A BASIC REVIEW OF CHEMICALS IN WATER

Ca^{2+} ← VALENCE = 2+
"combining power"
and electrical charge on ion

CALCIUM
ION

ATOMIC WEIGHT = 40 amu
= 40 grams/mole
mg/millimole

(ONE MOLE = 6.02×10^{23} molecules for ALL elements)

EQUIVALENT WEIGHT

$$\equiv \frac{\text{ATOMIC WEIGHT}}{\text{VALENCE}} = 20 \text{ g/mol}$$

CO_3^{2-} ← VALENCE = 2−

CARBONATE
ION

~~ATOMIC~~ MOLECULAR WEIGHT = C = 12
30 = 16 × 3
60.0 g/mol

EQUIVALENT WEIGHT
= ?

MORE ON EQUIVALENTS"

- $1 \text{ EQ} \equiv 1 \text{ mol}/\text{VALENCE}$

$$\underset{\text{VALENCE } 2-}{CO_3^{2-}} + \underset{\text{VALENCE } 1+}{2H^+} \rightarrow H_2CO_3$$

∴ $2H^+$'s will combine with 1 CO_3^{2-}

- BUT if WE NORMALIZE to valence

then: 1 eq CO_3^{2-} COMBINES WITH 1 eq H^+

$$\rightarrow \frac{1 \text{ mole } CO_3^{2-}}{2} + \frac{1 \text{ Mole } H^+}{1} \Rightarrow \frac{1 \text{ mole } H_2CO_3}{2}$$

$$\rightarrow \tfrac{1}{2} \text{ mol} + 1 \text{ mol} \rightarrow \tfrac{1}{2} \text{ mol}$$

$$\rightarrow 1 \text{ eq} + 1 \text{ eq} \rightarrow 1 \text{ eq}$$

HOW DO "EQUIVALENT WEIGHTS" WORK?

Ex: $CO_3^{2-} + 2H^+ \rightarrow H_2CO_3$

CARBONATE — HYDROGEN IONS ("PROTONS") — CARBONIC ACID

And we get protons from ACIDS

$HCl \rightarrow H^+ + Cl^-$

HYDROCHLORIC ACID — CHLORIDE

Suppose we want to turn 100g of $CaCO_3$ into $Ca^{2+} + H_2CO_3$?

$HCl + CaCO_{3(s)} \rightarrow Ca^{2+} + H_2CO_3$

$$\frac{100\text{ g } CaCO_3}{50\text{ g/mol EQ.WT}} = 2\text{ "equivalents" of } CaCO_3$$

$$2\text{ equivalents } HCl \Rightarrow \frac{(36.5 + 1.0)\text{ g/mol}}{1\text{ VALENCE}} = \left(37.5\,\frac{g}{eq}\right) \times 2\text{ eq}$$

$$= 75\text{ g } HCl \quad (\text{ANS})$$

EQUIVALENTS ALSO "AUTOMATICALLY" SORT OUT ELECTRICAL CHARGE BALANCES

All water solutions are (overall) electrically neutral.

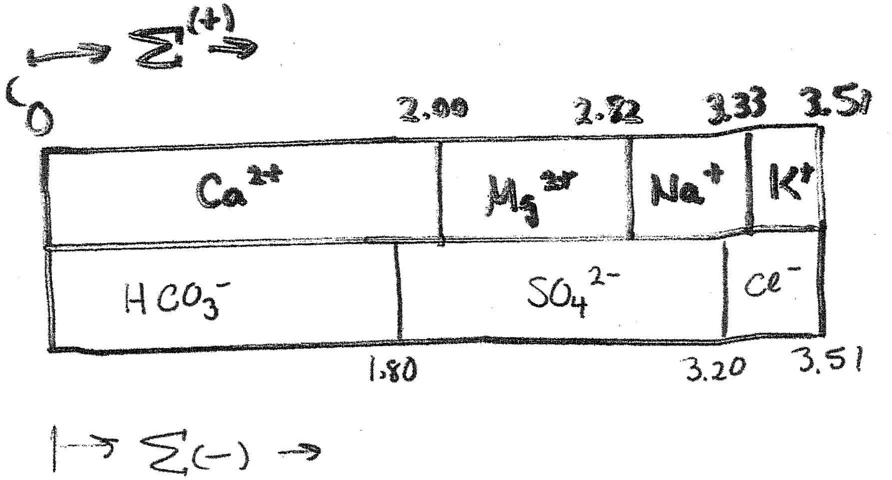
∴ All (+) ions must sum to total of the (−) ions

∴ Σ Equivalents of cations (plus ions) = Σ Equivalents of anions (minus ions)

Ex:

		EQUIV.WT	meq/L	
Ca^{2+}	40 mg/L	20.0 mg/meq	2.0	Σ = 3.51 meq/L
Mg^{2+}	10 mg/L	12.2	0.82	
Na^+	11.7 mg/L	23.0	0.51	
K^+	7.0 mg/L	39.1	0.18	
HCO_3^-	110 mg/L	61.0	1.80	Σ = 3.51
SO_4^{2-}	67.2 mg/L	48.0	1.40	
Cl^-	11.0 mg/L	35.5	0.31	

↑
LAB ANALYSIS



meq/L BAR GRAPH

HELPS US SEE WHAT IS BALANCING WHAT

▷ (Esp. useful for designing water softening)

▷ Geochemistry

EQUILIBRIUM REACTIONS

$$aA + bB \rightleftharpoons cC + dD$$

EXAMPLE: ADD Carbon dioxide to water:

$$(1)CO_2 + (1)\ H_2O \rightleftharpoons (1)CO_3^{2-} + 2H^+$$

REACTION RATES:

FORWARD RATE $= k_f[A]^a[B]^b$

REVERSE RATE $= k_r[C]^c[D]^d$

Due to statistical probability of $A \leftrightarrow B$ or $C \leftrightarrow D$ colliding

AND AT EQUILIBRIUM:

FORWARD RATE = REVERSE RATE

$$k_f[A]^a[B]^b = k_r[C]^c[D]^d$$

$$\therefore \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{k_f}{k_r} \equiv K_{equil}$$

EXAMPLE: $$\frac{[CO_3^{2-}][H^+]^2}{[CO_2][H_2O]} = K = 7.2\times10^{-19}\ M$$
$$= 10^{-18.14}$$

ACID-BASE EQUILIBRIA

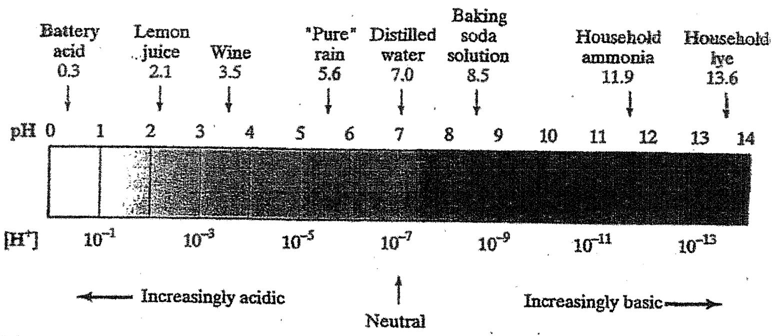
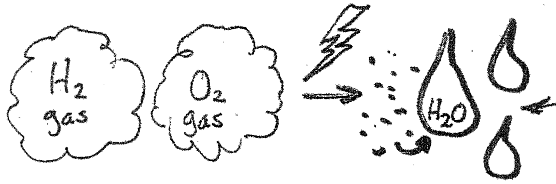


FIGURE 2.2 The pH scale.

Why is pure (neutral) water at $pH = 7.00$?

$\{H^+\} = 10^{-7.00}$



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

WATER DISSOCIATES

$$K = \frac{[H^+][OH^-]}{[H_2O]} = 1.8 \times 10^{-16} \text{ M}$$

BUT the concentration of H_2O is HUGE & ~CONSTANT

$$\frac{1000 \text{ g}}{\text{L}} \times \frac{\text{mol}}{18 \text{ g}} = 55.4 \frac{\text{mol}}{\text{L}} \quad \text{So: } [H^+][OH^+] = (1.8 \times 10^{-16})(55.4)$$

$$\therefore [H^+][OH^-] = 10^{-14.0} \text{ M}^2$$

$$K_w = [H^+][OH^-] = 10^{-14.0}$$

PURE H_2O:

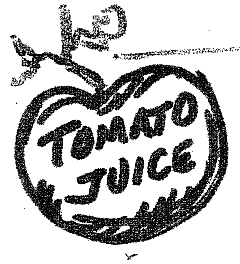
$$H_2O \rightleftharpoons H^+ + OH^-$$

$$[H^+] = [OH^-]$$

$$\therefore [H^+]^2 = 10^{-14.0} \quad \text{or} \quad [OH^-]^2 = 10^{-14.0}$$

$$[H^+] = 10^{-7.0} \quad [OH^-] = 10^{-7.0}$$

NEUTRAL SOLUTION



CITRIC ACID: $H{:}Cit \rightleftharpoons H^+ + Cit^-$

ADDS SOME EXTRA PROTONS (H^+'s)

$pH = 4.1 \qquad pH \equiv -\log[H^+]$

$$[H^+] = 10^{-4.1} = \boxed{7.9 \times 10^{-5} \text{ M}}$$

(~1000x more H^+ THAN PURE H_2O)

$$K_w = [H^+][OH^-]$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-4.1}} = 10^{-9.9} = \boxed{1.3 \times 10^{-10} \text{ M}}$$

(~1000x LESS OH^- THAN PURE H_2O)

$$-\log[OH^-] = 14.0 - pH$$

SOLUBILITY OF GASES IN H_2O

$$\left[\begin{matrix}\text{Dissolved}\\ \text{GAS}\end{matrix}\right] = K_H\, P_g$$

HENRYS LAW CONSTANT $\left[\frac{mol}{L}\cdot atm\right]$

PARTIAL PRESSURE OF GAS IN AIR $[atm]$

Ex: O_2 is 21% of AIR

$P_{O_2} = 0.21 \times 1atm = 0.21\ atm$

$P_{CO_2} = 3.3 \times 10^{-4}\ atm$

EXAMPLE 3: Sol'y of $[O_2]$

$[O_2] = (1.26\times10^{-3})(0.21)$

$= 2.65\times10^{-4}\ M$

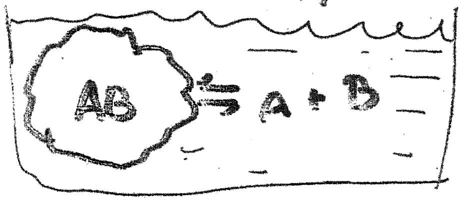
$\times\ 32\ g/mol$

$\boxed{= 8.5\ mg/L}$

TABLE 2.4 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

SOLUBILITY PRODUCT



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

concentration of solid is meaningless in solution, so define $[AB] = 1.000$

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

SOLUBILITY PRODUCT

Example

$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$ $\qquad [Ca^{2+}][F^-]^2 = 10^{-10.5}$

$[Ca^{2+}] = S$ $\qquad K_{sp} = S \times (2S)^2 = 10^{-10.5} = 4S^3$

$[F^-] = 2S$ $\qquad [Ca^{2+}] = 2\times10^{-4}\ M \qquad [F^-] = 4\times10^{-4}\ M$

TABLE 2.3 Selected solubility-product constants at 25°C

Equilibrium equation	K_{sp} at 25°C	Significance in environmental engineering
$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$	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).

pH of RAINWATER

$K_H^{CO_2} = 10^{-1.5}\ M \cdot atm$

$P_{CO_2} = 10^{-3.5}\ atm$

$[CO_2]_{aq} = (10^{-1.5}\ M \cdot atm)(10^{-3.5}\ atm) = 10^{-5.0}\ M$

$$\underset{}{CO_2 + H_2O} \rightleftharpoons \underset{\text{CARBONIC ACID}}{H_2CO_3} \rightleftharpoons H^+ + \underset{\text{BICARBONATE ION}}{HCO_3^-}$$

$$\frac{[H^+][HCO_3^-]}{[CO_2]_{aq}} = K_1 = 10^{-6.35}$$

We know that $[H^+] \approx [HCO_3^-]$ $\updownarrow$

$$\frac{[H^+]^2}{[CO_2]_{aq}} = 10^{-6.35} \Rightarrow [H^+]^2 = 10^{-6.35} \cdot \underset{\text{FROM above}}{10^{-5.0}}$$

$$[H^+] = \sqrt{10^{-11.35}} = 10^{-\frac{11.35}{2}} = 10^{-5.67}$$

$\therefore$ $\boxed{pH = 5.67}$ Natural rain is slightly ACIDIC