases, the story ends there. However, CO₂ is a special case because carbonic acid dissociates in water to generate H⁺.

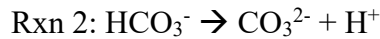


$$K_1 = \frac{a_{HCO_3^-} a_{H^+}}{a_{H_2CO_3}}$$

The equation for a_{H₂CO₃} can be substituted to yield:

$$K_1 K_{CO_2} P_{CO_2} = a_{HCO_3^-} a_{H^+}$$

Bicarbonate is inversely proportional to pH (when other cations are present to balance its charge)



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

Note: For pH > 7, a cation other than H⁺ must be present to maintain charge balance (i.e. balance the OH⁻ ions)

$$m_{H^+} + z_{cation} m_{cation} = m_{HCO_3(-)} + 2 m_{CO_3(2-)} + m_{OH(-)}$$

We can easily determine the K values, which are typically reported as pK, where pK = -log(K).

At 25°C:

pK _{CO₂} = 1.47	K _{CO₂} = 10 ^{-1.47}
pK ₁ = 6.35	K ₁ = 10 ^{-6.35}
pK ₂ = 10.33	K ₂ = 10 ^{-10.33}

These *acid dissociation constants* and the previous equations allow us to calculate pH from concentrations of dissolved carbonate species (and vice versa)

Example: What are the concentrations of carbonic acid and bicarbonate in a solution with *total activity of dissolved carbonate species* (H₂CO₃^{*}) equal to 10⁻² M and pH = 5.4?

Available information:

$$H_2CO_3^* = H_2CO_3 + HCO_3^- + CO_3^{2-} = 10^{-2} M$$

$$a_{H^+} = 10^{-5.4} M$$

*worked out on paper

Answers: solve for HCO₃⁻ first, which is equal to 2.0177x10⁻³M.

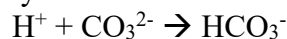
Then solve for carbonic acid = 1.7982 x10⁻²M. By the way, CO₃²⁻ = 2.3706 x10⁻⁸M

D. How does bicarbonate buffering relate to differences in stream water acidity?

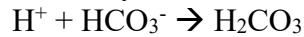
The buffering capacity of a watershed is influenced by the amount of carbonate minerals that are present:



If acid is added to the system:



If MORE acid is added to the system:



E. Alkalinity and Titrations

How do we actually quantify buffering capacity?

The *buffering capacity* of water in the environment is measured as *alkalinity* (equivalents)

Total alkalinity – the equivalent sum of the bases that are titratable with a strong acid; e.g. can accept a proton to form a neutral species

$$\text{Alk}_{\text{tot}} = m_{\text{HCO}_3^-} + 2 m_{\text{CO}_3^{2-}} + m_{\text{B(OH)}_4^-} + m_{\text{H}_3\text{SiO}_4^-} + m_{\text{organic anions}} + m_{\text{OH}^-} - m_{\text{H}^+}$$

In most natural environments, carbonate and bicarbonate are the dominant bases (all other species are negligible):

$$\text{Alkalinity} = m_{\text{HCO}_3^{(-)}} + 2 m_{\text{CO}_3^{(2-)}}$$

Charge balance requires that the concentrations of charges are equal:

$$\sum m_{\text{cations}} z_{\text{cations}} = \sum m_{\text{anions}} z_{\text{anions}}$$

$$m_{\text{Na}^+} + m_{\text{K}^+} + 2m_{\text{Ca}^{2+}} + 2m_{\text{Mg}^{2+}} = [m_{\text{Cl}^-} + 2m_{\text{SO}_4^{(2-)}}] + [m_{\text{HCO}_3^{(-)}} + 2m_{\text{CO}_3^{(2-)}}]$$

$$\sum m_{\text{cations}} z_{\text{cations}} = \sum m_{\text{conserv,anions}} z_{\text{conserv,anions}} + \text{Alkalinity}$$

$$\text{Alkalinity} \left(\frac{eq}{L} \right) = \sum m_{\text{cations}} z_{\text{cations}} - \sum m_{\text{conserv,anions}} z_{\text{conserv,anions}}$$

Alkalinity is measured by titration:

Titration – addition of a solution of known concentration (titrant) to a solution of unknown concentration (titrand)

e.g., addition of a strong acid to a solution with unknown alkalinity

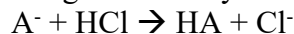
- acid is added until it exceeds the buffering capacity of the solution
- the amount of acid that is added is used to determine the concentration of the unknown
- the end point can be monitored by changes in pH (either indicator solutions or direct pH measurement)

Video demonstration of example titration – weak acid and strong base:

<https://www.youtube.com/watch?v=RCokW8HbGEw>

End point

(i) titration of base with strong acid: nearly all of the base is converted to its conjugate acid



(ii) titration of acid with strong base: nearly all of the acid is converted to its conjugate base



At the end point for case (ii), $\text{pK}_a = \text{pH} - \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$ (Henderson-Hasselbalch equation)

- pH is measured in the solution

- $[A^-]$ is approximately equal to the initial concentration of HA
- $[HA]$ at the end point is determined by proton mass balance (the proton condition)

Proton condition: All protons are derived from the initial species HA and mass balance on protons must be maintained.

At the end point, $[HA] = [OH^-] - [H^+]$