

Basic Chemistry Concepts II

Today's lecture

- More on equilibrium chemistry
- Reaction kinetics
- Concentration units in water
- Carbonate system

Chemical equilibrium: acid-base equilibria

- Ionization of water: $H_2O + H_2O = H_3O^+ + OH^-$

$$K = \frac{\{OH^-\}\{H_3O^+\}}{\{H_2O\}^2}$$

$$\{H_2O\} = \gamma_{H_2O} \cdot [H_2O], \quad \gamma_{H_2O} \approx 1, \quad [H_2O] = 55.6 M$$

- Dissociation constant of water, K_w

$$K_w = K \cdot \{H_2O\}^2 = \{OH^-\}\{H_3O^+\}$$

Chemical equilibrium: acid-base equilibria

$$K_w = \{OH^-\} \{H_3O^+\} \quad \text{or} \quad K_w = \{OH^-\} \{H^+\}$$

$$pK_w = 14 \quad (\text{at } 25^\circ\text{C})$$

$$pH < 7 \longrightarrow \{H^+\} > \{OH^-\}, \quad \text{acidic}$$

$$pH > 7 \longrightarrow \{H^+\} < \{OH^-\}, \quad \text{basic}$$

Acid dissociation constant



- Acid dissociation constant, K_a

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

- Strong acid = strong tendency to dissociate = high K_a = low pK_a
- Weak acid = only a small fraction dissociates = low K_a = high pK_a

Acid dissociation constant

Acid	Reaction	pKa	
Hydrochloric acid	$\text{HCl} = \text{H}^+ + \text{Cl}^-$	≈ -3	} Strong
Nitric acid	$\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$	-1	
Sulfuric acid	$\text{H}_2\text{SO}_4 = \text{H}^+ + \text{HSO}_4^-$	≈ -3	
Bisulfate	$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$	1.9	
Acetic acid	$\text{CH}_3\text{COOH} = \text{H}^+ + \text{CH}_3\text{COO}^-$	4.75	} Weak
Carbonic acid	$\text{H}_2\text{CO}_3^* = \text{H}^+ + \text{HCO}_3^-$	6.35	
	$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	10.33	
Phosphoric acid	$\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$	2.12	
	$\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}$	7.20	
	$\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}$	12.32	

Acid dissociation constant

Q: If 100 mg of H_2SO_4 (MW=98) is added to water, bringing the final volume to 1.0 L, what is the final pH?

Acid dissociation constant

Q: A solution of HOCl is prepared in water by adding 15 mg HOCl to a volumetric flask, and adding water to the 1.0 L mark. The final pH is measured to be 7.0. What are the concentrations of HOCl and OCl?
(T = 25°C)

Chemical equilibrium: gas dissolution

- Henry's Law: partial pressure of a chemical in the gas phase is linearly proportional to the concentration of the chemical in the aqueous phase

$$P_{\text{gas}} = kC^*$$

where P_{gas} = partial pressure in the gas phase

C^* = concentration in the water

k = constant

Reaction kinetics

- Reaction kinetics: study of the speed at which reactions proceed



$$r_A = \frac{d[A]}{dt} = -k[A]^\alpha [B]^\beta$$

r_A = reaction rate w.r.t. chemical A [conc./time]

k = reaction rate constant

$\alpha + \beta$ = reaction order

Reaction kinetics

Reaction order	Rate expression	Units on k
Zero	$r_A = -k$	$(\text{conc.})(\text{time})^{-1}$
First	$r_A = -k[A]$	$(\text{time})^{-1}$
Second	$r_A = -k[A]^2$	$(\text{conc.})^{-1}(\text{time})^{-1}$
Second	$r_A = -k[A][B]$	$(\text{conc.})^{-1}(\text{time})^{-1}$

- Half-life ($t_{1/2}$): time required for the concentration to reach $\frac{1}{2}$ of its initial conc.

Concentration units in water

- Weight percent, P

$$P = \frac{W}{W + W_0} \times 100\%$$

W = mass of substance (g)

W_0 = mass of solvent (g)

- ppm, ppb, ppt
- Molarity, M
- Normality, N (acid-base reaction)

$$N = nM$$

n = no. of protons transferred

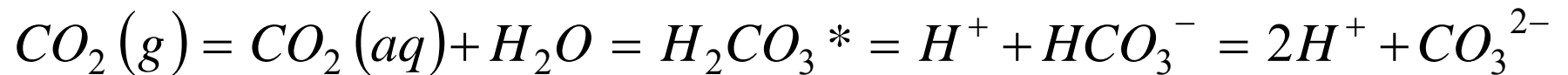
Concentration units in water

Q: Commercial H_2SO_4 is often purchased as a 93 wt% solution. Find the concentration of this solutions in units of mg/L, molarity, and normality.

(H_2SO_4 specific gravity = 1.839, $T=15^\circ\text{C}$)

Carbonate system

- Buffer: a solution that resists large changes in pH
- A solution of weak acid and its salt is a buffer
- Atmospheric CO₂ produces a natural buffer:



Carbonate system

Acid dissociation:



1. Closed system: constant C_T

$$[H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] = C_T$$

$$[H_2CO_3^*] = C_T \left(1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2} \right)^{-1}$$

Carbonate system

1. Closed system

$$pH < pK_{a1}: \quad \log[H_2CO_3^*] \approx \log C_T$$

$$pH = pK_{a1}: \quad \log[H_2CO_3^*] \approx \log(0.5C_T)$$

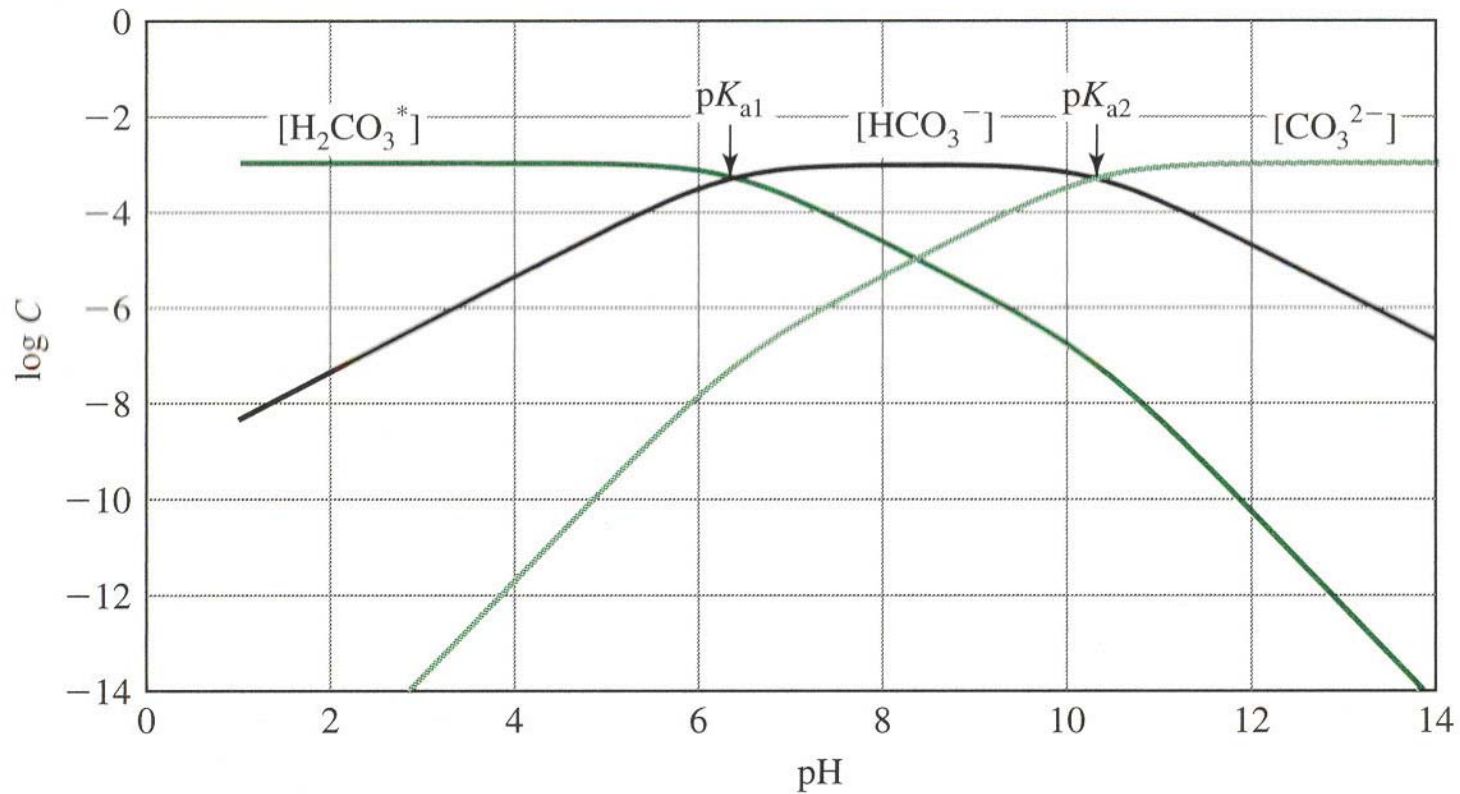
$$pK_{a1} < pH < pK_{a2}: \quad \log[H_2CO_3^*] \approx pK_{a1} + \log C_T - pH$$

$$pH = pK_{a2}: \quad \log[H_2CO_3^*] \approx pK_{a1} + \log(0.5C_T) - pH$$

$$pH > pK_{a2}: \quad \log[H_2CO_3^*] \approx pK_{a1} + pK_{a2} + \log C_T - 2pH$$

Carbonate system

1. Closed system



Carbonate system

2. Open system: constant $[H_2CO_3^*]$

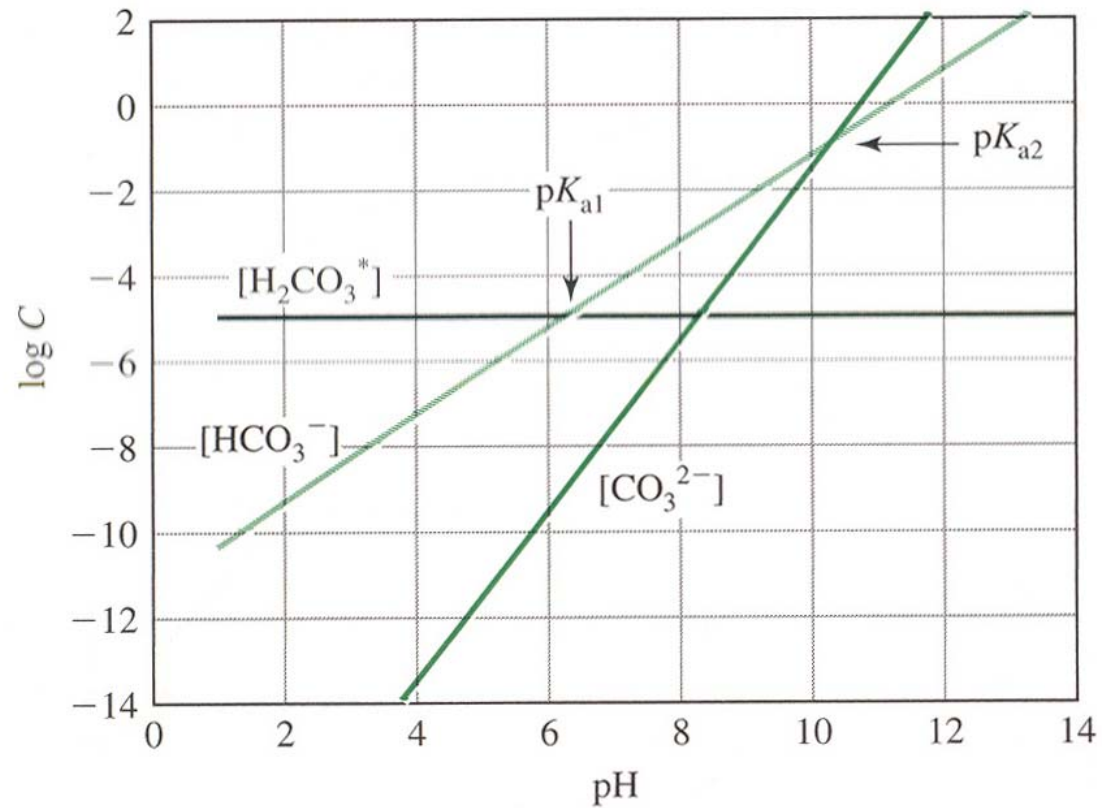
$$\begin{aligned}[H_2CO_3^*] &= K_H P_{CO_2} = (10^{-1.47} \text{ M} \cdot \text{atm}^{-1})(10^{-3.53} \text{ atm}) \\ &= 10^{-5.0} \text{ M} \quad (\text{at } 25^\circ\text{C}), \text{ ambient air}\end{aligned}$$

$$\log[HCO_3^-] = -pK_{a1} + \log(K_H P_{CO_2}) + pH = -11.35 + pH$$

$$\begin{aligned}\log[CO_3^{2-}] &= -pK_{a1} - pK_{a2} + \log(K_H P_{CO_2}) + 2pH \\ &= -21.68 + 2pH\end{aligned}$$

Carbonate system

2. Open system



Alkalinity

- Alkalinity: sum of all titratable bases to a pH of approximately 4.5 (in *N*)

$$\text{Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

$$\text{Carbonate alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

(bicarbonate and carbonate are major contributors of alkalinity in natural waters)

Reading assignment

- Textbook Ch2 p. 52-75