

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

CO_3^{2-} ← VALENCE = 2-

CARBONATE ION
 ATOMIC WEIGHT = $\frac{C=12}{3O=16 \times 3}$
 MOLECULAR
 60.0 g/mol

EQUIVALENT WEIGHT = ?

CONCENTRATION UNITS:

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

For most water/wastewater constituents use

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

Because one Liter \approx 1000 g
 and 1000 mg in a gram

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

Likewise:

$1 \frac{\mu\text{g}}{\text{L}} (\frac{\text{microgram}}{\text{liter}}) = 1 \text{ part per billion}$
 (Ppb)

Older Days: $\frac{\text{grains}}{\text{gallon}}$ ← fuggedaboutit...

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

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

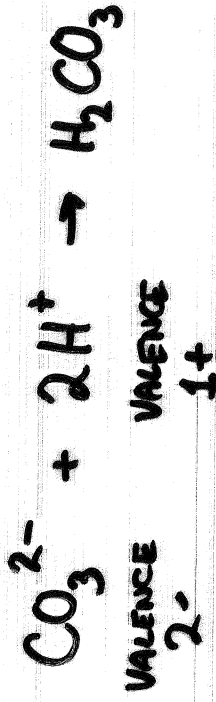
$$\therefore \frac{1 \text{ gal}}{1 \text{ million gal}} = 1 \text{ ppm} \approx 1 \text{ mg/L}$$
$$= \frac{8.34 \text{ lb}}{\text{MG}} = 1 \text{ mg/L}$$

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 $(0.5)(8.34) = 4.17 \text{ lb per MG}$

MORE ON "EQUIVALENTS"

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



$\therefore 2\text{H}^+$; will combine with 1 CO_3^{2-}

BUT if WE NORMALIZE to valence

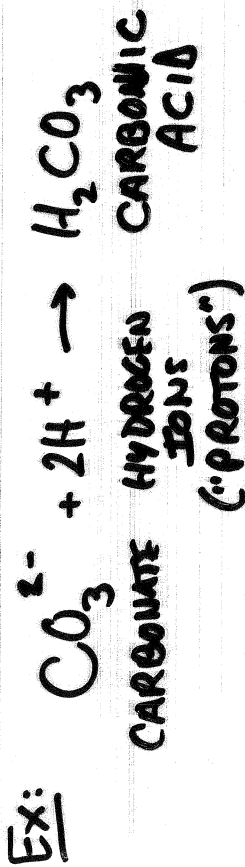
then: $\frac{1 \text{ eq CO}_3^{2-}}{2}$ COMBINES WITH $\frac{1 \text{ eq H}^+}{1}$

$$\Rightarrow \frac{1 \text{ mole CO}_3^{2-}}{2} + \frac{1 \text{ mole H}^+}{1} \Rightarrow \frac{1 \text{ mole H}_2\text{CO}_3}{2}$$

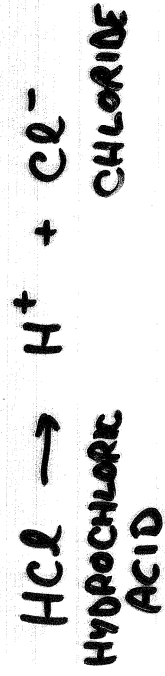
$$\Rightarrow \frac{1}{2} \text{ mol} + 1 \text{ mol} \rightarrow \frac{1}{2} \text{ mol}$$

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

HOW DO "EQUIVALENT WEIGHTS" WORK?



And we get protons from ACIDS



Suppose we want to turn 100g of CaCO_3 into $\text{Ca}^{2+} + \text{H}_2\text{CO}_3$?



$\frac{100 \text{ g CaCO}_3}{50 \text{ g/mol Eq.WT}} = 2 \text{ "equivalents" of CaCO}_3$

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

= 75 g HCl (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

∴ $\sum \text{Equivalents of cations (plus ions)} = \sum \text{Equivalents of anions (minus ions)}$

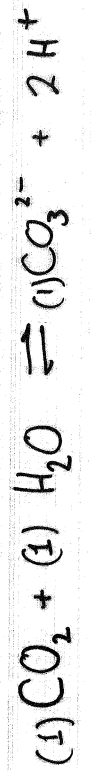
	mg/L	Eq. WT $\frac{\text{mg}}{\text{meq}}$	meq/L
Ex: Ca^{2+}	40 mg/L	20.0 $\frac{\text{mg}}{\text{meq}}$	2.0
Mg^{2+}	10 mg/L	12.2	0.82
Na^+	11.7 mg/L	23.0	0.51
K^+	7.0 mg/L	39.1	0.18
HCO_3^-	110 mg/L	61.0	1.80
SO_4^{2-}	67.2 mg/L	48.0	1.40
Cl^-	11.0 mg/L	35.5	0.31
			$\Sigma = 3.51$

LAB ANALYSIS

EQUILIBRIUM REACTIONS



EXAMPLE: ADD Carbon dioxide to water:



REACTION RATES:

$$\text{FORWARD RATE} = k_f [A]^a [B]^b$$

$$\text{REVERSE RATE} = k_r [C]^c [D]^d$$

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

AND AT EQUILIBRIUM:

$$\text{FORWARD RATE} = \text{REVERSE RATE}$$

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

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

EXAMPLE:

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

$\rightarrow \Sigma^{(+)} \rightarrow$

	2.00	2.72	333	3.51
Ca ²⁺				
Mg ²⁺				
HCO ₃ ⁻	1.80		3.20	3.51
SO ₄ ²⁻				
Na ⁺				
K ⁺				
Cl ⁻				

$\rightarrow \Sigma^{(-)} \rightarrow$

meq/L BAR GRAPH

HELPS US SEE WHAT IS BALANCING

WHAT

(Esp. useful for designing water softening)

ACID-BASE EQUILIBRIA

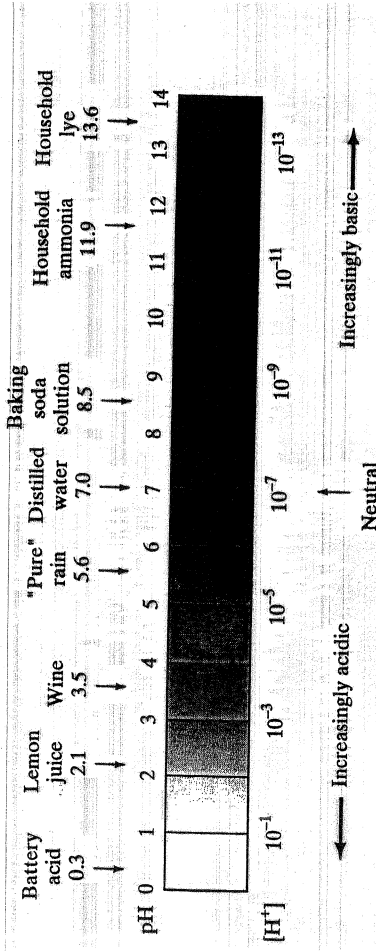
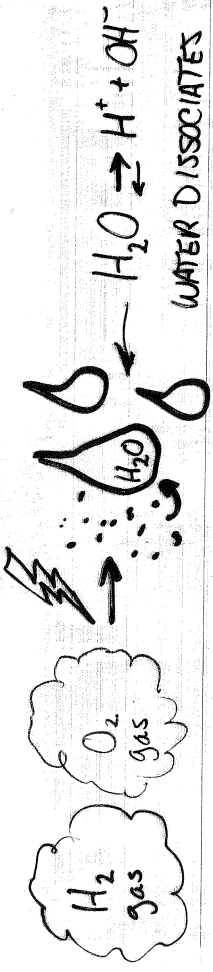


FIGURE 2.2 The pH scale.

Why is (neutral) pure water at $\text{pH} = 7.00$?

$$[\text{H}^+] = 10^{-7.00}$$



$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = 1.8 \times 10^{-16} \text{ M}$$

BUT the concentration of H_2O is HUGE & ~CONSTANT

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

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

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

PURE H_2O :



$$[\text{H}^+] = [\text{OH}^-]$$

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

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

NEUTRAL SOLUTION



CITRIC ACID: $\text{H}_3\text{Cit} \rightleftharpoons \text{H}^+ + \text{Cit}^-$
 ADDS SOME EXTRA PROTONS (H^+ 's)

$$\text{pH} = 4.1 \quad \text{pH} \equiv -\log[\text{H}^+]$$

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

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

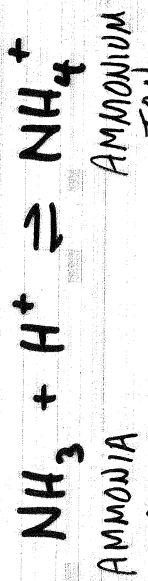
$$K_w = [\text{H}^+][\text{OH}^-]$$

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

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

$$-\log[\text{OH}^-] = 14.0 - \text{pH}$$

AMMONIA STRIPPING & pH



VOLATILE NONVOLATILE

$$\frac{[\text{NH}_4^+]}{[\text{NH}_3] + [\text{NH}_4^+]} = 10^{9.2} \quad \frac{[\text{NH}_3]}{[\text{NH}_3] + [\text{NH}_4^+]} = \frac{1}{1 + 10^{9.2 - \text{pH}}}$$

FRACTION THAT'S NH_3

$$= \frac{1}{1 + \frac{[\text{NH}_4^+]}{[\text{NH}_3]}} = \frac{1}{1 + 10^{9.2 - \text{pH}}}$$

pH	$\frac{[\text{NH}_3]}{[\text{NH}_3] + [\text{NH}_4^+]}$
4	0.000005
6	0.0005
8	0.052
9	0.35
10	0.85
12	0.99

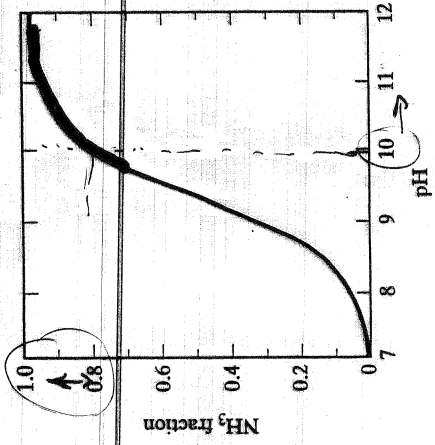


FIGURE 2.3 Dependence of the ammonia fraction on pH (Example 2.8).

SOLUBILITY PRODUCT

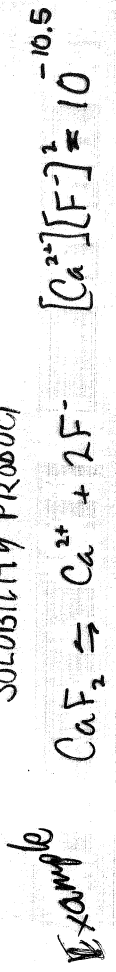


$$\frac{[\text{A}]^a [\text{B}]^b}{\text{AB-solid}} = K$$

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

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

SOLUBILITY PRODUCT



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

$$[\text{F}^-] = 2s \quad [\text{Ca}^{2+}] = 2 \times 10^{-4} \text{ M} \quad [\text{F}^-] = 4 \times 10^{-4} \text{ M}$$

TABLE 2.3 Selected solubility-product constants at 25°C

Equilibrium equation	K_{sp} at 25°C	Significance in environmental engineering
$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	5×10^{-9}	Hardness removal, scaling
$\text{CaSO}_4 \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-}$	2×10^{-5}	Flue gas desulfurization
$\text{Cu(OH)}_2 \rightleftharpoons \text{Cu}^{2+} + 2\text{OH}^-$	2×10^{-19}	Heavy metal removal
$\text{Al(OH)}_3 \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-$	1×10^{-32}	Coagulation
$\text{Ca}_3(\text{PO}_4)_2 \rightleftharpoons 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$	1×10^{-27}	Phosphate removal
$\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-$	3×10^{-11}	Fluoridation

Source: Sawyer et al. (1994).

