

Environmental Engineering FE CBT Exam

Knowledge: Environmental Chemistry with 15 Example Problems

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1 Quick-Reference Environmental Chemistry Equation Matrix

Topic	Primary Mathematical Equation / Formulation	Key Parameters & Application Notes
Molarity & Normality Equivalents as CaCO₃	$M = \frac{n}{V_L}, N = M \times z = \frac{\text{mass}}{\text{EW} \cdot V_L}$ mg/L as CaCO ₃ = mg/L of species $\times \frac{50.0 \text{ g/eq}}{\text{EW of species}}$	z = valence/charge, $\text{EW} = \frac{\text{MW}}{z}$ EW of CaCO ₃ = 50.0 g/eq = 50.0 mg/meq
Ionic Strength (I)	$I = \frac{1}{2} \sum_{i=1}^n C_i z_i^2$	C_i = molar conc. (M), z_i = ionic charge
Activity Coefficient (Davies)	$\log_{10} \gamma_i = -0.509 z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$	Valid for $I \leq 0.5$ M at 25°C
Weak Acid pH	$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}, [\text{H}^+] \approx \sqrt{K_a C_a}$	Valid if $C_a/K_a > 100$
Carbonate Alpha Fractions	$\alpha_0 = \frac{[\text{H}^+]^2}{D}, \alpha_1 = \frac{K_{a1}[\text{H}^+]}{D}, \alpha_2 = \frac{K_{a1}K_{a2}}{D}$	$D = [\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}$
Total Alkalinity	$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$	Molar or eq/L basis; conversion to mg/L CaCO ₃
Solubility Product	$\text{A}_x\text{B}_y(s) \rightleftharpoons x\text{A}^{y+} + y\text{B}^{x-}, K_{sp} = [\text{A}^{y+}]^x [\text{B}^{x-}]^y$	Activity units $\approx$ M at low ionic strength
Langelier Index (LSI)	$\text{LSI} = \text{pH} - \text{pH}_s, \text{pH}_s = (9.30 + A + B) - (C + D)$	LSI > 0: Scaling; LSI < 0: Corrosive
pE and E_h Relation	$\text{pE} = -\log_{10}\{e^-\} = \frac{E_h F}{2.303 RT} = \frac{E_h (\text{in mV})}{59.16 \text{ mV}}$	At 25°C (298.15 K)
Nernst Equation	$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{0.05916}{n} \log_{10} Q$	Q = reaction quotient
Octanol-Water / Carbon	$K_{oc} = \frac{K_d}{f_{oc}}, \log_{10} K_{oc} = 1.00 \log_{10} K_{ow} - 0.21$	f_{oc} = fraction organic carbon
Retardation Factor (R)	$R = 1 + \frac{\rho_b}{\theta} K_d = 1 + \frac{\rho_b}{\theta} f_{oc} K_{oc}$	ρ_b = bulk density, θ = porosity
Freundlich Isotherm	$q = K_f C^{1/n} \implies \log_{10} q = \log_{10} K_f + \frac{1}{n} \log_{10} C$	q = adsorbed mass / adsorbent mass
Henry's Law Constant	$P_i = K_H C_i, H' = \frac{C_g}{C_w} = \frac{K_H}{RT}$	H' = dimensionless Henry's constant
First-Order Decay	$C(t) = C_0 e^{-kt}, t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$	k = rate constant (time ⁻¹)
Arrhenius Temp. Adjust	$k_T = k_{20} \cdot \theta^{(T-20)}, \ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$	$R = 8.314 \text{ J/mol} \cdot \text{K}$
Gas Conc. Conversion	$\text{ppm}_v = \frac{\text{mg/m}^3 \times RT}{P \times \text{MW} \times 10^3} = \frac{\text{mg/m}^3 \times 24.45}{\text{MW}}$	At 1 atm and 25°C (298.15 K)

2 Chemical Stoichiometry, Units of Concentration, & Ionic Activity

2.1 Units of Concentration in Aqueous Systems

In environmental engineering, chemical species in water are expressed in various units depending on whether mass, moles, charges, or equivalent reactivity governs the process.

2.1.1 Mass Concentrations

Mass concentration represents the mass of solute dissolved per unit volume of solution:

$$C_{\text{mass}} = \frac{\text{mass of solute (mg)}}{\text{Volume of solution (L)}} = \text{mg/L} \quad (1)$$

For dilute aqueous solutions at standard temperature (20°C to 25°C), the density of water is approximately $\rho_w \approx 1.00 \text{ kg/L} = 1,000,000 \text{ mg/L}$. Therefore:

$$1 \text{ mg/L} \approx 1 \text{ part per million by weight (ppm}_w\text{)} \quad (2)$$

$$1 \text{ } \mu\text{g/L} \approx 1 \text{ part per billion by weight (ppb}_w\text{)} \quad (3)$$

2.1.2 Molar Concentration (Molarity)

Molarity (M) expresses the number of moles of solute per liter of solution:

$$M = \frac{n}{V_L} = \frac{\text{mass (g)}}{\text{MW (g/mol)} \times V_L \text{ (L)}} = \frac{\text{mg/L}}{\text{MW (g/mol)} \times 1000 \text{ mg/g}} \quad (4)$$

2.1.3 Equivalent Weight and Normality

In acid-base, precipitation, and redox reactions, chemical species react based on equivalent units of reactive capacity (e.g., moles of H^+ , moles of electrons e^- , or ionic charges z).

Equivalent Weight (EW) Formulation

$$\text{Equivalent Weight (EW)} = \frac{\text{Molecular Weight (MW)}}{z} \quad \left[\frac{\text{g}}{\text{eq}} \right] \text{ or } \left[\frac{\text{mg}}{\text{meq}} \right] \quad (5)$$

where z is the valence factor (equivalent number):

- **Acid-Base Reactions:** z = number of replaceable H^+ or OH^- ions per mole.
- **Precipitation/Salts:** z = total absolute positive or negative charge per mole of salt.
- **Redox Reactions:** z = number of moles of electrons transferred per mole of species.

Normality (N): Number of equivalents per liter of solution:

$$N = M \times z = \frac{\text{mass (g)}}{\text{EW (g/eq)} \times V_L \text{ (L)}} = \frac{\text{mg/L}}{\text{EW (mg/meq)}} \quad \left[\frac{\text{eq}}{\text{L}} \right] \text{ or } \left[\frac{\text{meq}}{\text{L}} \right] \quad (6)$$

2.2 Conversion to mg/L as CaCO_3

In water chemistry and municipal water treatment, multivalent cations (hardness) and buffering species (alkalinity) are conventionally expressed in terms of calcium carbonate equivalents (mg/L as CaCO_3).

The molecular weight of calcium carbonate is $\text{MW}_{\text{CaCO}_3} = 100.087 \text{ g/mol} \approx 100.0 \text{ g/mol}$. Since calcium exists as Ca^{2+} ($z = 2$), its equivalent weight is:

$$\text{EW}_{\text{CaCO}_3} = \frac{100.087 \text{ g/mol}}{2 \text{ eq/mol}} = 50.04 \text{ g/eq} \approx 50.0 \text{ mg/meq} \quad (7)$$

Conversion to Calcium Carbonate Equivalents

$$\text{Concentration as CaCO}_3 \text{ (mg/L)} = \text{Concentration of species (mg/L)} \times \frac{\text{EW of CaCO}_3}{\text{EW of species}} \quad (8)$$

$$\text{Concentration as CaCO}_3 \text{ (mg/L)} = \text{Concentration of species (mg/L)} \times \frac{50.0}{\left(\frac{\text{MW}}{z}\right)} \quad (9)$$

Species / Ion	Formula	MW (g/mol)	Valence (z)	EW (g/eq)
Calcium	Ca^{2+}	40.08	2	20.04
Magnesium	Mg^{2+}	24.31	2	12.16
Sodium	Na^+	22.99	1	22.99
Bicarbonate	HCO_3^-	61.02	1	61.02
Carbonate	CO_3^{2-}	60.01	2	30.00
Hydroxide	OH^-	17.01	1	17.01
Hydrogen Ion	H^+	1.008	1	1.008
Sulfate	SO_4^{2-}	96.06	2	48.03
Chloride	Cl^-	35.45		35.45

2.3 Ionic Strength and Non-Ideal Activity Corrections

In real environmental waters containing dissolved salts, electrostatic interactions between ions reduce the effective concentration (activity) of reactants compared to their analytical molar concentrations.

2.3.1 Ionic Strength (I) Calculation

Ionic strength quantifies the total electrical field strength of dissolved ions in solution:

Ionic Strength Equation

$$I = \frac{1}{2} \sum_{i=1}^n C_i z_i^2 \quad (10)$$

where C_i is the molar concentration (M) of ion i , and z_i is the charge of ion i .

An empirical estimation based on Total Dissolved Solids (TDS in mg/L) or Electrical Conductivity (EC in $\mu\text{S}/\text{cm}$) is frequently utilized when complete ion analyses are unavailable:

$$I \approx 2.5 \times 10^{-5} \times \text{TDS (mg/L)} \quad (11)$$

$$I \approx 1.6 \times 10^{-5} \times \text{EC } (\mu\text{S}/\text{cm}) \quad (12)$$

2.3.2 Activity Coefficients and Activity

The thermodynamic activity (a_i) of a chemical species represents its effective concentration in chemical equilibrium equations:

$$a_i = \gamma_i [C_i] \quad (13)$$

where γ_i is the single-ion activity coefficient (dimensionless), and $[C_i]$ is the molar concentration.

As $I \rightarrow 0$ (infinitely dilute solution), $\gamma_i \rightarrow 1.0$, and $a_i \rightarrow [C_i]$. For finite ionic strengths, $\gamma_i < 1.0$ for charged ions. Uncharged neutral molecules (e.g., dissolved H_2CO_3^* , dissolved O_2 , organic solvents) have $\gamma_i \approx 1.0$ at moderate ionic strengths.

Activity Coefficient Models

1. Debye-Hückel Limiting Law ($I < 0.005$ M):

$$\log_{10} \gamma_i = -A z_i^2 \sqrt{I} \quad (14)$$

where $A \approx 0.509$ for water at 25°C .

2. Extended Debye-Hückel Equation ($I < 0.1$ M):

$$\log_{10} \gamma_i = -\frac{0.509 z_i^2 \sqrt{I}}{1 + B \cdot a_i^\circ \sqrt{I}} \quad (15)$$

where $B \approx 0.328 \times 10^8 \text{ cm}^{-1} \text{ M}^{-1/2}$, and a_i° is the effective hydrated ion diameter (in Ångströms).

3. Davies Equation ($I \leq 0.5$ M):

$$\log_{10} \gamma_i = -0.509 z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (16)$$

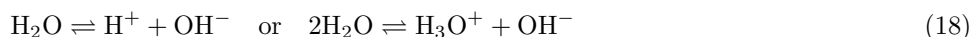
Critical FE Exam Tip: Equilibrium Constants with Activity

When solving equilibrium calculations in non-dilute waters ($I > 0.01$ M), replace molar concentrations with activities. The conditional equilibrium constant K' expressed in molarities relates to the thermodynamic equilibrium constant K via:

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \times \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} = K' \cdot \Gamma_\gamma \quad (17)$$

3 Acid-Base Chemistry & The Carbonate System**3.1 Fundamental Acid-Base Equilibrium**

According to Brønsted-Lowry theory, an acid is a proton (H^+) donor and a base is a proton acceptor. Water undergoes self-ionization (autoprotolysis):

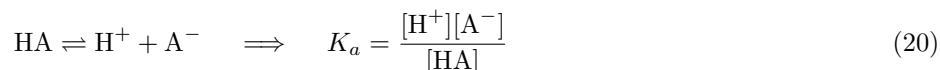


The ion product constant of water at 25°C (298.15 K) is:

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \implies pK_w = pH + pOH = 14.00 \quad (19)$$

3.1.1 Monoprotic Weak Acid Dissociation

For a weak acid HA dissociating in water:



If C_a is the analytical total acid concentration and $C_a/K_a > 100$, the dissociation fraction is small ($[HA] \approx C_a$), giving the simplified quadratic solution:

$$[H^+] \approx \sqrt{K_a C_a} \implies pH \approx \frac{1}{2} (pK_a - \log_{10} C_a) \quad (21)$$

For exact calculations or dilute weak acids, use the full quadratic relation:

$$[H^+]^2 + K_a[H^+] - K_a C_a = 0 \implies [H^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a C_a}}{2} \quad (22)$$

3.2 The Aqueous Carbonate System

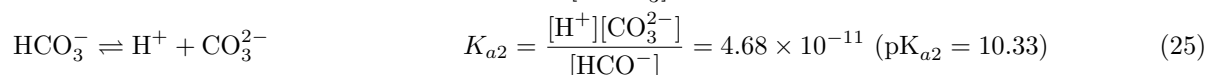
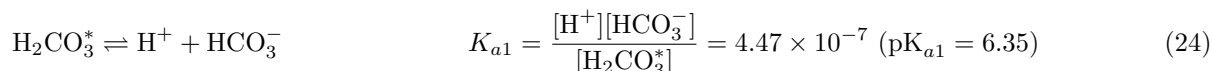
The carbonate system is the principal acid-base buffer in natural freshwaters, oceans, and water treatment systems.

3.2.1 Carbonate Species Equilibria

In environmental water chemistry, $[CO_{2(aq)}]$ and $[H_2CO_3]$ are combined into a single composite species denoted as $[H_2CO_3^*]$:

$$[H_2CO_3^*] = [CO_{2(aq)}] + [H_2CO_3] \approx [CO_{2(aq)}] \quad (23)$$

The stepwise dissociation reactions and equilibrium constants at 25°C are:



3.2.2 Total Inorganic Carbon (CT) and Ionization Fractions (α)

The total dissolved inorganic carbon concentration (C_T) is the sum of all carbonate species:

$$C_T = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (26)$$

The ionization fractions ($\alpha_0, \alpha_1, \alpha_2$) represent the fractional distribution of C_T as a function of pH ($[\text{H}^+]$):

Carbonate System Alpha Fractions

$$\alpha_0 = \frac{[\text{H}_2\text{CO}_3^*]}{C_T} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \quad (27)$$

$$\alpha_1 = \frac{[\text{HCO}_3^-]}{C_T} = \frac{K_{a1}[\text{H}^+]}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \quad (28)$$

$$\alpha_2 = \frac{[\text{CO}_3^{2-}]}{C_T} = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \quad (29)$$

Note that $\alpha_0 + \alpha_1 + \alpha_2 = 1.0$ at all pH values.

- **pH < 5.0:** $\alpha_0 \approx 1.0$; dissolved carbon dioxide (H_2CO_3^*) dominates.
- **pH = 6.35 ($\text{p}K_{a1}$):** $\alpha_0 = \alpha_1 = 0.50$; equal concentrations of H_2CO_3^* and HCO_3^- .
- **pH 7.0 – 9.0:** $\alpha_1 \approx 1.0$; bicarbonate (HCO_3^-) is the predominant species.
- **pH = 10.33 ($\text{p}K_{a2}$):** $\alpha_1 = \alpha_2 = 0.50$; equal concentrations of HCO_3^- and CO_3^{2-} .
- **pH > 11.0:** $\alpha_2 \approx 1.0$; carbonate ion (CO_3^{2-}) dominates.

3.3 Alkalinity and Acidity Calculations

Alkalinity is a measure of the capacity of water to neutralize acids without a significant change in pH (acid-neutralizing capacity, ANC). In natural unpolluted waters, alkalinity is imparted primarily by carbonate species and hydroxyl ions.

3.3.1 Total and Phenolphthalein Alkalinity Formulas

Total Alkalinity Formulation

Molar / Equivalent Basis (eq/L):

$$[\text{Alk}]_{\text{total}} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad [\text{eq/L}] \quad (30)$$

Mass Basis as CaCO_3 (mg/L):

$$\text{Total Alkalinity (mg/L as CaCO}_3) = [\text{Alk}]_{\text{total}} (\text{eq/L}) \times 50,000 \text{ mg/eq} \quad (31)$$

Phenolphthalein Alkalinity (Endpoint pH = 8.3):

$$[\text{Alk}]_P = [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}_2\text{CO}_3^*] - [\text{H}^+] \quad [\text{eq/L}] \quad (32)$$

3.3.2 Species Distribution from Titration Alkalinity Data

By measuring Total Alkalinity (T) and Phenolphthalein Alkalinity (P) via standard acid titration, the individual concentrations of Hydroxide (OH^-), Carbonate (CO_3^{2-}), and Bicarbonate (HCO_3^-) are computed using the standard FE exam relationship matrix:

3.4 Open vs. Closed Carbonate Systems

Titration Condition	Hydroxide (OH^-)	Carbonate (CO_3^{2-})	Bicarbonate (HCO_3^-)
$P = 0$	0	0	T
$P < \frac{1}{2}T$	0	$2P$	$T - 2P$
$P = \frac{1}{2}T$	0	$2P = T$	0
$P > \frac{1}{2}T$	$2P - T$	$2(T - P)$	0
$P = T$	T	0	0

Table 1: *
All values P , T , OH^- , CO_3^{2-} , and HCO_3^- expressed in mg/L as CaCO_3 .

3.4.1 Closed Carbonate System

In a closed system, there is no mass exchange of carbon dioxide gas across the air-water interface ($C_T = \text{constant}$). Adding acid or base changes the pH and redistributes $\alpha_0, \alpha_1, \alpha_2$, but C_T remains fixed.

3.4.2 Open Carbonate System

For an open system, $\text{PCO}_2 = 10^{-3.5} \text{ atm} = 3.162 \times 10^{-4} \text{ atm}$, approximately 316 ppmv (316 micro-atm at 1 atm). 415 ppmv corresponds to $4.15 \times 10^{-4} \text{ atm}$ and is a separate assumption.

Open Carbonate System Equations

1. Henry's Law for Dissolved Carbon Dioxide:

$$[\text{H}_2\text{CO}_3^*] = K_H P_{\text{CO}_2} = (10^{-1.47} \text{ M/atm})(10^{-3.5} \text{ atm}) = 1.07 \times 10^{-5} \text{ M} \quad (\text{constant at } 25^\circ\text{C}) \quad (33)$$

2. Total Inorganic Carbon (C_T) as Function of pH:

$$C_T = \frac{[\text{H}_2\text{CO}_3^*]}{\alpha_0} = \frac{K_H P_{\text{CO}_2}}{\alpha_0} \quad (34)$$

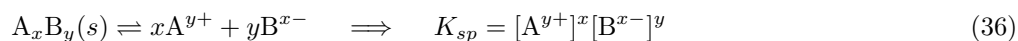
3. **Equilibrium pH of Pure Water Open to Atmosphere:** In pure distilled water open to air, alkalinity is zero ($[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] = [\text{H}^+]$). At $\text{pH} < 6$, $[\text{HCO}_3^-] \approx \frac{K_{a1}[\text{H}_2\text{CO}_3^*]}{[\text{H}^+]}$, leading to:

$$[\text{H}^+] \approx \sqrt{K_{a1} K_H P_{\text{CO}_2}} = \sqrt{(4.47 \times 10^{-7})(1.07 \times 10^{-5})} = 2.19 \times 10^{-6} \text{ M} \implies \text{pH} = 5.66 \quad (35)$$

4 Precipitation, Solubility Products, & Complexation

4.1 Solubility Product Constant (K_{sp}) and Molar Solubility

For a sparingly soluble salt $\text{A}_x\text{B}_y(s)$ dissolving in water:



If s is the molar solubility (moles of solid dissolved per liter of pure water):

$$[\text{A}^{y+}] = x \cdot s, \quad [\text{B}^{x-}] = y \cdot s \implies K_{sp} = (xs)^x (ys)^y = x^x y^y s^{x+y} \quad (37)$$

$$s = \left(\frac{K_{sp}}{x^x y^y} \right)^{\frac{1}{x+y}} \quad (38)$$

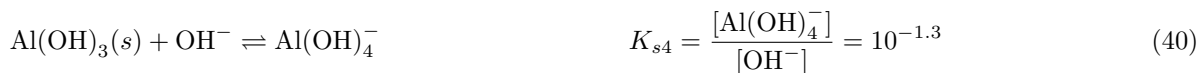
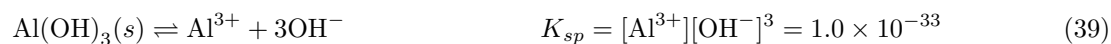
4.2 The Common Ion Effect

Adding a soluble salt containing a common ion (A^{y+} or B^{x-}) shifts the equilibrium to the left according to Le Chatelier's principle, dramatically decreasing the molar solubility s of the sparingly soluble salt.

4.3 Amphoteric Metal Hydroxide Solubility

Many environmental metals (e.g., Al^{3+} , Fe^{3+} , Zn^{2+} , Cr^{3+}) precipitate as hydroxide solids, but dissolve at both low pH (forming free metal cations) and high pH (forming soluble hydroxo-complex anions).

For aluminum hydroxide $\text{Al}(\text{OH})_3(s)$:



Total dissolved aluminum concentration C_{Al} is:

$$C_{\text{Al}} = [\text{Al}^{3+}] + [\text{Al}(\text{OH})_4^-] = \frac{K_{sp}}{[\text{OH}^-]^3} + K_{s4}[\text{OH}^-] = \frac{K_{sp}[\text{H}^+]^3}{K_w^3} + \frac{K_{s4}K_w}{[\text{H}^+]} \quad (41)$$

Setting $\frac{dC_{\text{Al}}}{d[\text{H}^+]} = 0$ yields the pH of minimum solubility ($\text{pH} \approx 6.0$ to 6.5 for $\text{Al}(\text{OH})_3$).

4.4 Municipal Water Softening Chemistry

4.4.1 Hardness Classification

Hardness is defined as the sum of all multivalent metallic cations in water, predominantly Ca^{2+} and Mg^{2+} :

$$\text{Total Hardness (TH)} = \text{Calcium Hardness (CH)} + \text{Magnesium Hardness (MH)} \quad [\text{mg/L as CaCO}_3] \quad (42)$$

Hardness is partitioned relative to Total Alkalinity (Alk):

Carbonate vs. Non-Carbonate Hardness

- If $\text{TH} > \text{Alk}$:

$$\text{Carbonate Hardness (CH)} = \text{Alk}, \quad \text{Non-Carbonate Hardness (NCH)} = \text{TH} - \text{Alk} \quad (43)$$

- If $\text{TH} \leq \text{Alk}$:

$$\text{Carbonate Hardness (CH)} = \text{TH}, \quad \text{Non-Carbonate Hardness (NCH)} = 0 \quad (44)$$

4.4.2 Chemical Softening Stoichiometry (Lime-Soda Ash Process)

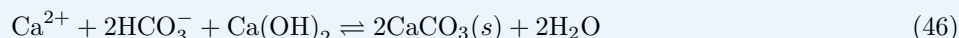
Softening precipitates Ca^{2+} as calcium carbonate ($\text{CaCO}_3(s)$) and Mg^{2+} as magnesium hydroxide ($\text{Mg}(\text{OH})_2(s)$) by adding hydrated lime ($\text{Ca}(\text{OH})_2$) and soda ash (Na_2CO_3).

Lime and Soda Ash Chemical Reactions

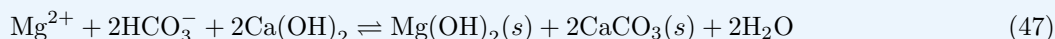
1. **Neutralization of Free Carbon Dioxide:** (Consumes Lime, forms no hardness)



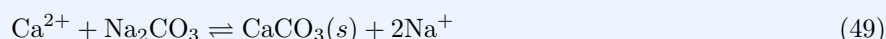
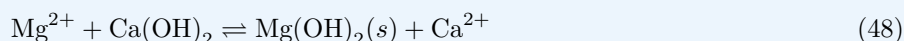
2. **Precipitation of Calcium Carbonate Hardness:** (Consumes Lime)



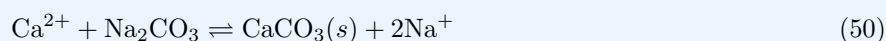
3. **Precipitation of Magnesium Carbonate Hardness:** (Consumes 2 moles Lime)



4. **Precipitation of Magnesium Non-Carbonate Hardness:** (Consumes Lime + Soda Ash)



5. **Precipitation of Calcium Non-Carbonate Hardness:** (Consumes Soda Ash)



Total Chemical Dosage Requirements (in meq/L)

$$\text{Lime } [\text{Ca}(\text{OH})_2] \text{ Dosage (meq/L)} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{Mg}^{2+}] + \text{Excess} \quad (51)$$

$$\text{Soda Ash } [\text{Na}_2\text{CO}_3] \text{ Dosage (meq/L)} = [\text{NCH}] = \text{TH} - \text{Alk} + \text{Excess} \quad (52)$$

To convert meq/L to mg/L: multiply Lime meq/L by $\text{EW}_{\text{Ca}(\text{OH})_2} = 37.05 \text{ mg/meq}$; multiply Soda Ash meq/L by $\text{EW}_{\text{Na}_2\text{CO}_3} = 53.0 \text{ mg/meq}$.

4.5 Water Stability Indices: Langelier Saturation Index (LSI)

The Langelier Saturation Index assesses the propensity of water to precipitate CaCO_3 scale or dissolve protective pipe linings (corrosive water):

$$\text{LSI} = \text{pH} - \text{pH}_s \quad (53)$$

where pH_s is the saturation pH at which water is in exact thermodynamic equilibrium with solid CaCO_3 :

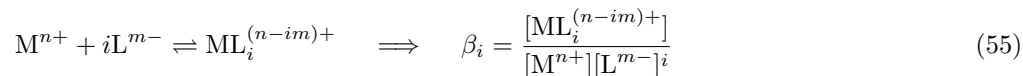
$$\text{pH}_s = (9.30 + A + B) - (C + D) \quad (54)$$

- $A = \frac{\log_{10}(\text{TDS}) - 1}{10}$, $B = -13.12 \log_{10}(T_K) + 34.55$
- $C = \log_{10}[\text{Ca}^{2+} \text{ as } \text{CaCO}_3] - 0.40$, $D = \log_{10}[\text{Total Alk as } \text{CaCO}_3]$

LSI Value	Water Condition	Water Treatment Action / Significance
$\text{LSI} > +0.5$	Scale-Forming	Supersaturated with CaCO_3 ; scale precipitates in pipes and heat exchangers.
$-0.5 \leq \text{LSI} \leq +0.5$	Balanced / Neutral	Near thermodynamic equilibrium; non-corrosive, non-scaling.
$\text{LSI} < -0.5$	Corrosive	Undersaturated; dissolves protective carbonate coating, corrodes metallic pipes.

4.6 Coordination Chemistry and Complexation

Transition metals form soluble coordination complexes with inorganic ligands (OH^- , Cl^- , NH_3 , F^-) and organic chelating agents (EDTA, NTA, humic acids):



Complexation increases the apparent total solubility of toxic heavy metals in natural waters and prevents metal hydroxide precipitation during treatment.

5 Oxidation-Reduction (Redox) Chemistry & pE-pH Diagrams

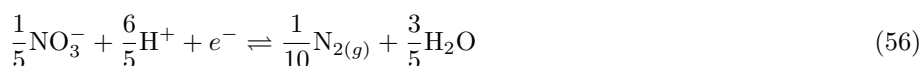
5.1 Redox Fundamentals and Balancing Half-Reactions

Oxidation is the loss of electrons (increase in oxidation state); reduction is the gain of electrons (decrease in oxidation state). Environmental redox half-reactions are standardized per mole of electrons transferred ($1e^-$).

5-Step Method for Balancing Environmental Half-Reactions

1. Balance all key non-H and non-O atoms.
2. Balance oxygen atoms (O) by adding liquid water (H_2O).
3. Balance hydrogen atoms (H) by adding protons (H^+).
4. Balance net electrical charge by adding electrons (e^-).
5. Divide the entire reaction by the coefficient of e^- to normalize per $1e^-$.

Example: Reduction of Nitrate to Nitrogen Gas ($\text{NO}_3^- \rightarrow \text{N}_2$):



5.2 Thermodynamic Formulations: pE, Eh, and Nernst Equation

5.2.1 Relationship Between pE and Reduction Potential Eh

Electron activity (pE) is defined as the negative logarithm of effective electron activity:

$$\text{pE} = -\log_{10}\{e^-\} \quad (57)$$

High pE ($> +10$) indicates strongly oxidizing (aerobic) environments; low or negative pE (< -2) indicates strongly reducing (anaerobic) environments.

pE and E_h Conversion Equation

$$\text{pE} = \frac{F}{2.303RT} E_h \quad (58)$$

At standard temperature ($25^\circ\text{C} = 298.15\text{ K}$), $\frac{2.303RT}{F} = 0.05916\text{ V} = 59.16\text{ mV}$. Therefore:

$$\text{pE} = \frac{E_h \text{ (in mV)}}{59.16\text{ mV}} = \frac{E_h \text{ (in V)}}{0.05916\text{ V}} \quad (59)$$

5.2.2 Standard pE° and Nernst Equation

For a general half-reaction written as a reduction per $1e^-$:

$$\text{Ox} + e^- \rightleftharpoons \text{Red} \quad \Rightarrow \quad \text{pE}^\circ = \frac{1}{n} \log_{10} K_{\text{red}} = \frac{E^\circ \text{ (in V)}}{0.05916} \quad (60)$$

The Nernst equation expresses pE under non-standard concentrations:

$$\text{pE} = \text{pE}^\circ - \log \left(\frac{[\text{Red}]}{[\text{Ox}]} \right) \quad (61)$$

5.3 Environmental Redox Ladder (Electron Acceptor Sequence)

Microorganisms harvest free energy by coupling the oxidation of organic matter (CH_2O) to the reduction of terminal electron acceptors in order of decreasing thermodynamic energy yield (ΔG°):

Redox Process / Zone	Reduction Half-Reaction (per $1e^-$)	$\text{pE}^\circ(w)$ at pH 7.0	$E_h^\circ(w)$ (mV)
1. Aerobic Respiration	$\frac{1}{4}\text{O}_{2(g)} + \text{H}^+ + e^- \rightleftharpoons \frac{1}{2}\text{H}_2\text{O}$	+13.75	+814
2. Denitrification	$\frac{1}{2}\text{NO}_3^- + \frac{9}{8}\text{H}^+ + e^- \rightleftharpoons \frac{1}{2}\text{N}_2 + \frac{3}{8}\text{H}_2\text{O}$	+12.65	+748
3. Manganese Reduction	$\frac{1}{2}\text{MnO}_2 + \frac{1}{2}\text{CO}_2 + \text{H}^+ + e^- \rightarrow \frac{1}{2}\text{MnCO}_3 + \frac{1}{2}\text{H}_2\text{O}$	+8.90	+527
4. Iron Reduction	$\text{Fe}(\text{OH})_{3(s)} + 3\text{H}^+ + e^- \rightleftharpoons \text{Fe}^{2+} + 3\text{H}_2\text{O}$	+0.20	+12
5. Sulfate Reduction	$\frac{1}{8}\text{SO}_4^{2-} + \frac{9}{8}\text{H}^+ + e^- \rightleftharpoons \frac{1}{8}\text{HS}^- + \frac{1}{2}\text{H}_2\text{O}$	-3.75	-222
6. Methanogenesis	$\frac{1}{8}\text{CO}_2 + \text{H}^+ + e^- \rightarrow \frac{1}{8}\text{CH}_4 + \frac{1}{4}\text{H}_2\text{O}$	-4.13	-244

5.4 pE-pH Dominance Diagrams (Pourbaix Diagrams)

5.4.1 Water Stability Boundaries

Aqueous chemical reactions are bounded by the thermodynamic stability limits of liquid water:

Water Stability Limits at 1 atm and 25°C

1. Upper Boundary (Oxidation of H_2O to O_2):

$$\text{pE} = 20.75 - \text{pH} \implies E_h = 1.23 \text{ V} - 0.05916 \cdot \text{pH} \quad (62)$$

2. Lower Boundary (Reduction of H^+ to H_2):

$$\text{pE} = -\text{pH} \implies E_h = 0.00 \text{ V} - 0.05916 \cdot \text{pH} \quad (63)$$

5.4.2 Boundary Line Derivation Principles

- **Vertical Lines:** Pure acid-base equilibria (dependent on pH, independent of pE).
- **Horizontal Lines:** Pure electron transfer reactions (dependent on pE, independent of pH).
- **Sloped Lines:** Coupled electron and proton transfer reactions ($\text{pE} = \text{pE}^\circ - \frac{m}{n}\text{pH}$).

6 Environmental Organic Chemistry & Phase Partitioning

6.1 Nomenclature and Properties of Priority Organic Pollutants

6.2 Phase Partitioning Coefficients

6.2.1 Octanol-Water Partition Coefficient (K_{ow})

K_{ow} measures the hydrophobic partitioning of an organic chemical between *n*-octanol and water:

$$K_{ow} = \frac{C_{\text{octanol}}}{C_{\text{water}}} \left[\frac{\text{mg/L}}{\text{mg/L}} \right] \text{ (dimensionless)} \quad (64)$$

High log K_{ow} (> 4.0) indicates strong bioaccumulation potential in aquatic organisms and fatty tissues.

Class	Representative Chemicals	Environmental Behavior & Relevance
BTEX Compounds	Benzene, Toluene, Ethylbenzene, Xylenes	Volatile, aromatic petroleum constituents; LNAPLs (float on water table), relatively water-soluble.
Chlorinated Solvents	PCE, TCE, 1,1,1-TCA, Carbon Tetrachloride, Vinyl Chloride	Dense Non-Aqueous Phase Liquids (DNAPLs; sink in aquifers), persistent, recalcitrant under aerobic conditions.
PAHs	Naphthalene, Phenanthrene, Benzo[a]pyrene	Polycyclic aromatic hydrocarbons; hydrophobic, high $\log_{10} K_{ow}$, adsorb strongly to soils/sediments.
PFAS Compounds	PFOA, PFOS, GenX	Per- and polyfluoroalkyl substances; fluorinated surfactants, extreme chemical stability, mobile in groundwater.

6.2.2 Soil Organic Carbon Partition Coefficient (K_{oc})

Soil adsorption of non-polar organic molecules is driven primarily by organic matter content (f_{oc}):

$$K_d = \frac{C_{soil}}{C_{water}} = f_{oc} \cdot K_{oc} \implies K_{oc} = \frac{K_d}{f_{oc}} \quad (65)$$

Empirical Karickhoff relation:

$$\log_{10} K_{oc} = 1.00 \log_{10} K_{ow} - 0.21 \quad (66)$$

6.2.3 Solute Retardation Factor (R) in Aquifers

Adsorption onto soil matrices slows the linear migration velocity of a contaminant plume relative to seepage groundwater velocity:

Retardation Factor Equation

$$R = \frac{v_s}{v_c} = 1 + \frac{\rho_b}{\theta} K_d = 1 + \frac{\rho_b}{\theta} f_{oc} K_{oc} \quad (67)$$

where v_s is seepage velocity, v_c is contaminant velocity, ρ_b is aquifer dry bulk density (kg/L or g/cm³), and θ is total porosity.

6.3 Adsorption Isotherm Models

Adsorption isotherms describe the equilibrium mass of contaminant adsorbed per unit mass of adsorbent (q = mg/g) as a function of aqueous concentration (C = mg/L):

1. Linear Isotherm:

$$q = K_d C \quad (68)$$

2. Freundlich Isotherm (Empirical Multi-Layer Adsorption):

$$q = K_f C^{1/n} \implies \log_{10} q = \log_{10} K_f + \frac{1}{n} \log_{10} C \quad (69)$$

3. Langmuir Isotherm (Monolayer Adsorption on Fixed Sites):

$$q = \frac{q_{\max} K_L C}{1 + K_L C} \implies \frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} K_L} \left(\frac{1}{C} \right) \quad (70)$$

6.4 Henry's Law and Volatilization

Henry's Law describes the equilibrium distribution of a volatile pollutant between gas phase and liquid phase:

$$P_i = K_H C_w \quad \left[\text{atm} = \left(\frac{\text{atm} \cdot \text{m}}{\text{mol}} \right) \left(\frac{\text{mol}}{\text{m}} \right) \right] \quad (71)$$

$$H' = \frac{C_g}{C_w} = \frac{K_H}{RT} \quad (\text{dimensionless Henry's constant}) \quad (72)$$

If $H' > 10^{-3}$, volatilization from surface water is significant.

7 Chemical Kinetics & Atmospheric Gas Chemistry

7.1 Chemical Reaction Kinetics

Order (n)	Differential Law	Integrated Rate Law	Half-Life ($t_{1/2}$)	Units of k
Zero ($n = 0$)	$\frac{dC}{dt} = -k$	$C(t) = C_0 - kt$	$t_{1/2} = \frac{C_0}{2k}$	$\text{mg/L} \cdot \text{time}^{-1}$
First ($n = 1$)	$\frac{dC}{dt} = -kC$	$C(t) = C_0 e^{-kt}$	$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$	time^{-1}
Second ($n = 2$)	$\frac{dC}{dt} = -kC^2$	$\frac{1}{C(t)} = \frac{1}{C_0} + kt$	$t_{1/2} = \frac{1}{kC_0}$	$\text{L/mg} \cdot \text{time}^{-1}$

7.2 Temperature Dependence of Reaction Rates

1. Arrhenius Equation:

$$k = Ae^{-E_a/RT} \implies \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (73)$$

where E_a is activation energy (J/mol), $R = 8.314 \text{ J/mol} \cdot \text{K}$, and T is in Kelvin.

2. Modified Streeter-Phelps Temperature Formula (Biological Processes):

$$k_T = k_{20} \cdot \theta^{(T-20)} \quad (74)$$

where $\theta = 1.047$ for wastewater BOD decay (20°C to 30°C) and $\theta = 1.135$ (4°C to 20°C).

7.3 Atmospheric Gas Laws and Unit Conversions

Ideal gas law: $PV = nRT$. At standard conditions ($P = 1.0 \text{ atm}$, $T = 25^\circ\text{C} = 298.15 \text{ K}$), 1 mole of gas = 24.45 L.

Gas Concentration Conversion Formula

$$\text{ppm}_v = \frac{\text{mg/m}^3 \times RT}{P \times \text{MW} \times 10^3} = \frac{\text{mg/m}^3 \times 24.45}{\text{MW}} \quad \text{at } 25^\circ\text{C}, 1.0 \text{ atm} \quad (75)$$

$$\text{mg/m}^3 = \frac{\text{ppm}_v \times \text{MW}}{24.45} \quad \text{at } 25^\circ\text{C}, 1.0 \text{ atm} \quad (76)$$

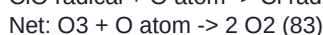
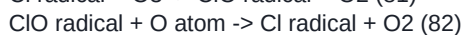
7.4 Stratospheric Ozone Photochemistry

7.4.1 Chapman Mechanism (Natural Steady-State)



7.4.2 Catalytic Stratospheric Ozone Destruction Cycles

Example: chlorine-catalyzed ozone destruction cycle:



A single chlorine radical ($\text{Cl}^\bullet$) can destroy over 100,000 ozone molecules before terminating into reservoir species (HCl , ClONO_2).

8 Overview of 15 FE-Style Practice Problems

No.	Problem Topic & Scenario Description	Primary Equation / Concept Tested	Page
1	Normality and mg/L as CaCO_3 conversion for multi-tation water	$\text{mg/L as CaCO}_3 = \sum C_i \times \frac{50.0}{\text{EW}_i}$	15
2	Activity coefficient calculation using Davies equation	$\log_{10} \gamma_i = -0.509 z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right)$	16
3	Weak acid pH and degree of ionization in industrial effluent	$[\text{H}^+] \approx \sqrt{K_a C_a}$, $\text{pH} = -\log_{10} [\text{H}^+]$	17
4	Total Alkalinity and species distribution from titration data	T, P titration relationships	17
5	Open carbonate system equilibrium pH open to atmospheric CO_2	$[\text{H}_2\text{CO}_3^*] = K_H P_{\text{CO}_2}$, $[\text{H}^+] \approx \sqrt{K_{a1} K_H P_{\text{CO}_2}}$	18
6	Barium sulfate solubility in presence of common sulfate ion	$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$	18
7	Chemical softening lime and soda ash dosage requirements	$\text{Lime} = \text{CO}_2 + \text{Alk} + \text{Mg}^{2+}$, $\text{Soda Ash} = \text{NCH}$	19
8	Langelier Saturation Index (LSI) calculation for water pipe	$\text{LSI} = \text{pH} - \text{pH}_s$	20
9	Balancing redox reaction and calculating pE from E_h	$pE = \frac{E_h (\text{mV})}{59.16 \text{ mV}}$	20
10	Soil organic carbon partitioning (K_{oc}) and retardation factor (R)	$R = 1 + \frac{\rho_b}{\theta} f_{oc} K_{oc}$	21
11	Freundlich adsorption isotherm calculation for activated carbon	$q = K_f C^{1/n}$	21
12	Atmospheric conversion from ppm_v to $\mu\text{g}/\text{m}^3$ for sulfur dioxide	$\text{mg}/\text{m}^3 = \frac{\text{ppm}_v \times \text{MW}}{24.45}$	22
13	First-order reaction rate constant and CSTR retention time	$C = \frac{C_0}{1+k\tau}$, $t_{1/2} = \frac{\ln 2}{k}$	22
14	Arrhenius activation energy calculation for biological decay	$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$	23
15	Minimum solubility pH determination for amphoteric metal hydroxide	$\frac{dC_{\text{Al}}}{d[\text{H}^+]} = 0$	24

9 15 Example Problems

Example Problem 1: Hardness Calcium Carbonate Equivalent Calculations

A groundwater sample analyzed in a water quality laboratory yields the following cation concentrations:

- $\text{Ca}^{2+} = 68.0 \text{ mg/L}$ (MW = 40.08 g/mol)
- $\text{Mg}^{2+} = 24.3 \text{ mg/L}$ (MW = 24.31 g/mol)
- $\text{Na}^+ = 46.0 \text{ mg/L}$ (MW = 22.99 g/mol)

What is the **Total Hardness** of this groundwater sample expressed in mg/L as CaCO_3 ?

Select the correct answer:

- (A) 170.0 mg/L as CaCO_3
- (B) 270.0 mg/L as CaCO_3
- (C) 370.0 mg/L as CaCO_3
- (D) 410.0 mg/L as CaCO_3

Solution

Step 1: Determine Equivalent Weights (EW) for multivalent hardness ions. Hardness is caused exclusively by multivalent cations (Ca^{2+} and Mg^{2+}). Monovalent sodium (Na^+) does not contribute to hardness.

$$\text{EW}_{\text{Ca}^{2+}} = \frac{40.08 \text{ g/mol}}{2 \text{ eq/mol}} = 20.04 \text{ g/eq} = 20.04 \text{ mg/meq} \quad (84)$$

$$\text{EW}_{\text{Mg}^{2+}} = \frac{24.31 \text{ g/mol}}{2 \text{ eq/mol}} = 12.155 \text{ g/eq} = 12.16 \text{ mg/meq} \quad (85)$$

Step 2: Convert mass concentrations to milliequivalents per liter (meq/L).

$$[\text{Ca}^{2+}] \text{ (meq/L)} = \frac{68.0 \text{ mg/L}}{20.04 \text{ mg/meq}} = 3.393 \text{ meq/L} \quad (86)$$

$$[\text{Mg}^{2+}] \text{ (meq/L)} = \frac{24.3 \text{ mg/L}}{12.155 \text{ mg/meq}} = 1.999 \text{ meq/L} \quad (87)$$

Step 3: Convert total hardness meq/L to mg/L as CaCO_3 ($\text{EW}_{\text{CaCO}_3} = 50.0 \text{ mg/meq}$):

$$\text{Total Hardness} = (3.393 + 1.999) \text{ meq/L} \times 50.0 \text{ mg/meq} = 5.392 \text{ meq/L} \times 50.0 \text{ mg/meq} = 269.6 \approx 270.0 \text{ mg/L as } \text{CaCO}_3 \quad (88)$$

Correct Choice: (B)

Example Problem 2: Activity Coefficient Calculation using Davies Equation

An industrial wastewater solution contains 0.010 M CaCl_2 and 0.020 M MgSO_4 . Using the Davies equation at 25°C, what is the single-ion activity coefficient ($\gamma_{\text{Ca}^{2+}}$) for calcium ions in this solution?

Select the correct answer:

- (A) 0.363
- (B) 0.468
- (C) 0.621
- (D) 0.842

Solution

Step 1: Dissociate salts into individual ionic species and concentrations.

- $0.010 \text{ M CaCl}_2 \rightarrow 0.010 \text{ M Ca}^{2+} + 0.020 \text{ M Cl}^-$
- $0.020 \text{ M MgSO}_4 \rightarrow 0.020 \text{ M Mg}^{2+} + 0.020 \text{ M SO}_4^{2-}$

Step 2: Calculate Ionic Strength (I).

$$I = \frac{1}{2} \left[C_{\text{Ca}^{2+}}(+2)^2 + C_{\text{Cl}^-}(-1)^2 + C_{\text{Mg}^{2+}}(+2)^2 + C_{\text{SO}_4^{2-}}(-2)^2 \right] \quad (89)$$

$$I = \frac{1}{2} [(0.010)(4) + (0.020)(1) + (0.020)(4) + (0.020)(4)] = \frac{1}{2} [0.040 + 0.020 + 0.080 + 0.080] = \frac{0.220}{2} = 0.110 \text{ M} \quad (90)$$

Step 3: Apply the Davies Equation for Ca^{2+} ($z = 2$).

$$\log_{10} \gamma_{\text{Ca}^{2+}} = -0.509(2)^2 \left(\frac{\sqrt{0.110}}{1 + \sqrt{0.110}} - 0.3(0.110) \right) \quad (91)$$

$$\sqrt{0.110} = 0.33166 \quad (92)$$

$$\frac{0.33166}{1 + 0.33166} = \frac{0.33166}{1.33166} = 0.24906 \quad (93)$$

$$0.24906 - 0.3(0.110) = 0.24906 - 0.0330 = 0.21606 \quad (94)$$

$$\log_{10} \gamma_{\text{Ca}^{2+}} = -2.036 \times 0.21606 = -0.4399 \quad (95)$$

$$\gamma_{\text{Ca}^{2+}} = 10^{-0.4399} = 0.363 \quad (96)$$

Correct Choice: (A)

Example Problem 3: Weak Acid Disassociation and pH Calculation

An industrial wastewater stream contains acetic acid (CH_3COOH , $K_a = 1.75 \times 10^{-5}$) at a total concentration of $C_a = 0.050$ M. Assuming dilute behavior, what is the pH of this effluent?

Select the correct answer:

- (A) 2.03
- (B) 3.03
- (C) 4.30
- (D) 5.06

Solution

Step 1: Check applicability of weak acid approximation.

$$\frac{C_a}{K_a} = \frac{0.050}{1.75 \times 10^{-5}} = 2857 > 100 \quad \Rightarrow \quad \text{Approximation holds.} \quad (97)$$

Step 2: Calculate $[\text{H}^+]$.

$$[\text{H}^+] \approx \sqrt{K_a C_a} = \sqrt{(1.75 \times 10^{-5})(0.050)} = \sqrt{8.75 \times 10^{-7}} = 9.354 \times 10^{-4} \text{ M} \quad (98)$$

Step 3: Compute pH.

$$\text{pH} = -\log_{10}(9.354 \times 10^{-4}) = 3.029 \approx 3.03 \quad (99)$$

Correct Choice: (B)

Example Problem 4: Total Alkalinity from Titration Data

A 100.0 mL water sample is titrated with 0.020 N H_2SO_4 . Titration to the phenolphthalein endpoint (pH 8.3) requires 4.0 mL of acid ($P = 4.0$ mL). Titration continues to the bromocresol green endpoint (pH 4.5), requiring an additional 12.0 mL of acid (Total volume $T = 16.0$ mL). What are the concentrations of Bicarbonate (HCO_3^-) and Carbonate (CO_3^{2-}) alkalinity in mg/L as CaCO_3 ?

Select the correct answer:

1. $\text{HCO}_3^- = 80$ mg/L, $\text{CO}_3^{2-} = 80$ mg/L
2. $\text{HCO}_3^- = 40$ mg/L, $\text{CO}_3^{2-} = 80$ mg/L
3. $\text{HCO}_3^- = 80$ mg/L, $\text{CO}_3^{2-} = 40$ mg/L
4. $\text{HCO}_3^- = 160$ mg/L, $\text{CO}_3^{2-} = 0$ mg/L

Solution

Step 1: Calculate P and T alkalinity in mg/L as CaCO_3 .

$$\text{Alkalinity (mg/L as CaCO}_3) = \frac{V_{\text{acid}} (\text{mL}) \times N_{\text{acid}} (\text{eq/L}) \times 50,000 \text{ mg/eq}}{V_{\text{sample}} (\text{mL})} \quad (100)$$

$$P = \frac{(4.0 \text{ mL})(0.020 \text{ N})(50,000)}{100.0 \text{ mL}} = 40.0 \text{ mg/L as CaCO}_3 \quad (101)$$

$$T = \frac{(16.0 \text{ mL})(0.020 \text{ N})(50,000)}{100.0 \text{ mL}} = 160.0 \text{ mg/L as CaCO}_3 \quad (102)$$

Step 2: Evaluate titration condition. Here $P = 40.0$ and $\frac{1}{2}T = 80.0$. Since $0 < P < \frac{1}{2}T$:

- Hydroxide Alkalinity (OH^-) = 0
- Carbonate Alkalinity (CO_3^{2-}) = $2P = 2(40.0) = 80.0$ mg/L as CaCO_3
- Bicarbonate Alkalinity (HCO_3^-) = $T - 2P = 160.0 - 80.0 = 80.0$ mg/L as CaCO_3

Correct Choice: (A)

Example Problem 5: Open Carbonate System Equilibrium pH

Rainwater falls through pristine atmosphere with a carbon dioxide partial pressure of $P_{\text{CO}_2} = 10^{-3.5}$ atm. Given $K_H = 10^{-1.47}$ M/atm and $K_{a1} = 4.47 \times 10^{-7}$, what is the equilibrium pH of this unpolluted rainwater?

Select the correct answer:

- (A) 4.20
- (B) 5.66
- (C) 6.35
- (D) 7.00

Solution

Step 1: Calculate dissolved carbonic acid $[\text{H}_2\text{CO}_3^*]$.

$$[\text{H}_2\text{CO}_3^*] = K_H P_{\text{CO}_2} = (10^{-1.47})(10^{-3.5}) = 10^{-4.97} = 1.072 \times 10^{-5} \text{ M} \quad (103)$$

Step 2: Set up charge balance for pure water open to air. Since alkalinity is zero, $[\text{H}^+] \approx [\text{HCO}_3^-]$.

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} \implies [\text{H}^+]^2 = K_{a1}[\text{H}_2\text{CO}_3^*] \quad (104)$$

$$[\text{H}^+] = \sqrt{(4.47 \times 10^{-7})(1.072 \times 10^{-5})} = \sqrt{4.79 \times 10^{-12}} = 2.189 \times 10^{-6} \text{ M} \quad (105)$$

Step 3: Calculate pH.

$$\text{pH} = -\log_{10}(2.189 \times 10^{-6}) = 5.66 \quad (106)$$

Correct Choice: (B)

Example Problem 6: Barium Sulfate Solubility with Common Ion Effect

The solubility product of barium sulfate is $K_{sp} = 1.1 \times 10^{-10}$ at 25°C. What is the molar solubility of BaSO_4 in a solution containing 0.050 M Na_2SO_4 ?

Select the correct answer:

- 1. 1.05×10^{-5} M
- 2. 2.20×10^{-9} M
- 3. 5.50×10^{-12} M
- 4. 2.20×10^{-10} M

Solution

Step 1: Determine initial sulfate ion concentration from dissolved Na_2SO_4 .



Step 2: Express equilibrium concentrations in terms of molar solubility s .

$$[\text{Ba}^{2+}] = s, \quad [\text{SO}_4^{2-}] = 0.050 + s \approx 0.050 \text{ M} \quad (\text{since } s \ll 0.050) \quad (108)$$

Step 3: Substitute into K_{sp} expression.

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = s(0.050) = 1.1 \times 10^{-10} \quad (109)$$

$$s = \frac{1.1 \times 10^{-10}}{0.050} = 2.20 \times 10^{-9} \text{ M} \quad (110)$$

Correct Choice: (B)

Example Problem 7: Chemical Softening Lime and Soda Ash Dosages

A hard water sample has the following chemical characterization:

- Free $\text{CO}_2 = 1.0 \text{ meq/L}$
- $\text{Ca}^{2+} = 4.0 \text{ meq/L}$
- $\text{Mg}^{2+} = 1.5 \text{ meq/L}$
- Total Alkalinity (HCO_3^-) = 3.5 meq/L

Calculate the required stoichiometric dosages of hydrated lime $[\text{Ca}(\text{OH})_2]$, $\text{EW} = 37.05 \text{ mg/meq}$ and soda ash $[\text{Na}_2\text{CO}_3]$, $\text{EW} = 53.0 \text{ mg/meq}$ in mg/L .

Select the correct answer:

- (A) Lime = 222.3 mg/L , Soda Ash = 106.0 mg/L
 (B) Lime = 222.3 mg/L , Soda Ash = 212.0 mg/L
 (C) Lime = 185.3 mg/L , Soda Ash = 106.0 mg/L
 (D) Lime = 259.4 mg/L , Soda Ash = 106.0 mg/L

Solution

Step 1: Calculate Total Hardness (TH) and Non-Carbonate Hardness (NCH).

$$\text{TH} = [\text{Ca}^{2+}] + [\text{Mg}^{2+}] = 4.0 + 1.5 = 5.5 \text{ meq/L} \quad (111)$$

Since $\text{TH} (5.5) > \text{Alk} (3.5)$:

$$\text{NCH} = \text{TH} - \text{Alk} = 5.5 - 3.5 = 2.0 \text{ meq/L} \quad (112)$$

Step 2: Calculate Lime dosage requirement in meq/L.

$$\text{Lime Dosage} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{Mg}^{2+}] = 1.0 + 3.5 + 1.5 = 6.0 \text{ meq/L} \quad (113)$$

Convert to mg/L :

$$\text{Lime (mg/L)} = 6.0 \text{ meq/L} \times 37.05 \text{ mg/meq} = 222.3 \text{ mg/L} \quad (114)$$

Step 3: Calculate Soda Ash dosage requirement in meq/L.

$$\text{Soda Ash Dosage} = [\text{NCH}] = 2.0 \text{ meq/L} \quad (115)$$

Convert to mg/L :

$$\text{Soda Ash (mg/L)} = 2.0 \text{ meq/L} \times 53.0 \text{ mg/meq} = 106.0 \text{ mg/L} \quad (116)$$

Correct Choice: (A)

Example Problem 8: Langelier Saturation Index (LSI) Calculation

A water distribution line carries treated water at 25°C ($T_K = 298.15$ K) with pH = 7.80, TDS = 320 mg/L, Calcium Hardness = 150 mg/L as CaCO_3 , and Total Alkalinity = 100 mg/L as CaCO_3 . Given the LSI empirical parameters $A = 0.15$, $B = 2.10$, $C = 1.78$, $D = 2.00$, what is the LSI and the scaling/corrosive state of this water?

Select the correct answer:

- (A) LSI = -0.13 (Slightly corrosive)
- (B) LSI = +0.03 (Balanced / slightly scaling)
- (C) LSI = +0.87 (Strongly scaling)
- (D) LSI = -0.87 (Strongly corrosive)

Solution

Step 1: Calculate saturation pH (pH_s).

$$\text{pH}_s = (9.30 + A + B) - (C + D) \quad (117)$$

$$\text{pH}_s = (9.30 + 0.15 + 2.10) - (1.78 + 2.00) = 11.55 - 3.78 = 7.77 \quad (118)$$

Step 2: Calculate LSI.

$$\text{LSI} = \text{pH} - \text{pH}_s = 7.80 - 7.77 = +0.03 \quad (\text{Balanced / neutral range}) \quad (119)$$

Correct Choice: (B)

Example Problem 9: Redox Balancing and pE Calculation

An aerobic aquifer sample has a measured reduction potential of $E_h = +532.4$ mV at 25°C. What is the electron activity (pE) of this groundwater?

Select the correct answer:

- (A) +4.20
- (B) +9.00
- (C) +12.50
- (D) -3.15

Solution

Step 1: Apply the pE– E_h relation at 25°C.

$$\text{pE} = \frac{E_h \text{ (in mV)}}{59.16 \text{ mV}} \quad (120)$$

$$\text{pE} = \frac{532.4 \text{ mV}}{59.16 \text{ mV}} = 9.00 \quad (121)$$

Correct Choice: (B)

Example Problem 10: Soil Organic Carbon Partitioning and Plume Retardation

A spill of trichloroethylene (TCE, $\log_{10} K_{ow} = 2.42$) occurs in a sandy aquifer with bulk density $\rho_b = 1.65$ kg/L, porosity $\theta = 0.30$, and organic carbon content $f_{oc} = 0.0050$ (0.50%). Using Karickhoff's equation ($\log_{10} K_{oc} = 1.00 \log_{10} K_{ow} - 0.21$), calculate the contaminant retardation factor (R).

Select the correct answer:

- (A) $R = 1.45$
- (B) $R = 3.23$
- (C) $R = 5.46$
- (D) $R = 11.20$

Solution

Step 1: Calculate K_{oc} using Karickhoff's relation.

$$\log_{10} K_{oc} = 1.00(2.42) - 0.21 = 2.21 \implies K_{oc} = 10^{2.21} = 162.2 \text{ L/kg} \quad (122)$$

Step 2: Calculate distribution coefficient K_d .

$$K_d = f_{oc} \cdot K_{oc} = (0.0050)(162.2 \text{ L/kg}) = 0.811 \text{ L/kg} \quad (123)$$

Step 3: Calculate Retardation Factor R .

$$R = 1 + \frac{\rho_b}{\theta} K_d = 1 + \left(\frac{1.65 \text{ kg/L}}{0.30} \right) (0.811 \text{ L/kg}) = 1 + (5.50)(0.811) = 1 + 4.46 = 5.46 \quad (124)$$

Correct Choice: (C)

Example Problem 11: Freundlich Isotherm Adsorption Calculation

Granular activated carbon (GAC) is used to adsorb phenol from water. Isotherm testing establishes Freundlich constants $K_f = 2.0$ (mg/g)(L/mg) $^{1/n}$ and $1/n = 0.50$. What mass of phenol (q in mg/g) is adsorbed at an equilibrium concentration of $C = 16.0$ mg/L?

Select the correct answer:

- (A) 4.0 mg/g
- (B) 8.0 mg/g
- (C) 16.0 mg/g
- (D) 32.0 mg/g

Solution

Step 1: Apply Freundlich equation.

$$q = K_f C^{1/n} = (2.0)(16.0)^{0.50} = (2.0)(\sqrt{16.0}) = (2.0)(4.0) = 8.0 \text{ mg/g} \quad (125)$$

Correct Choice: (B)

Example Problem 12: Atmospheric Unit Conversion (ppmv to $\mu\text{g}/\text{m}^3$)

An air quality monitoring station measures sulfur dioxide (SO_2 , $\text{MW} = 64.06 \text{ g/mol}$) at a concentration of 0.150 ppm_v at 25°C and 1.0 atm . What is this concentration in $\mu\text{g}/\text{m}^3$?

Select the correct answer:

1. $150 \mu\text{g}/\text{m}^3$
2. $393 \mu\text{g}/\text{m}^3$
3. $572 \mu\text{g}/\text{m}^3$
4. $840 \mu\text{g}/\text{m}^3$

Solution

Step 1: Apply gas unit conversion equation at 25°C and 1 atm .

$$\text{mg}/\text{m}^3 = \frac{\text{ppm}_v \times \text{MW}}{24.45} = \frac{(0.150)(64.06)}{24.45} = \frac{9.609}{24.45} = 0.393 \text{ mg}/\text{m}^3 \quad (126)$$

Step 2: Convert mg/m^3 to $\mu\text{g}/\text{m}^3$.

$$0.393 \text{ mg}/\text{m}^3 \times 1000 \mu\text{g}/\text{mg} = 393 \mu\text{g}/\text{m}^3 \quad (127)$$

Correct Choice: (B)

Example Problem 13: First-Order Reaction Kinetics Half-Life

A toxic organic chemical degrades in a CSTR via first-order decay kinetics. Laboratory tests establish a half-life of $t_{1/2} = 12.0 \text{ days}$. What hydraulic retention time ($\tau = V/Q$) is required in an ideal CSTR to achieve 90% removal efficiency?

Select the correct answer:

- (A) 36.0 days
- (B) 72.0 days
- (C) 156.0 days
- (D) 174.0 days

Solution

Step 1: Calculate reaction rate constant k .

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.69315}{12.0 \text{ days}} = 0.05776 \text{ day}^{-1} \quad (128)$$

Step 2: Apply CSTR steady-state mass balance for first-order decay.

$$C = \frac{C_0}{1 + k\tau} \implies \frac{C}{C_0} = 1 - 0.90 = 0.10 \quad (129)$$

$$0.10 = \frac{1}{1 + k\tau} \implies 1 + k\tau = 10.0 \implies k\tau = 9.0 \quad (130)$$

$$\tau = \frac{9.0}{k} = \frac{9.0}{0.05776 \text{ day}^{-1}} = 155.8 \approx 156.0 \text{ days} \quad (131)$$

Correct Choice: (C)

Example Problem 14: Arrhenius Activation Energy Calculation

The biological decay rate constant for a pharmaceutical compound in activated sludge is measured as $k_1 = 0.20 \text{ day}^{-1}$ at $T_1 = 20^\circ\text{C}$ (293.15 K) and $k_2 = 0.50 \text{ day}^{-1}$ at $T_2 = 35^\circ\text{C}$ (308.15 K). What is the activation energy, E_a , for this decay reaction?

Select the correct answer:

- (A) 18.5 kJ/mol
- (B) 45.9 kJ/mol
- (C) 76.2 kJ/mol
- (D) 112.0 kJ/mol

Solution

Step 1: Apply the Arrhenius equation.

$$\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2), R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \quad (132)$$

$$\ln(0.50/0.20) = \ln(2.50) = 0.9163 \quad (133)$$

$$1/293.15 - 1/308.15 = 0.00016599 \text{ K}^{-1} \quad (134)$$

Step 2: Solve for E_a .

$$E_a = [(0.9163)(8.314)]/0.00016599 = 45,895 \text{ J/mol} \approx 45.9 \text{ kJ/mol} \quad (135)$$

Correct Choice: (B)

Example Problem 15: Minimum Hydroxide Solubility of Amphoteric Aluminum

The total dissolved aluminum concentration C_{Al} in equilibrium with solid $\text{Al}(\text{OH})_3(s)$ is governed by:

$$C_{\text{Al}} = 1.0 \times 10^9 [\text{H}^+]^3 + 1.0 \times 10^{-15} [\text{H}^+]^{-1} \quad [\text{mol/L}] \quad (137)$$

At what pH does the minimum solubility of aluminum hydroxide occur?

Select the correct answer:

- (A) 4.50
- (B) 6.12
- (C) 8.50
- (D) 10.50

Solution

Step 1: Differentiate C_{Al} with respect to $[\text{H}^+]$ and set to zero.

$$\frac{dC_{\text{Al}}}{d[\text{H}^+]} = 3.0 \times 10^9 [\text{H}^+]^2 - 1.0 \times 10^{-15} [\text{H}^+]^{-2} = 0 \quad (138)$$

$$3.0 \times 10^9 [\text{H}^+]^4 = 1.0 \times 10^{-15} \implies [\text{H}^+]^4 = \frac{1.0 \times 10^{-15}}{3.0 \times 10^9} = 3.333 \times 10^{-25} \quad (139)$$

Step 2: Take the 4th root.

$$[\text{H}^+] = (3.333 \times 10^{-25})^{0.25} = 7.598 \times 10^{-7} \text{ M} \quad (140)$$

Step 3: Calculate optimal pH.

$$\text{pH} = -\log_{10}(7.598 \times 10^{-7}) = 6.12 \text{ (Choice B)} \quad (141)$$

Correct Choice: (B)