Advanced Redox Technology (ART) Lab
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Environmental Chemistry-2

- Equilibrium and the Carbonate System

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Chemical Equilibrium

- Most chemical reactions are reversible, to some extent

$$aA + bB \Leftrightarrow cC + dD$$

- If forward and reverse reactions are proceeding at the same rate, the system is in **equilibrium**.

  No changes in chemical speciation with time.

- **Some examples:**
  - Acid/base reactions affecting pH
  - Solubility products affecting precipitation
  - Solubility of gases in water

Chemical Equilibrium

- At equilibrium, relative abundance of reactants and products given by:

$$K = \frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b} \approx \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where, K = equilibrium constant, { } = activity, [ ] = molar concentration

- Concentration for dissolved species must be in <u>moles/liter</u> (not mg/L or ppm)

- If solids or liquid water, assumed to be in excess and are not included

  Activity = 1

- All concentration units are in mole/L

  Except for gases in atmosphere – they use partial pressure

Chemical Equilibrium

√ **Various types of K exist**

- Ionization constants, $\mathrm{K_i}$
- Acidity and basicity constants, $\mathrm{K_a}$, $\mathrm{K_b}$
- Dissociation constants
- Solubility product constants, $\mathrm{K_{sp}}$
- Water dissociation constant, $\mathrm{K_w} = 10^{-14}$
  - Governs pH of solution

- Note:
  - Capital K for equilibrium constants
  - Lowercase k for rate constants

Chemical Equilibrium

- Molecules may dissolve to form ions
  - Cations: + charge (e.g., Na^{+})
  - Anions: - charge (e.g., Cl^{-})

- Charge must be balanced

$$A_2B \Leftrightarrow 2A^{+} + B^{-2}$$

- In this case, K is a dissociation/ionization constant

$$K_i = \frac{[A^{+}]^2[B^{-2}]}{[A_2B]}$$

Chemical Equilibrium

- *K* can range over large orders of magnitude
  - Water dissociation constant $K_w = 10^{-14}$
  - Acetic acid $K_a \approx 5.0 \text{ x } 10^4$

- Convenient to use logarithmic notation
  - p [ ] = - log [ ]
  - pK = - log K
  - K = 10^{-pk}

Acid–Base Equilibrium

- **Dissociation of acid**

$$\underbrace{HA}_{\text{acid}} \Leftrightarrow \underbrace{A^-}_{\text{base}} + \underbrace{H^+}_{\text{proton}} \quad \Rightarrow \quad K_a = \frac{[A^-][H^+]}{[HA]} = \frac{[\text{base}][H^+]}{[\text{acid}]}$$

When pH = pK_a, get 50% dissociation

- **Typical values (higher K_a, lower pK_a = stronger acid)**

Stronger acid

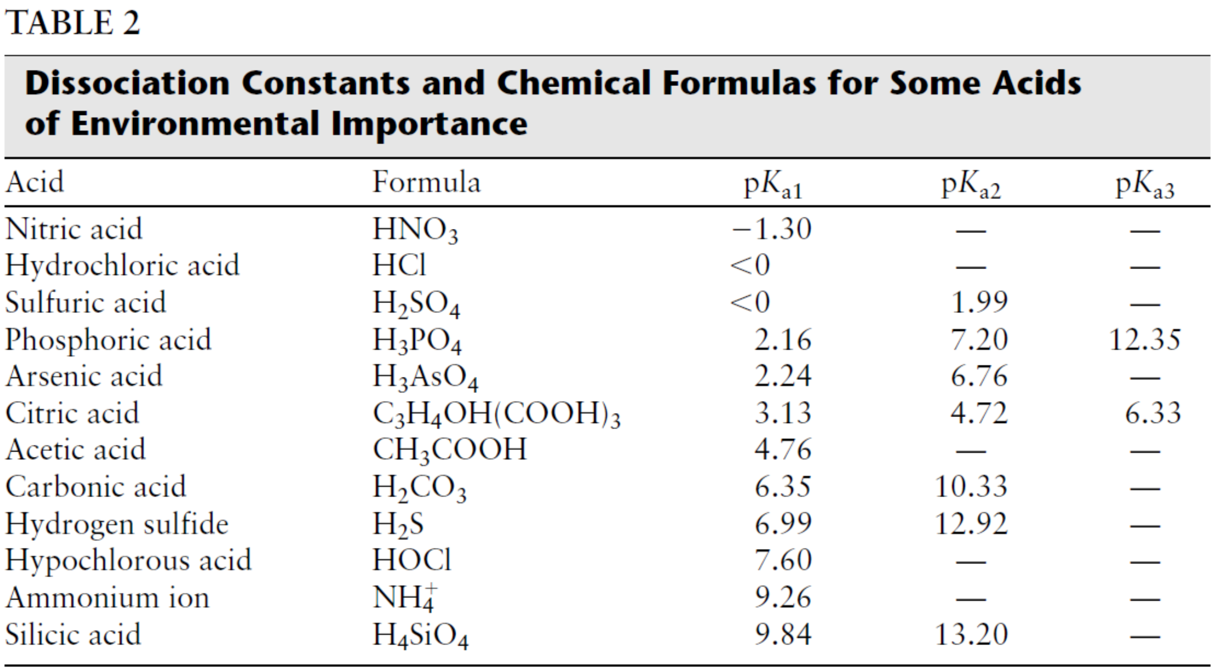


TABLE 2

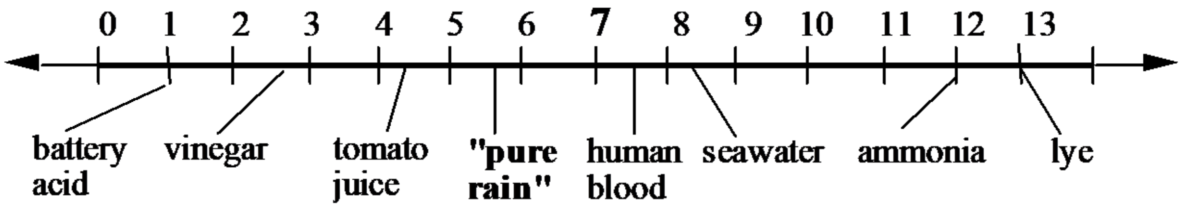
Dissociation Constants and Chemical Formulas for Some Acids of Environmental Importance

Acid	Formula	pK_{a1}	pK_{a2}	pK_{a3}
Nitric acid	HNO_3	−1.30	—	—
Hydrochloric acid	HCl	<0	—	—
Sulfuric acid	H_2SO_4	<0	1.99	—
Phosphoric acid	H_3PO_4	2.16	7.20	12.35
Arsenic acid	H_3AsO_4	2.24	6.76	—
Citric acid	$C_3H_4OH(COOH)_3$	3.13	4.72	6.33
Acetic acid	CH_3COOH	4.76	—	—
Carbonic acid	H_2CO_3	6.35	10.33	—
Hydrogen sulfide	H_2S	6.99	12.92	—
Hypochlorous acid	$HOCl$	7.60	—	—
Ammonium ion	NH_4^+	9.26	—	—
Silicic acid	H_4SiO_4	9.84	13.20	—

Acid–Base Equilibrium

- **pH**

  pH = -log [H⁺]



- Water dissociation

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

  $K_w = [H^+][OH^-] = 1\text{x}10^{-14}$ (at 25 °C)

  pH + pOH = 14

- Neutral water, $[H^+] = [OH^-]$

  $K_w = [H^+][OH^-] = 10^{-14}$

  $\Rightarrow [H^+][H^+] = [H^+]^2 = 10^{-14}$

  $\Rightarrow [H^+] = 1\text{x}10^{-7}$

  $\Rightarrow$ pH = 7

Significance of pH

- Indicates whether solution is:
  - Acidic (pH < 7, H^+)
  - Basic (pH > 7, OH^-)
- Aquatic life is pH-sensitive
  - pH has a dramatic impact on biodiversity
- pH control is important for water & wastewater treatment
  - It affects dissolution/solubility of solids/gases, which can be manipulated to remove some pollutants by precipitation (metals) or by volatilization (NH_3, H_2S)
  - Corrosion vs. clogging problems
- Industrial waste can be at pH extremes
  - May need neutralization

Example

- What is $[H^+]$ and $[OH^-]$ in the solution of pH = 11.9 at 25°C?

Ammonia Removal

- Nitrogen dissolved in industrial or municipal waste waters can be problematic.

  N can be often found as ammonia ($NH_{3,}$ strippable) or ammonium ion ($NH_4^+{}_,$ polar and very soluble)

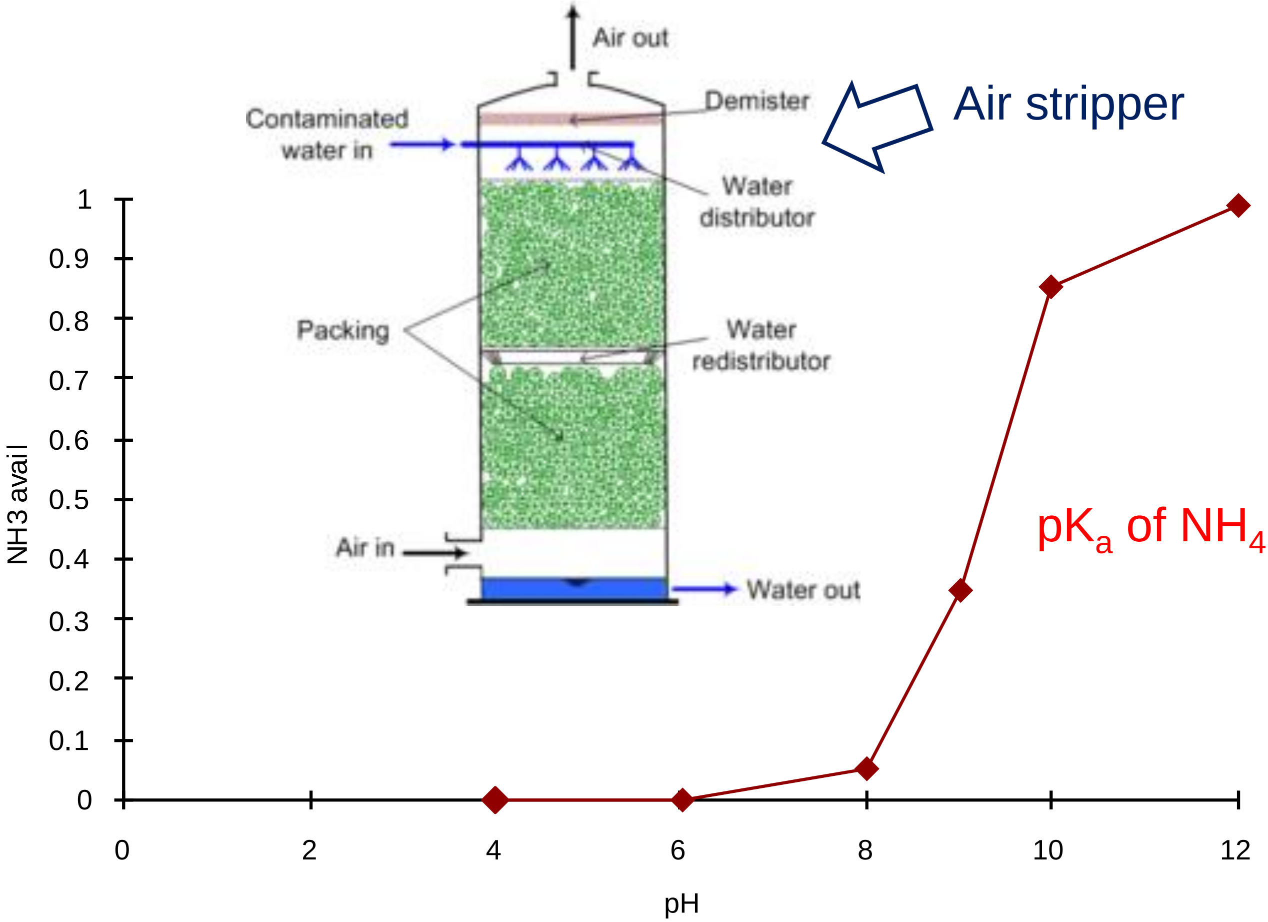
gas soluble

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$$

Exploiting this reaction (law of mass action), adding a base (OH^-) shifts reaction to the left (strip NH_3)

Ammonia Removal

- Ammonia (NH_3) is not very soluble in water (volatile), whereas ammonium (NH_4^+) is.
- Increase pH to convert N to volatile ammonia



Air stripper

pK_a of $NH_4^+ = 9.4$

Solubility Product

- Dissolution of solid or precipitation of soluble compounds

$$\text{solid} \Leftrightarrow aA + bB$$

- At equilibrium,

$$K = \frac{[A]^a [B]^b}{[\text{solid}]}$$

- Solubility product:

$K_{sp} = [A]^a [B]^b =$ **solubility product**

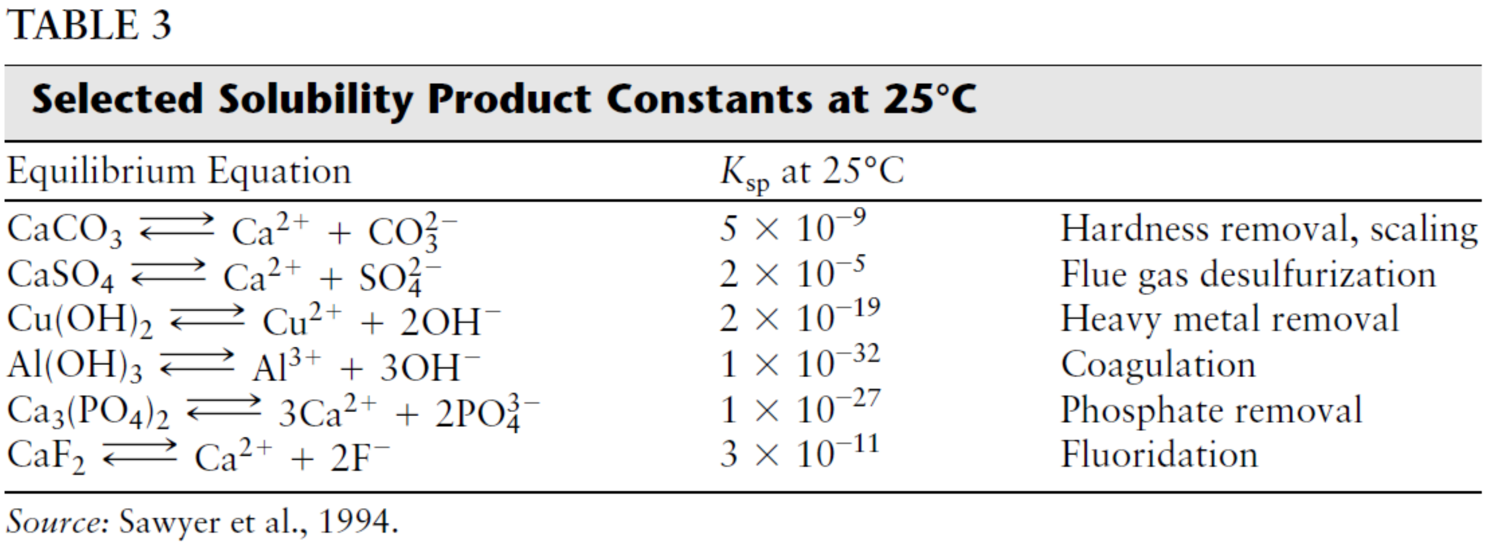


TABLE 3

Selected Solubility Product Constants at 25°C

Equilibrium Equation	K_{sp} at 25°C	
$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$	5×10^{-9}	Hardness removal, scaling
$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$	2×10^{-5}	Flue gas desulfurization
$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^-$	2×10^{-19}	Heavy metal removal
$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$	1×10^{-32}	Coagulation
$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$	1×10^{-27}	Phosphate removal
$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$	3×10^{-11}	Fluoridation

Source: Sawyer et al., 1994.

Example

- CaF_2 (solid) is dissolved in water.

  What will the equilibrium concentration of F^- be in mg/L?

  *Use the solubility product of CaF_2 in the previous table.

Example (solution)

- Dissociation of CaF_2

$$CaF_2 \Leftrightarrow Ca^{2+} + 2F^-$$

When one mole of Ca^{2+} is released, two moles of F^- will be released.

- Solubility product:

$K_{sp} = 3 \times 10^{-11}$

Solubility of Gases in Water

✓ Henry's Law

Describes how much gases can dissolve into water (at equilibrium)

$$\text{Henry's Law:}\quad [\text{gas}] = K_H P_g$$

[gas] : concentration of dissolved gas in liquid (mol/L)

K_h : Henry's Law Constant (mol/L·atm)

P_g : partial pressure of gas in air (atm)

- Henry's Law constants are temperature-dependent.

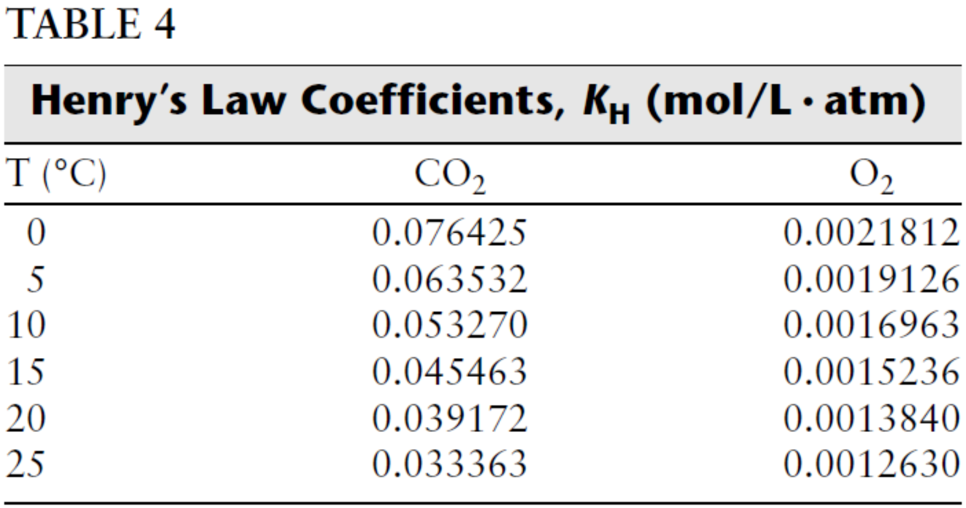


TABLE 4

Henry's Law Coefficients, K_H (mol/L · atm)

T (°C)	CO_2	O_2
0	0.076425	0.0021812
5	0.063532	0.0019126
10	0.053270	0.0016963
15	0.045463	0.0015236
20	0.039172	0.0013840
25	0.033363	0.0012630

Example

- There's water on the table outside on a cold day (10°C) in Denver (@ 1525 m).

  How much CO_2 will dissolve in the water (in mg/L) if its concentration in the atmosphere is 350 ppm_v?

  *Use the following equation to calculate the atmospheric pressure in Denver.

$$P = P_o - 1.15 \times 10^{-4}\ H\ (meters)$$

Example (solution)

Atmospheric pressure in Denver, P = 0.825 atm

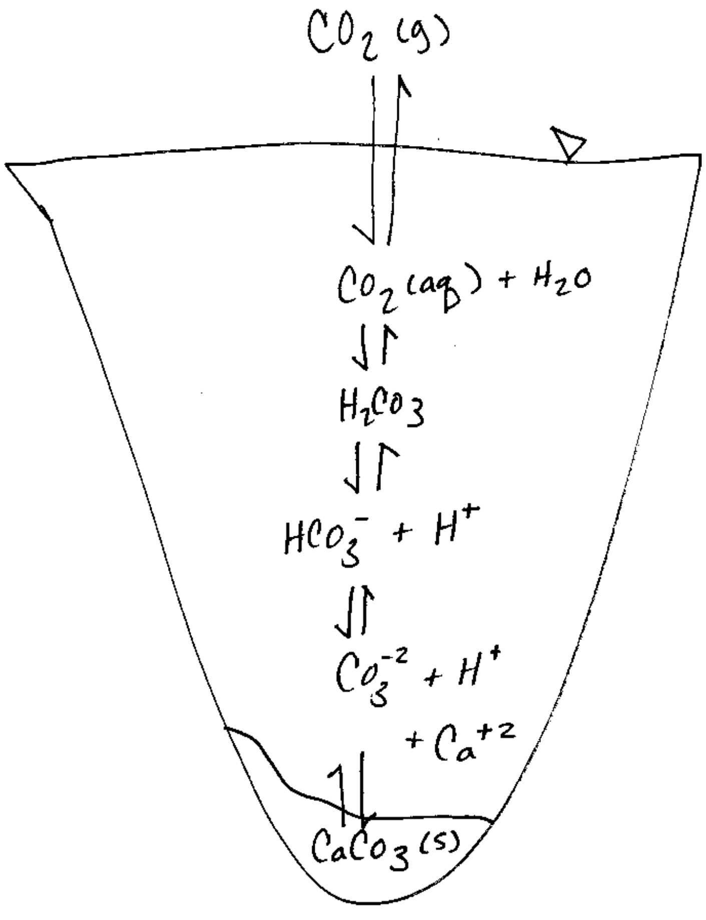
$$P_{O_2} = 0.21$$

Carbonate System

✓ **Carbonates**

- Largest reservoir of carbon on earth
- They control (buffer) pH in natural systems

- Four important chemical species:
  - $CO_{2(aqueous)}$
  - H_2CO_3 (carbonic acid)
  - HCO_3^- (bicarbonate ion)
  - CO_3^{2-} (carbonate ion)



The Carbonate System

Carbonate System

- Recall: atmospheric CO_2 dissolves in water
  - By Henry's Law: $[CO_{2(aq)}] = K_H P_{CO2}$

- What happens to $CO_{2(aq)}$?
  - It forms carbonic acid (weak acid) which dissociates

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

- Bicarbonate can dissociate further into carbonate

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

- In natural systems, limestone (solid) is abundant and dissolves

$$CaCO_{3(s)} \leftrightarrow Ca^{2+} + CO_3^{2-}$$

Carbonate System

- At equilibrium, governing equations are:

$$\frac{[H^+][HCO_3^-]}{[CO_{2(aq)}]} = K_1 = 4.47\times10^{-7}$$

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = K_2 = 4.68\times10^{-11}$$

$$[Ca^{2+}][CO_3^{2-}] = K_{sp} = 4.57\times10^{-9}$$

- Presence of solid carbonates
  - CO_3^{2-} source that consumes H^+ and increases pH

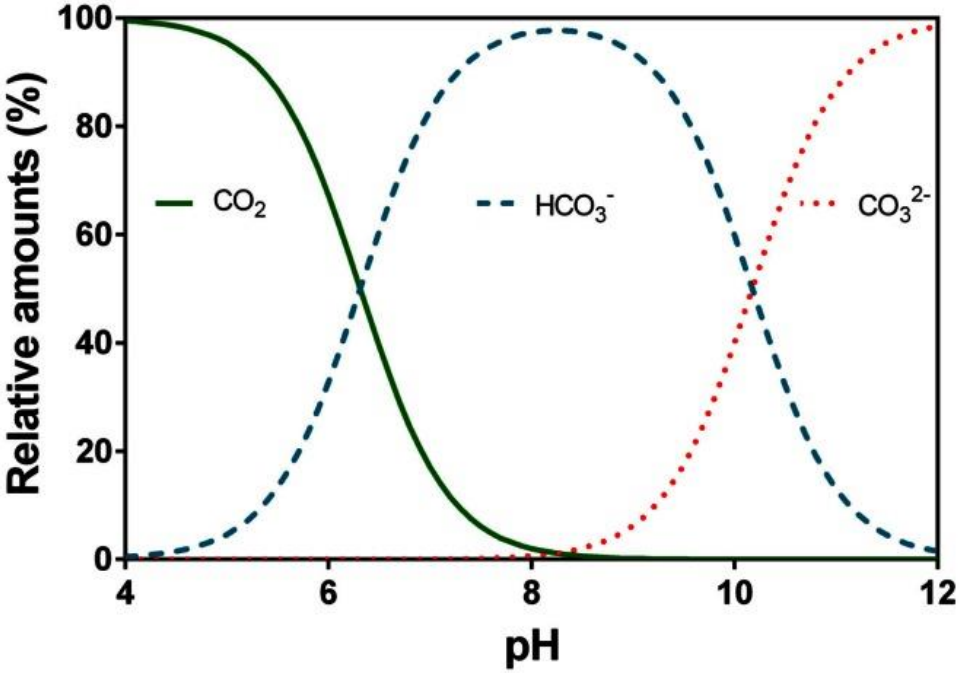
- If system is open to the atmosphere
  - CO_2 source that produces carbonic acid and lowers the pH

Carbonate System

- Relative carbonate concentration depends on pH

$$\frac{[CO_3^{2-}]}{[HCO_3^{-}]} = \frac{K_2}{[H^+]} = \frac{K_2}{10^{-pH}} = 4.68\times10^{pH-11}$$

- Thus, unless pH is very high, the carbonate concentration is small compared to bicarbonate
  - CO_3^{2-} can be ignored at near neutral pH



Example

- What is the pH of a soda pop in a bottle where pure CO_2 is present in the gas phase at 3 atm?

*Assume temperature is 25 °C

K_H (for CO_2) = 0.033363 mol/L·atm

$$\frac{[H^+][HCO_3^-]}{[CO_{2(aq)}]} = K_1 = 4.47\times10^{-7}$$

Example (solution)

- Assuming:
  - Negligible carbonate concentration (fairly low pH)
  - No solids
- Henry's Law
- Bicarbonate equilibrium governed by:

$$\frac{[H^+][HCO_3^-]}{[CO_{2(aq)}]} = K_1 = 4.47 \times 10^{-7}$$

- Thus,

Example (solution)

- Electroneutrality: sum of + charges = sum of - charges (Ignoring CO_3^{2-}):