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

---

CO_3^{2-} ← VALENCE = 2−

CARBONATE ION

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

EQUIVALENT WEIGHT
= ?

CONCENTRATION UNITS:

$$\frac{\text{mass of chemical}}{\text{volume of water}}$$

For most water/wastewater constituents use

$$\frac{\text{milligrams}}{\text{liter}} \equiv \frac{\text{mg}}{\text{L}}$$

Because one Liter ≈ 1000 g
and 1000 mg in a gram

$1 \frac{\text{mg}}{\text{L}} \approx$ 1 part per million
1 ppm

Likewise:
$1 \frac{\mu g}{L}$ $\left(\frac{\text{microgram}}{\text{Liter}}\right) \approx$ 1 part per billion (ppb)

Olden Days: $\frac{\text{grains}}{\text{gallon}}$ ← fugeddaboutit...

WATER/WW ANALYSES ALMOST ALWAYS IN mg/L (metric)

However design is still often in U.S. units so DOSAGES (added chemicals) convenient in POUNDS/GALLON

$$1 \text{ gal} = 8.34 \text{ lb}$$

$$\therefore \frac{1 \text{ gal}}{1 \text{ million gal}} = 1 \text{ ppm} \simeq 1 \text{ mg/L}$$

$$= \frac{8.34 \text{ lb}}{\text{MG}} = 1 \text{ mg/L}$$

That is 8.34 lb in a million gallons yields a final conc. of 1 mg/L.

E.g.: want 0.5 mg/L FLUORIDE in D/W
Add $(0.5)(8.34) = \underline{4.17}$ lb per MG

MORE ON "EQUIVALENTS"

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

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

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

BUT if WE NORMALIZE to valence then:

$\frac{1}{?}$ eq CO_3^{2-} COMBINES WITH $\frac{1}{?}$ 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 $Ca^{2+} + H_2CO_3$?

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

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

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

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

EQUIVALENTS ALSO "AUTOMATICALLY" SORT OUT ELECTRICAL CHARGE BALANCES

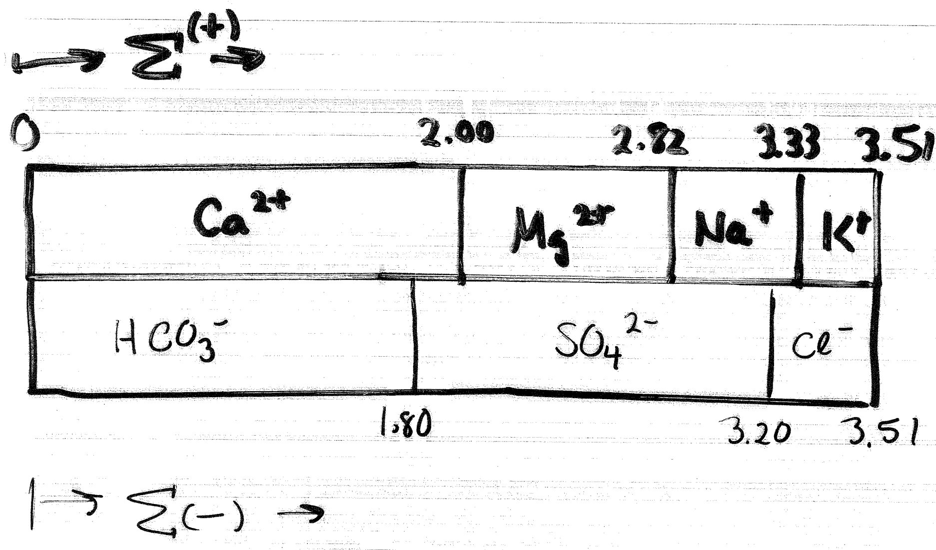
All water solutions are (overall) electrically neutral.

∴ 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 $\frac{mg}{meq}$	2.0	
Mg^{2+}	10 mg/L	12.2	0.82	
Na^+	11.7 mg/L	23.0	0.51	$\Sigma = 3.51$ meq/L
K^+	7.0 mg/L	39.1	0.18	
HCO_3^-	110 mg/L	61.0	1.80	
SO_4^{2-}	67.2 mg/L	48.0	1.40	$\Sigma = 3.51$
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)

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:

$$\frac{[CO_3^{2-}][H^+]^2}{[CO_2][H_2O]} = K = 7.2 \times 10^{-19}\,M$$

$$= 10^{-18.14}$$

ACID-BASE EQUILIBRIA

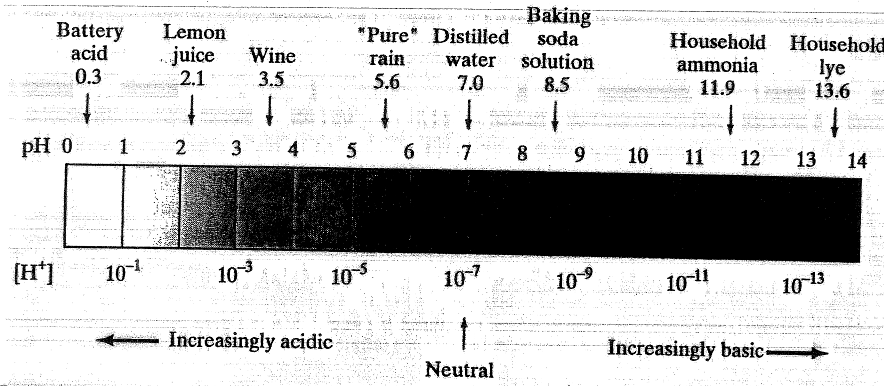
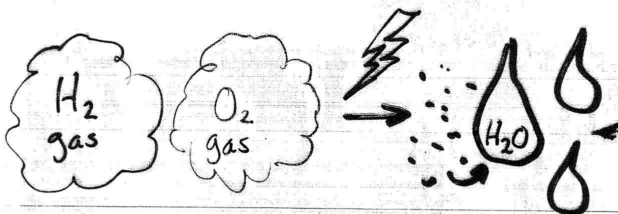


FIGURE 2.2 The pH scale.

Why is pure (neutral) water at pH = 7.00 ? $\{H^+\} = 10^{-7.00}$



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

WATER DISSOCIATES

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

BUT the concentration of H_2O is HUGE & ~CONSTANT

$$\frac{1000\,g}{L} \times \frac{mol}{18\,g} = 55.4\ \frac{mol}{L}$$ So: $[H^+][OH^+] = (1.8\times10^{-16})(55.4)$

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

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

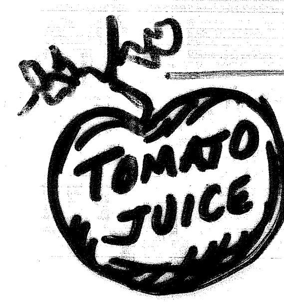
PURE H_2O: $H_2O \rightleftarrows H^+ + OH^-$

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

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

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

NEUTRAL SOLUTION



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

ADDS SOME EXTRA PROTONS [H^+'s]

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

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

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

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

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-4.1}} = 10^{-9.9} = \boxed{1.3\times10^{-10}\ M}$$

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

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

AMMONIA STRIPPING & pH

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

AMMONIA ↑ **VOLATILE**

AMMONIUM ION ↑ **NONVOLATILE**

$$\frac{[NH_4^+]}{[NH_3][H^+]} = 10^{9.2}$$

$$\boxed{\frac{[NH_3]}{[NH_3]+[NH_4^+]} = \frac{1}{1+\frac{[NH_4^+]}{[NH_3]}}}$$

FRACTION THAT'S NH_3

$$= \frac{1}{1+\frac{[NH_4]}{[NH_3]}} = \frac{1}{1+[H^+]10^{9.2}} = \frac{1}{1+10^{[9.2-pH]}}$$

pH	$\frac{[NH_3]}{[NH_3]+[NH_4^+]}$
4	0.000005
6	0.0005
8	0.052
9	0.35
10	0.85
12	0.99

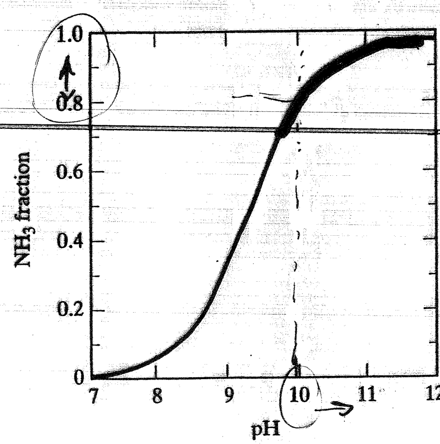
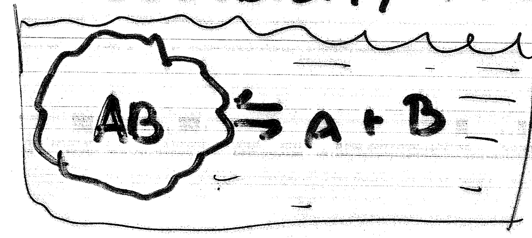


FIGURE 2.3 Dependence of the ammonia fraction on pH (Example 2.8).

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).

SOLUBILITY OF GASES IN H_2O

$$\begin{bmatrix}\text{Dissolved}\\ \text{GAS}\end{bmatrix} = K_H\, P_g$$

HENRYS LAW CONSTANT

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

PARTIAL PRESSURE OF GAS IN AIR

$[atm]$

Ex: O_2 is 21% of AIR

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

$= 0.21 atm$

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

EXAMPLE: Sol'y of $[O_2]$

$[O_2] = (1.26 \times 10^{-3})(0.21)$

$= 2.65 \times 10^{-4}$ M

$\times$ 32 g/mol

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

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