2.21 $AlPO_4 \rightarrow Al^{3+} + PO_4^{3-}$ $\quad K_{sp} = 10^{-22}$

$K_{sp} = [Al^{3+}][PO_4^{3-}]$ at eq. assume $[Al^{3+}] = [PO_4^{3-}]$

$\therefore \quad 10^{-22} = [PO_4^{3-}]^2$

$[PO_4^{3-}] = 10^{-11}\ mol/L \cdot \frac{95{,}000\ mg}{1\ mol} = \underline{\underline{9.5 \cdot 10^{-7}\ mg/L}}$ ←

2-22 DO_{sat} @ 2000m, 15°C and at 1 atm

$DO_{sat} = K_H P_g$ @ 15°C $K_H = 0.0015236$

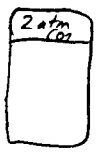
$DO_{sat} = (0.0015236)(0.22)(1\ atm) = 0.00031996\ mol/L \cdot \frac{32{,}000\ mg}{1\ mol\ O_2} = \underline{\underline{10.2\ mg/L}}$ ←

@ 2000 m

$P_g = 1 - 1.15 \cdot 10^{-4}(2000) = 0.77\ atm$

$DO_{sat} = (0.0015236)(0.22)(0.77) = 0.0002464 \frac{mol}{L} \cdot \frac{32{,}000\ mg}{1\ mol} = \underline{\underline{7.9\ mg/L}}$ ←

2.23



$CO_{2(aq)} = K_H P_g$

$= 0.033363\,(2) = 0.066676\ mol/L * \frac{44{,}000\ mg}{mol} = 2900\ mg/L = 2.9\ g/L$

2.24 $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$

$\frac{[H^+][HCO_3^-]}{[CO_{2\,aq}]} = 4.47 \cdot 10^{-7}$ $\qquad [H^+][OH^-] = 10^{-14}$

Charge equilibrium $\quad [H^+] = [HCO_3^-] + [OH^-]$

$[H^+] = (4.47 \cdot 10^{-7})(6.6 \cdot 10^{-2}\ mol/L)[H^+]^{-1} + 10^{-14}[H^+]^{-1}$

Solve for $[H^+]$

$[H^+]^2 = (4.47 \cdot 10^{-7})(6.6 \cdot 10^{-2}) + (1 \cdot 10^{-14})$

$[H^+] = 1.73 \cdot 10^{-4}\ mol/L$

$pH = -\log(0.000173) = 3.76$

2.25 @ 275 ppm

$[CO_2] = K_H P_g = 0.033363 \cdot 275 \cdot 10^{-6} = 9.17 \cdot 10^{-6}\ mol/L$

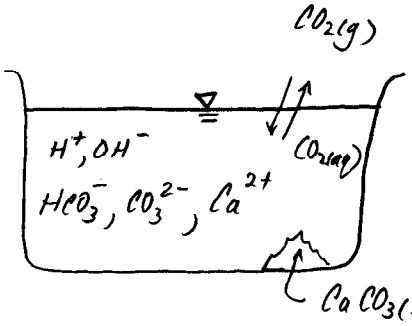
$[H^+]^2 \approx (4.47 \cdot 10^{-7})(9.17 \cdot 10^{-6}) + 10^{-14} = 4.11 \cdot 10^{-12}$ $\quad \therefore [H^+] \approx 2.0 \cdot 10^{-6}$

$pH = -\log(2.0 \cdot 10^{-6}) = 5.69$

Repeat for $P_g = 600 \cdot 10^{-6}$ $\quad pH = 5.52$

CIVE 3331 PROBLEM 2.26 11

Acid lakes can be periodically limed ($CaCO_3$) to increase the pH. Calculate pH of a lake with excess lime.



Assume system at STP (25°C, 1 atm)

① System is in equilibrium with atmosphere
② System is in equilibrium with $CaCO_3$ precipitate
③ Charge balance is neutral (no excess charge)

(a) $[CO_{2(aq)}] = K_H P_{CO_{2(g)}} = (0.033363 \frac{M}{L \cdot atm})(360 \cdot 10^{-6} atm)$

$= 1.2011 \cdot 10^{-5} \frac{mol}{L}$ (dissolution)

(b) $CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$ (carbonic acid, bicarbonate eq.)

(c) $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ (bicarbonate - carbonate eq.)

(d) $CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$ (solid-liquid equilibrium)

(e) $H^+ + 2Ca^{2+} = HCO_3^- + 2CO_3^{2-} + OH^-$ (charge balance)

(f) $[H^+][OH^-] = 1 \cdot 10^{-14}$

④ All "equilibria" & charge balance must be satisfied

(b) $\frac{[H^+][HCO_3^-]}{[CO_{2aq}]} = K_1 = 4.47 \cdot 10^{-7}\ m/L$

(c) $\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = K_2 = 4.68 \cdot 10^{-11}$

(d) $[Ca^{2+}][CO_3^{2-}] = K_{sp} = 4.57 \cdot 10^{-9}$

(f) $[H^+][OH^-] = 1 \cdot 10^{-14}$

(e) $H^+ + 2Ca^{2+} = HCO_3^- + 2CO_3^{2-} + OH^-$

known: $CO_{2(aq)}$, if we pick H^+ we can determine values for HCO_3^-, CO_3^{2-}, Ca^{2+}, OH^-

by trial & error, pick H^+ that satisfies all the equations!

1) $HCO_3^- = \frac{4.47\cdot10^{-7}\,[CO_{2aq}]}{H^+}$

2) $CO_3^{2-} = \frac{4.68\cdot10^{-11}\,[HCO_3^-]}{H^+} = \frac{4.68\cdot10^{-11}\times 4.47\cdot10^{-7}\,[CO_{2aq}]}{[H^+]^2}$

3) $Ca^{2+} = \frac{4.57\cdot10^{-9}}{CO_3^{2-}} = \frac{4.57\cdot10^{-9}\,[H^+]^2}{4.68\cdot10^{-11}\times 4.47\cdot10^{-7}\,[CO_{2aq}]}$

4) $OH^- = \frac{1\cdot10^{-14}}{H^+}$

5) Charge balance — beat to death with Excel or use algebra

$$[H^+] + 2\left[\frac{4.57\cdot10^{-9}\,[H^+]^2}{4.68\cdot10^{-11}\times 4.47\cdot10^{-7}\,[CO_{2aq}]}\right] - \frac{4.47\cdot10^{-7}\,[CO_{2(aq)}]}{[H^+]}$$

$$- 2\left[\frac{4.68\cdot10^{-11}\times 4.47\cdot10^{-7}\,[CO_{2aq}]}{[H^+]^2}\right] - \frac{1\cdot10^{-14}}{[H^+]} = 0$$

solve for H^+

by trial & error pH is somewhere between 8 & 9

pH = 8.27415 (too many sig. figs should be close)

Check

$H^+ = 10^{-8.27415} = 5.3192 \cdot 10^{-9}$

$HCO_3^- = 1.0093 \cdot 10^{-3}$

$CO_3^{2-} = 8.8806 \cdot 10^{-6}$

$Ca^{2+} = 5.1461 \cdot 10^{-4}$

$OH^- = 1.88 \cdot 10^{-6}$

charge balance

$[H^+] + 2[Ca^{2+}]$

$5.3192 \cdot 10^{-9} + 2\left(5.1461 \cdot 10^{-4}\right) = 1.0292 \cdot 10^{-3}$

$[HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$

$1.0093 \cdot 10^{-3} + 2\left(8.8806 \cdot 10^{-6}\right) + \left(1.88 \cdot 10^{-6}\right) = 1.0289 \cdot 10^{-3}$

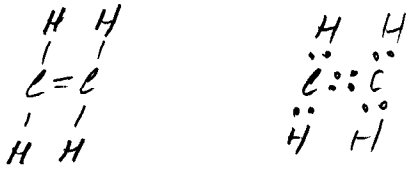
$$\begin{array}{rr} & 1.0292 \cdot 10^{-3} \\ \text{difference} & -1.0289 \cdot 10^{-3} \\ \hline & 2.588 \cdot 10^{-7} \end{array}$$

practically zero

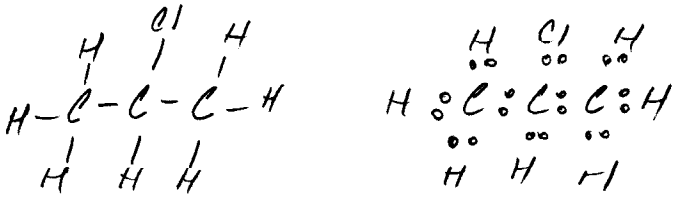
∴ $pH \approx 8.27$ for open system with excess solid present.

(compare to open system, no solid (no Ca) $pH = 5.63$)

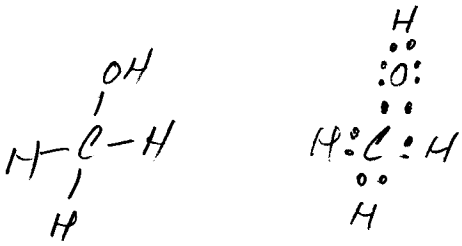
a) Ethylene



b) 2-chloropropane

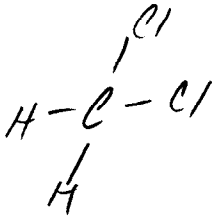


c) Methanol

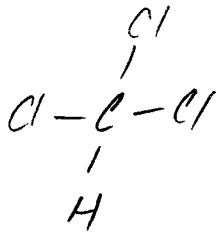


PROBLEM 2.38

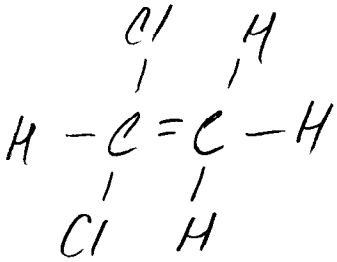
a) Dichloromethane



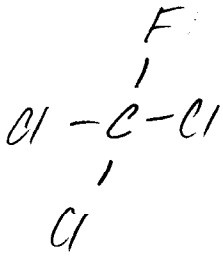
b) Trichloromethane



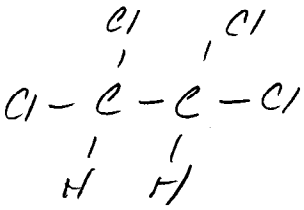
c) 1-1 Dichloroethylene



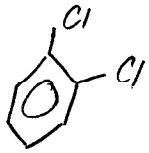
d) Trichlorofluoromethane



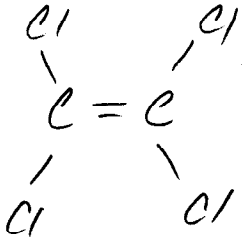
e) 1, 1, 2, 2 Tetrachloroethane



f) o-Dichlorobenzene



g) Tetrachloroethene



h) Dichlorofluoromethane