Chem Rxs, Stoich__________ Z Ch 2.9, 4; H Ch 1-2, 1-3, 7-1, 7-2, 16-4–16-6

"The world of chemical events is like a stage on which scene after scene is enacted in a continuous succession. The players on this stage are the elements. To each of them is assigned a characteristic role, either that of supernumerary or that of an actor playing a part."

Clemens Alexander Winkler, 1897

Almost all the chemical processes which occur in nature ... take place between substances in solution." **Friedrich Wilhelm Ostwald**, 1890
(Nobel Prize for Chemistry in 1909 "in recognition of his work on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction".)

4.4 - Types of Chemical Reactions

dissolution reactions (solvent, solute) - two (or more) substances form homogeneous mixture; dispersion on the level of individual molecules or ions

precipitation reactions - a substance exceeds its solubility in another, ppt

NO QUIZ TODAY

REVIEW FROM WEDNESDAY

Dissolution Reactions

$CH_3CH_2OH(\textit{l}) \rightarrow CH_3CH_2OH(\boldsymbol{aq})$

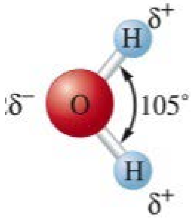
molecular compounds in water (*e.g.*, solid urea dissolving)

$$H_2NCONH_2(\boldsymbol{s}) \rightarrow H_2NCONH_2(\boldsymbol{aq})$$

ionic compounds in water **(dissociation, ionization)**

$$Na_2CO_3(\boldsymbol{s}) \rightarrow 2Na^+(\boldsymbol{aq}) + CO_3^-(\boldsymbol{aq})$$

water is polar



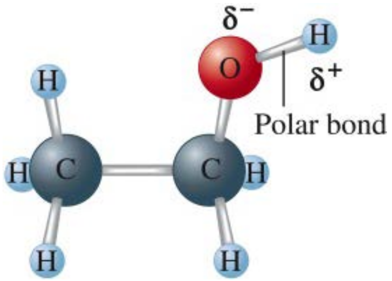
water is polar – unequal charge distribution

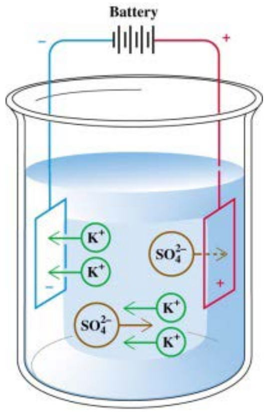
electrolytes (conduct electricity better than pure water)

strong: $Na_2CO_3(aq)$, $HCl(aq)$

weak (produce less ions => lower conductivity): ammonia, acetic acid

nonelectrolyte: ethanol, sugar





REVIEW FROM WEDNESDAY

Dissolution Reactions

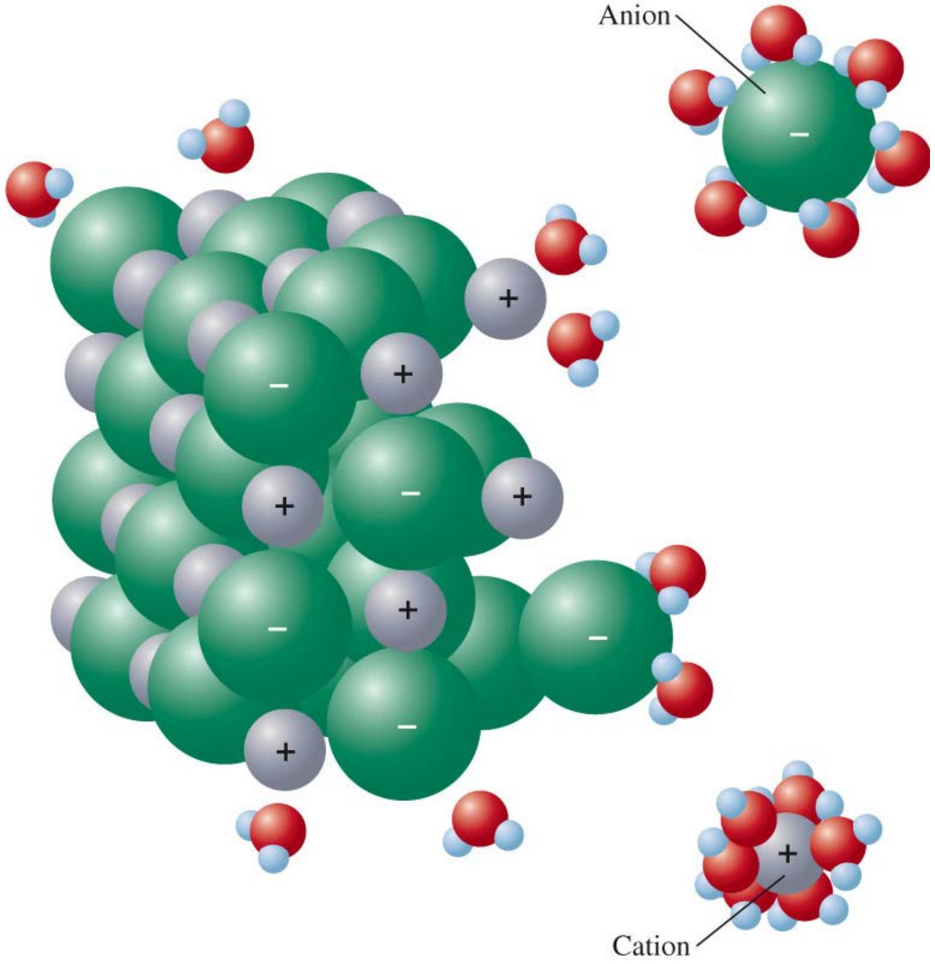


FIG II – Dissolution of NaCl in Water

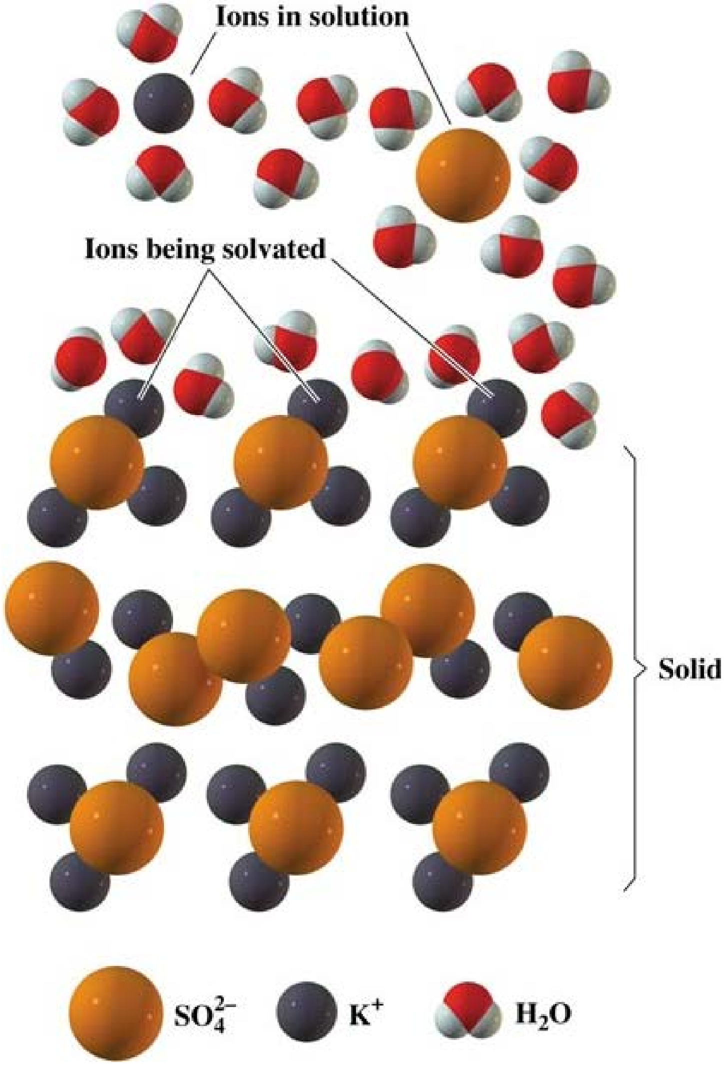


FIG I – Dissolution of K_2SO_4 in Water

Stoichiometry of Reactions in Solution

How to express composition: solute A + solvent = solution

mass percent = mass A / mass solution x 100

mole fraction, X_A = moles A / moles of solution

molarity, M_A = moles of A / 1 L of solution

molality, m_A = moles of A / 1 kg of solvent (later)

Molarity – Measuring Atoms in Solution

M = *n* / L

REVIEW FROM WEDNESDAY

Solutions

EX 2. What is the molarity of pure water? (M_{H2O} = 18.0152 g mol^{-1}, d = 1.00 g cm^{-3})

M = n / L how many moles of water are in a L? d = 1.00 g cm^{-3} =>

1000 g/L => M = (1000 / 18.0152) / L

= **55.5 M**

EX 3. What mass of silver nitrate is needed to make 100. mL of a 0.100 M $AgNO_3$ solution? (M_{AgNO3} = 169.874 g mol^{-1})

M = n / L = (m / M) / L

0.100 = (m / 169.874) / 0.100

=> m = **1.70 g**

REVIEW FROM WEDNESDAY

Diluting Solutions

When you **dilute or mix** solutions the total **number of moles of solute does not change** (1 is initial) $n_1 = M_1V_1 = n_2 = M_2V_2$ (2 is final)

EX 4. What is the molarity of the solution prepared by adding 29.0 mL of 17.4 M acetic acid to a 500-mL volumetric and filling with distilled water?

$$\boldsymbol{n_1 =} M_1V_1 = n_2 = M_2V_2 \Rightarrow M_2 = \boldsymbol{M_1V_1 / V_2}$$

$$= 29.0\ \mathbf{mL}\ (17.4) / 500\ \mathbf{mL} \quad \textbf{RATIO}$$

$$= 1.0092 \Rightarrow \mathbf{1.01\ M}$$

EX 5. How would you prepare 1.5 L of 0.10 M H_2SO_4 from a 16 M supply?

$$V_1 = M_2V_2 / M_1$$

$$= 0.10(1.5) / 16$$

$$= 0.0094\ \text{L} = \mathbf{9.4\ mL}$$

Mixing Solutions

When you **dilute or mix** solutions the total **number of moles of solute does not change**

$$n_{tot} = n_1 + n_2 = \mathrm{M}_1V_1 + \mathrm{M}_2V_2 = \mathrm{M}(V_1 + V_2)$$

EX 6. What is the molarity of the sodium chloride solution obtained from mixing 53 mL of 0.52 M NaCl with 62 mL of 0.47 M NaCl?

$$\mathrm{M} = [\,53(0.52) + 62(0.47)\,] / (53 + 62) = \mathbf{0.49\ M}$$

makes sense, between 0.47 and 0.62 M

REVIEW FROM WEDNESDAY

Density in Molarity Calculations

EX 7. A solution which is 5.50% (by mass) sulfuric acid (M = 98. 0778) has a density of 1.0352 g cm^{-3}. What is the molarity of the solution?

the power of ratios!

assume 100 g of solution

$$(5.50\text{ g }H_2SO_4 / 100\text{ g sol'n})\ (1\text{ mol }H_2SO_4 / 98.0778\text{ g }H_2SO_4)$$

$$\times\ (1.0352\text{ g sol'n} / 1\text{ cm}^3\text{ sol'n})\ (1000\text{ cm of sol'n} / \text{L sol'n})$$

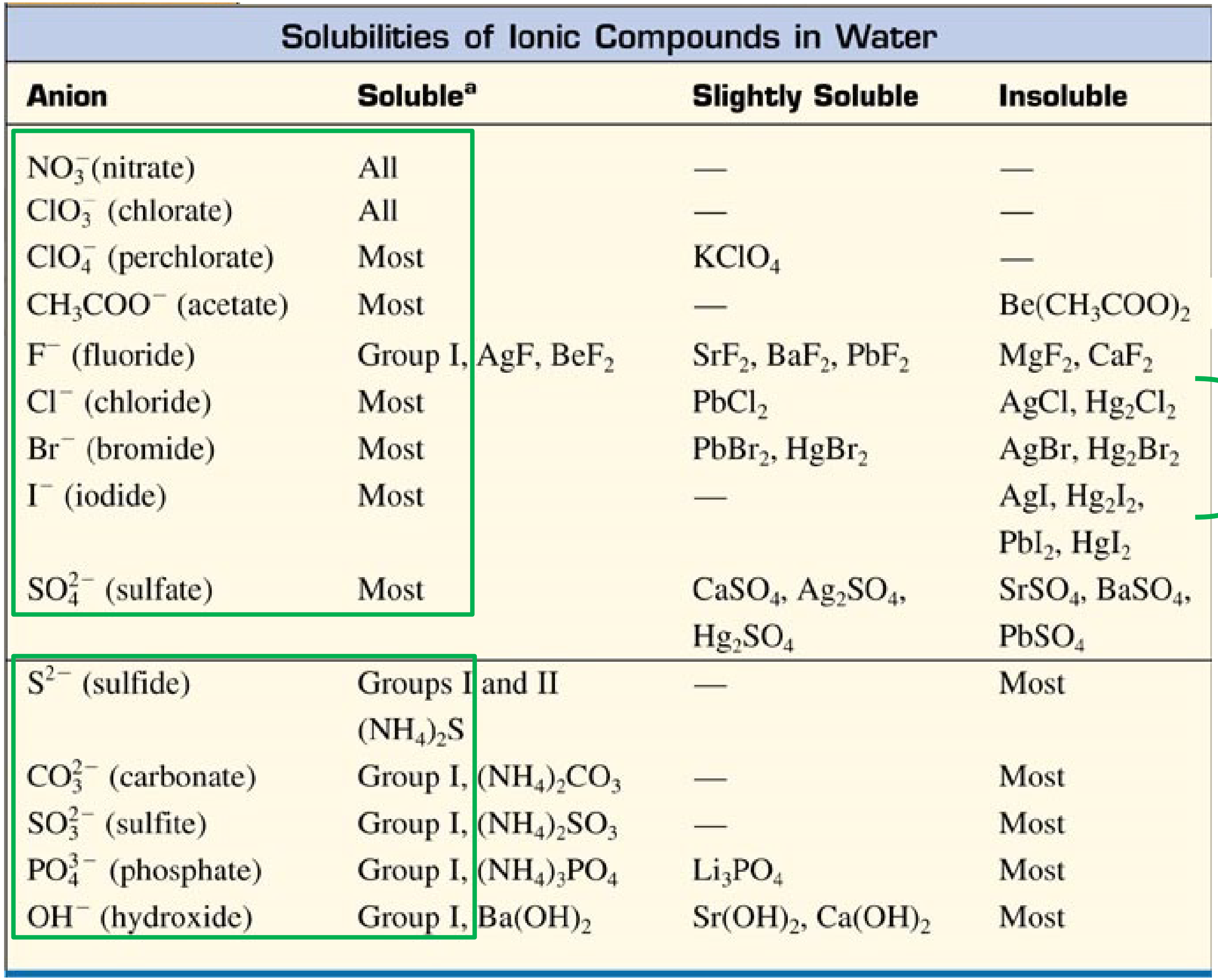
$$= \mathbf{0.581\ M}$$

Precipitation Reactions

STRATEGY (do not memorize solubility tables)

- write down formulas of reactants
- identify nature of reactants in solution (if ionic, what ions are in solution)
- consult solubility table for combination of cations/anions that will precipitate
- write balanced equation
- write total ionic equation
- write net ionic equation - omits spectator ions - **CHEMISTRY**

Solubility Rules



Solubilities of Ionic Compounds in Water

Anion	Soluble[a]	Slightly Soluble	Insoluble
NO_3^- (nitrate)	All	—	—
ClO_3^- (chlorate)	All	—	—
ClO_4^- (perchlorate)	Most	$KClO_4$	—
CH_3COO^- (acetate)	Most	—	$Be(CH_3COO)_2$
F^- (fluoride)	Group I, AgF, BeF_2	SrF_2, BaF_2, PbF_2	MgF_2, CaF_2
Cl^- (chloride)	Most	$PbCl_2$	$AgCl$, Hg_2Cl_2
Br^- (bromide)	Most	$PbBr_2$, $HgBr_2$	$AgBr$, Hg_2Br_2
I^- (iodide)	Most	—	AgI, Hg_2I_2, PbI_2, HgI_2
SO_4^{2-} (sulfate)	Most	$CaSO_4$, Ag_2SO_4, Hg_2SO_4	$SrSO_4$, $BaSO_4$, $PbSO_4$
S^{2-} (sulfide)	Groups I and II $(NH_4)_2S$	—	Most
CO_3^{2-} (carbonate)	Group I, $(NH_4)_2CO_3$	—	Most
SO_3^{2-} (sulfite)	Group I, $(NH_4)_2SO_3$	—	Most
PO_4^{3-} (phosphate)	Group I, $(NH_4)_3PO_4$	Li_3PO_4	Most
OH^- (hydroxide)	Group I, $Ba(OH)_2$	$Sr(OH)_2$, $Ca(OH)_2$	Most

Group I, NH_4^+ always soluble

Ag^+
Hg_2^{2+}

Precipitation Reactions

For example: if aqueous solutions of sodium chloride and silver nitrate were mixed, the solubility table identifies silver chloride as an insoluble species so

balanced equation:

$$\mathrm{NaCl}(aq) + \mathrm{AgNO_3}(aq) \rightarrow \mathrm{AgCl}(s) + \mathrm{NaNO_3}(aq)$$

total ionic equation: [never break apart (*s*), (*l*), (*g*)]

$$\mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq) + \mathrm{Ag^+}(aq) + \mathrm{NO_3^-}(aq) \rightarrow$$

$$\mathrm{AgCl}(s) + \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq)$$

net ionic equation (contains the **CHEMISTRY**):

$$\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \rightarrow \mathrm{AgCl}(s)$$

Precipitation Reactions

EX 8. Aqueous solutions of iron(III) bromide and potassium sulfide are mixed. Write a net ionic equation for the reaction.

balanced equation:

$$2\ FeBr_3(aq)\ +\ 3\ K_2S(aq)\ \rightarrow\ Fe_2S_3(s)\ +\ 6\ KBr(aq)$$

total ionic equation:

$$2\ Fe^{2+}(aq)\ +\ 6\ Br^{-}(aq)\ +\ 6\ K^{+}(aq)\ +\ 3\ S^{2-}(aq)\ \rightarrow\ Fe_2S_3(s)\ +\ 6\ K^{+}(aq)\ +\ 6\ Br^{-}(aq)$$

net ionic equation (contains the **CHEMISTRY**):

$$2\ Fe^{2+}(aq)\ +\ 3\ S^{2-}(aq)\ \rightarrow\ Fe_2S_3(s)$$

Precipitation Reactions

EX 9. Aqueous solutions of sodium hydroxide and magnesium chloride are mixed. Write a net ionic equation for the reaction.

balanced equation:

$$2\ \mathrm{NaOH}(aq) + \mathrm{MgCl_2}(aq) \rightarrow \mathrm{Mg(OH)_2}(s) + 6\ \mathrm{NaCl}(aq)$$

total ionic equation:

$$2\ \mathrm{Na^+}(aq) + 2\ \mathrm{OH^-}(aq) + \mathrm{Mg^{2+}}(aq) + 2\ \mathrm{Cl^-}(aq) \rightarrow$$
$$\mathrm{Mg(OH)_2}(s) + 2\ \mathrm{Na^+}(aq) + 2\ \mathrm{Cl^-}(aq)$$

net ionic equation (contains the **CHEMISTRY**):

$$\mathrm{Mg^{2+}}(aq) + 2\ \mathrm{OH^-}(aq) \rightarrow \mathrm{Mg(OH)_2}(s)$$

"There are three kinds of lies: lies, damned lies, and **statistics**." Benjamin Disraeli, 1895

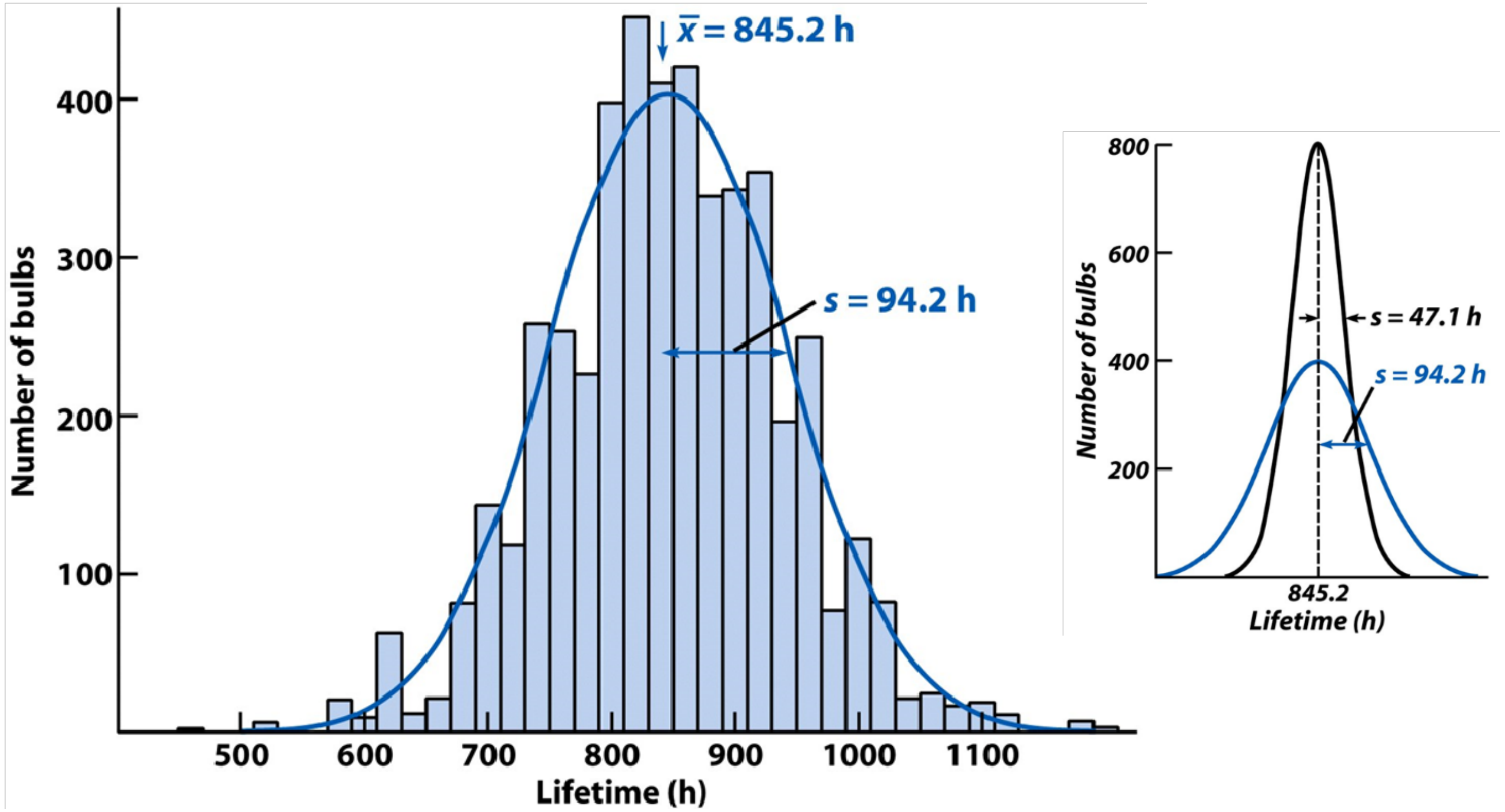
Statistics

H_Exp 5 (next week)

H Ch 4

H 4-1 - Gaussian Distribution

Central Limit Theorem – random variable



H 4-6 – Grubbs Test

To determine whether a particular data point can be excluded based upon its questionable veracity, form the Grubbs statistic, *G*.

$$G_{\text{calculated}} = \frac{|x_{\text{questionable}} - \langle x \rangle|}{s}$$

If $G_{\text{calculated}} > G_{\text{table}}$ then the point can be excluded with the chosen confidence level (here 95%). The mean and standard deviation will need to be recalculated. Hint: generally do not exclude a data point unless you are certain that an error occurred in its measurement. **Never** exclude more than one point. Always use a value of *G* of at least a 95% confidence level.

$G_{\text{calc}} < G_{\text{table}}$ => do not drop point

$G_{\text{calc}} > G_{\text{table}}$ => drop point

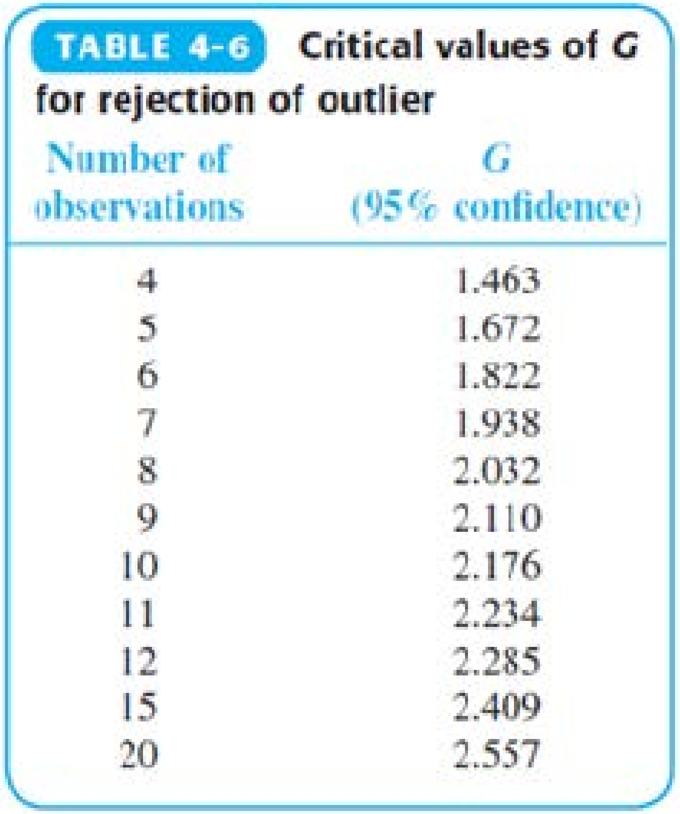


TABLE 4-6 Critical values of *G* for rejection of outlier

Number of observations	*G* (95% confidence)
4	1.463
5	1.672
6	1.822
7	1.938
8	2.032
9	2.110
10	2.176
11	2.234
12	2.285
15	2.409
20	2.557

H 4-2 – *F* Test: Comparison of Standard Deviations

To compare the standard deviations of two different sets of measurements to determine if they are or are not statistically the same

n_1 measurements, $<x_1>$ mean, s_1 standard deviation
n_2 measurements, $<x_2>$ mean, s_2 standard deviation

H 4-2 – *F* Test: Comparison of Standard Deviations

To compare the standard deviations of two different sets of measurements to determine if they are or are not statistically the same

n_1 measurements, $\langle x_1 \rangle$ mean, s_1 standard deviation
n_2 measurements, $\langle x_2 \rangle$ mean, s_2 standard deviation

determine

$$F_{\text{calculated}} = (s_1 / s_2)^2 \text{ where } F \geq 1$$

F_{table} = FINV(0.05,dof1,dof2), dof1 = $n_1 - 1$, dof2 = $n_2 - 1$

EXCEL

H 4-2 – *F* Test: Comparison of Standard Deviations

To compare the standard deviations of two different sets of measurements to determine if they are or are not statistically the same

n_1 measurements, $<x_1>$ mean, s_1 standard deviation
n_2 measurements, $<x_2>$ mean, s_2 standard deviation

determine

$$F_{\text{calculated}} = (s_1 / s_2)^2 \text{ where } \boldsymbol{F \geq 1}$$

$$F_{\text{table}} = \underset{\textbf{EXCEL}}{\text{FINV}}(0.05,\text{dof1},\text{dof2}),\ \text{dof1} = n_1 - 1,\ \text{dof2} = n_2 - 1$$

$F_{\text{calc}} < F_{\text{table}}$ => statistically the same at 95% confidence
$F_{\text{calc}} > F_{\text{table}}$ => statistically different

H 4-4 – Case 2 : Comparing Means

To compare the means of two different sets of measurements to determine if they are statistically the same or different

n_1 measurements, $\langle x_1 \rangle$ mean, s_1 standard deviation
n_2 measurements, $\langle x_2 \rangle$ mean, s_2 standard deviation

H 4-4 – Case 2 : Comparing Means

To compare the means of two different sets of measurements to determine if they are statistically the same or different

n_1 measurements, $\langle x_1 \rangle$ mean, s_1 standard deviation
n_2 measurements, $\langle x_2 \rangle$ mean, s_2 standard deviation

if $F_{\text{calc}} < F_{\text{table}}$

H 4-4 – Case 2 : Comparing Means

To compare the means of two different sets of measurements to determine if they are statistically the same or different

n_1 measurements, $<x_1>$ mean, s_1 standard deviation
n_2 measurements, $<x_2>$ mean, s_2 standard deviation

if $F_{\text{calc}} < F_{\text{table}}$

determine s_{pooled}, t_{calc}

t_{table} = TINV(0.05,**dof**)

EXCEL

$$t_{\text{calculated}} = \frac{|<x_1> - <x_2>|}{s_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

$$s_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$$

H 4-4 – Case 2 : Comparing Means

To compare the means of two different sets of measurements to determine if they are statistically the same or different

n_1 measurements, $<x_1>$ mean, s_1 standard deviation
n_2 measurements, $<x_2>$ mean, s_2 standard deviation

if $F_{\text{calc}} < F_{\text{table}}$

determine s_{pooled}, t_{calc}

t_{table} = TINV(0.05,**dof**)

EXCEL

$t_{\text{calc}} < t_{\text{table}}$ => stat. the same
$t_{\text{calc}} > t_{\text{table}}$ => stat. different

$$t_{\text{calculated}} = \frac{|<x_1> - <x_2>|}{s_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

$$s_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$$