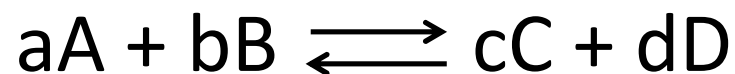


# Chemical equilibrium

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- For a reversible reaction



at chemical equilibrium,

$$\text{rate}(\text{forward rxn}) = \text{rate}(\text{reverse rxn})$$

- Equilibrium constant,  $K$

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

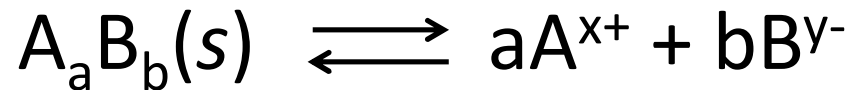
For pure solid, activity = 1

For gases, activity = partial pressure

# Chemical equilibrium: solubility

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- For a precipitation-dissolution reaction



$$K = \frac{\{A^{x+}\}^a \cdot \{B^{y-}\}^b}{\{A_a B_b\}}$$

as  $\{A_a B_b\} = 1$  (pure solid),  $K = \{A^{x+}\}^a \{B^{y-}\}^b$

- Solubility product,  $K_s = \{A^{x+}\}^a \{B^{y-}\}^b$

# Ionic strength

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- Recall that  $\{i\} = \gamma[i]$ :

$$K_s = \{A^{x+}\}^a \{B^{y-}\}^b = (\gamma_A [A^{x+}])^a \cdot (\gamma_B [B^{y-}])^b$$

- Ionic strength,  $I$ : measure of interaction among ions in a solution

$$I = \frac{1}{2} \sum C_i z_i^2$$

$C_i$  = molarity of the  $i^{\text{th}}$  ion

$z_i$  = charge of the  $i^{\text{th}}$  ion

# Calculating activity coefficients

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- Davies equation (for  $I < 0.5$  M):

$$\log \gamma = -Az^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$$

$A \approx 0.5$  for water at  $25^\circ\text{C}$

$z$  = charge of the ion

# Selected solubility products (@ 25°C)

Substance	Equilibrium Reaction	$pK_s$	Application
Aluminum hydroxide	$\text{Al(OH)}_3 (s) \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-$	32.9	Coagulation
Aluminum phosphate	$\text{AlPO}_4 (s) \rightleftharpoons \text{Al}^{3+} + \text{PO}_4^{3-}$	22.0	Phosphate removal
Calcium carbonate (aragonite)	$\text{CaCO}_3 (s) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	8.34	Softening, corrosion control
Ferric hydroxide	$\text{Fe(OH)}_3 (s) \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^-$	38.57	Coagulation, iron removal
Ferric phosphate	$\text{FePO}_4 (s) \rightleftharpoons \text{Fe}^{3+} + \text{PO}_4^{3-}$	21.9	Phosphate removal
Magnesium hydroxide	$\text{Mg(OH)}_2 (s) \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$	11.25	Removal of calcium and magnesium
Dolomite (CaMg(CO <sub>3</sub> ) <sub>2</sub> ) (ordered)	$\text{CaMg(CO}_3)_2 \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$	17.09	Weathering of dolomitic minerals
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ \rightleftharpoons 2\text{Al}^{3+} + 2\text{Si(OH)}_4 + \text{H}_2\text{O}$	7.44	Weathering of kaolinite clays
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	4.58	Weathering of gypsum minerals

# Chemical equilibrium: solubility

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Q: Added 30g of  $\text{CaCO}_3$  in water of make 1.00 L solution containing 0.01 M NaCl. Assuming  $\text{Ca}^{2+}$  in solution is at equilibrium with  $\text{CaCO}_3(s)$ , what would be the  $\text{Ca}^{2+}$  concentration?

( $T = 25^\circ\text{C}$ ,  $pK_s$  for  $\text{CaCO}_3 = 8.48$ )

# Chemical equilibrium: acid-base equilibria

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- 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	pK <sub>a</sub>	
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:** 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<sup>-</sup>? (T = 25°C)

# Chemical equilibrium: gas dissolution

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- 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  $P_{\text{gas}}$  = partial pressure in the gas phase

$C^*$  = concentration in the water

$k$  = constant

# Caveat!

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- The equilibrium/solubility product constants do not tell anything about the reaction rate!
- Differentiate equilibrium and kinetics

# Reading assignment

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- Textbook Ch2 p. 44-56

# Reaction kinetics

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- 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

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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

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- 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)

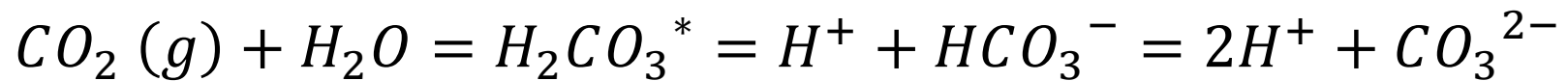
$$N = nM$$

$n$  = no. of protons transferred

# Carbonate system

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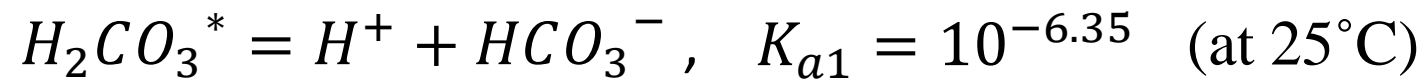
- Buffer: a solution that resists large changes in pH
- A solution of weak acid and its salt is a buffer
- Atmospheric  $\text{CO}_2$  produces a natural buffer:



# Carbonate system

---

Acid dissociation:



Define  $C_T$  as:

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

# Carbonate system

---

Then:

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

$$[HCO_3^-] = \frac{K_{a1}}{[H^+]} \cdot [H_2CO_3^*]$$

$$[CO_3^{2-}] = \frac{K_{a1}K_{a2}}{[H^+]^2} \cdot [H_2CO_3^*]$$

➡ If  $C_T$  is known, we can obtain the concentration of each species at a certain pH

# Carbonate system

---

Now, think of

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]}$$

$$pH - pK_{a1} = \log \frac{[HCO_3^-]}{[H_2CO_3^*]}$$

If  $pH < pK_{a1}$ ,  $[H_2CO_3^*] > [HCO_3^-]$

*(If  $pH - pK_{a1} = -2$ ,  $[H_2CO_3^*] = 100[HCO_3^-]$ )*

If  $pH > pK_{a1}$ ,  $[H_2CO_3^*] < [HCO_3^-]$

*(If  $pH - pK_{a1} = 2$ ,  $[HCO_3^-] = 100 [H_2CO_3^*]$ )*

# Carbonate system

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This applies to  $\text{HCO}_3^-$  -  $\text{CO}_3^{2-}$  relationship as well:

If  $\text{pH} < \text{pK}_{a2}$ ,  $[\text{HCO}_3^-] > [\text{CO}_3^{2-}]$

If  $\text{pH} > \text{pK}_{a2}$ ,  $[\text{HCO}_3^-] < [\text{CO}_3^{2-}]$

Actually this principle applies to any acids:

If  $\text{pH} < \text{pK}_a$ , associated (protonated) form dominates

If  $\text{pH} > \text{pK}_a$ , dissociated (deprotonated) form dominates

# Carbonate system

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## 1. Closed system: $C_T$ is constant

Solving for  $\text{pH} < \text{p}K_{a1}$  region as an example

At this pH range,  $\text{H}_2\text{CO}_3^*$  dominant:

$$C_T \approx [\text{H}_2\text{CO}_3^*] \quad \Rightarrow \quad \log[\text{H}_2\text{CO}_3^*] \approx \log C_T$$

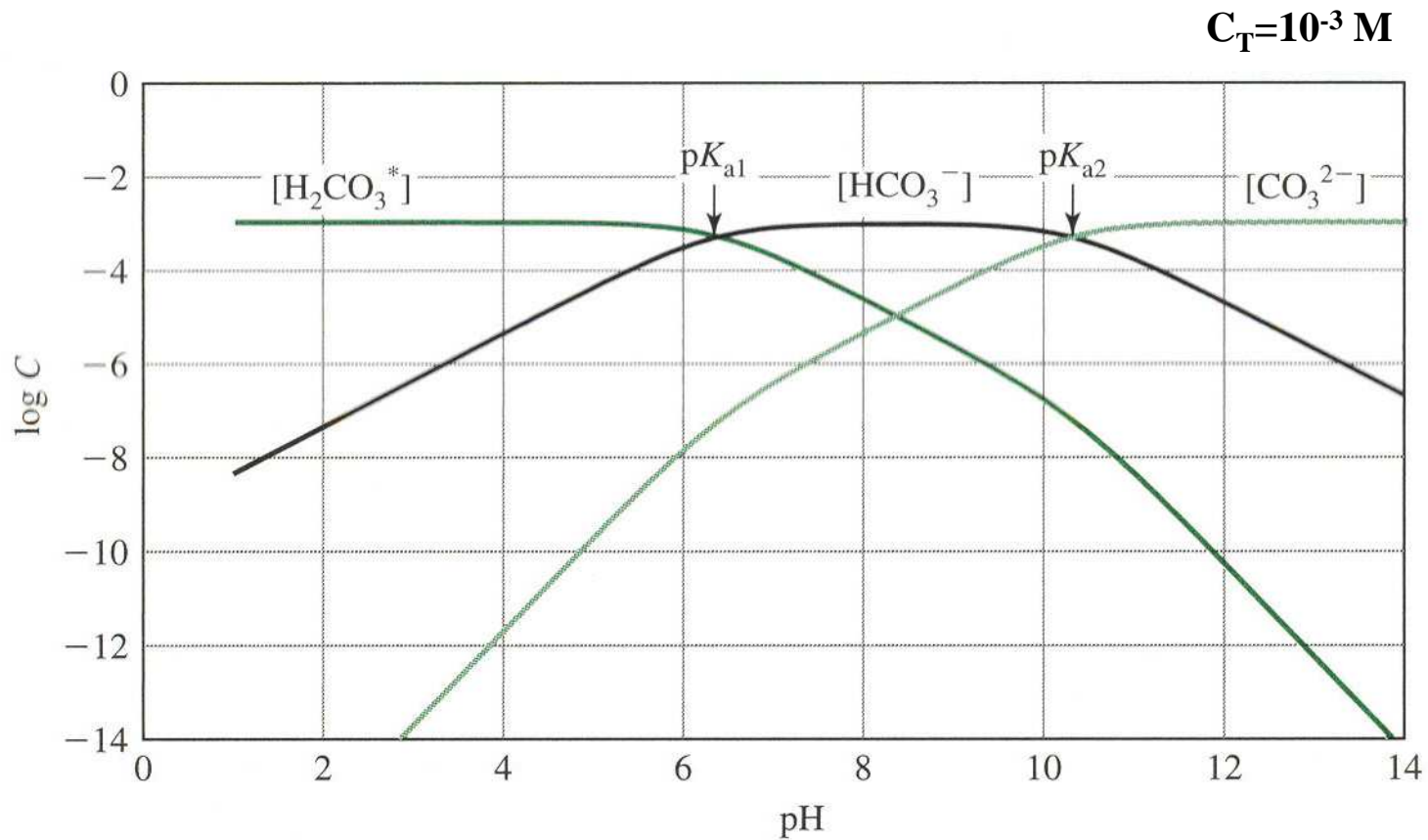
$$[\text{HCO}_3^-] = \frac{K_{a1}}{[\text{H}^+]} \cdot [\text{H}_2\text{CO}_3^*] \quad \Rightarrow \quad \log[\text{HCO}_3^-] = \log C_T - \text{p}K_{a1} + \text{pH}$$

$$[\text{CO}_3^{2-}] = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2} \cdot [\text{H}_2\text{CO}_3^*] \quad \Rightarrow \quad \log[\text{CO}_3^{2-}] = \log C_T - \text{p}K_{a1} - \text{p}K_{a2} + 2\text{pH}$$

# Carbonate system

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## 1. Closed system



Davis & Masten (2014)



# Carbonate system

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

$$[H_2CO_3^*] = K_H P_{CO_2} = (10^{-1.47} \text{ M/atm})(10^{-3.53} \text{ atm})$$

$$= 10^{-5.00} \text{ M} \quad (\text{at } 25^\circ\text{C}), \text{ ambient air}$$

$$[HCO_3^-] = \frac{K_{a1}}{[H^+]} \cdot [H_2CO_3^*] \quad \Rightarrow \quad \log[HCO_3^-] = \log(K_H P_{CO_2}) - pK_{a1} + pH$$
$$= -11.35 + pH$$

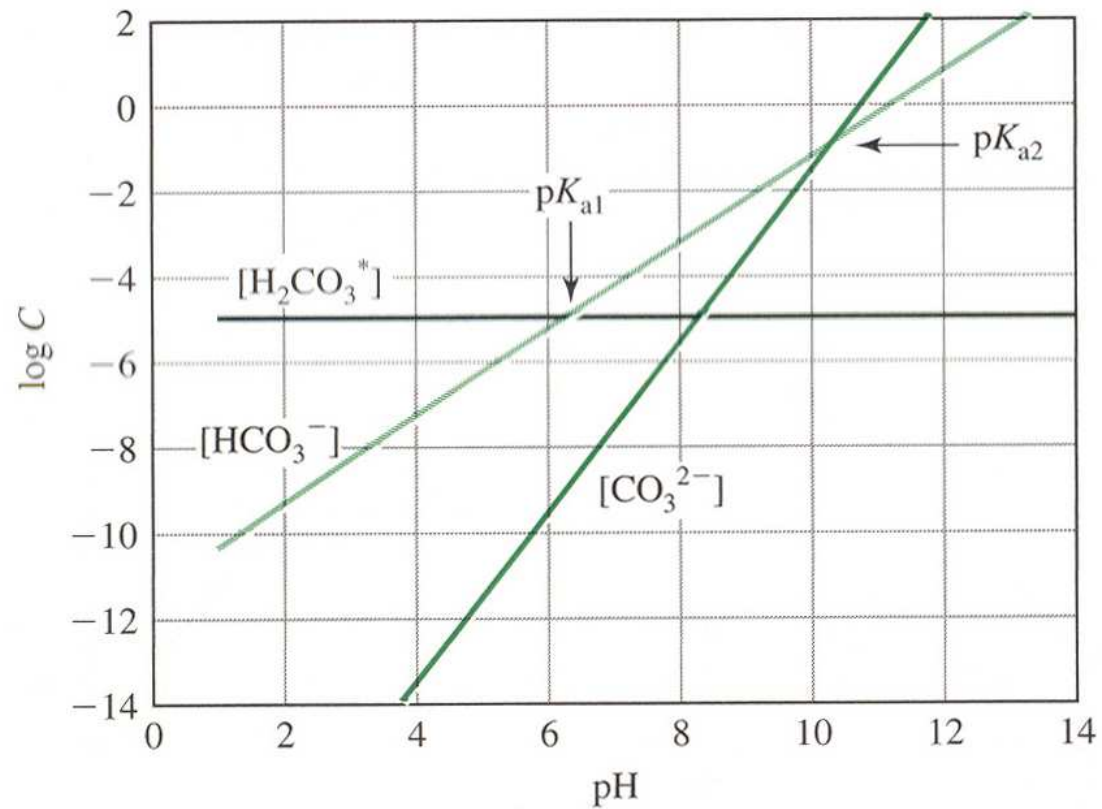
$$[CO_3^{2-}] = \frac{K_{a1}K_{a2}}{[H^+]^2} \cdot [H_2CO_3^*]$$

$$\Rightarrow \quad \log[CO_3^{2-}] = \log(K_H P_{CO_2}) - pK_{a1} - pK_{a2} + pH = -21.68 + 2pH$$

# Carbonate system

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## 2. Open system



# Alkalinity

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- Alkalinity: sum of all titratable bases to a pH of approximately 4.5

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

*Include  $\text{B(OH)}_4^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{SiO(OH)}_3^-$ , etc. if significant*

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

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

# Alkalinity

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- Unit of alkalinity
  - Using molarity for each species, we get “eq/L”
  - “eq”: equivalent, moles of H<sup>+</sup> ion in an acid-base solution or electrons in a redox reaction
  - More common unit is “mg/L as CaCO<sub>3</sub>”
  - Unit conversion: 1 meq/L = 10<sup>-3</sup> eq/L = 50 mg/L as CaCO<sub>3</sub>

# Reading assignment

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- Textbook Ch2 p. 56-75