ANALYTICAL CHEMISTRY STUDY GUIDE

CHAPTER 1 CHEMICAL MEASUREMENTS

Concentrations

I. M —> Molarity, expressed in mol/L

II. F —> Formality, expressed in mol/L

III. N —> Normality, expressed in equivalent/L

ie. HCl — — — —-> H+ + Cl- can be expressed 1M or 1N

Exercise: Calculate the formal concentration of 5.0g NaCl in 1.0L of water.

1:1 ratio

$$5.0gNaCl \times \frac{1mol}{59.44g/mol} = 0.086F$$

%Composition

I. Percent by Weight, %wt:

II. Percent Volume , %vol

III. Percent weight by volume

$$\frac{solute(g)}{total(g)} \times 100 \qquad \frac{solute(L)}{total(L)} \times 100 \qquad \frac{solute(g)}{volume(L)} \times 100$$

Exercise: How many grams of sodium sulfate (MM 119g/mol) should be weighed out to prep 500mL of 0.100M solution?

MM $_{\text{sodium sulfate}}$= 142g/mol

$$142g/mol \div \frac{500mL}{1.0L} \times 0.100M$$
$$= 7.10g$$

How much sulphuric acid (94 wt%, density 1.831g/mol) are needed to prepare 1.00L of a 0.100M solution?

MM= 98.079g/mol

0.1 mol needed

$$0.1mol \times \frac{98.1g}{mol} = 9.81g$$
$$9.81g \times \frac{100}{94} = 10.436g$$

Dilutions

$$M1V1 = M2V2$$
$$C1V1 = C2V2$$

ie. 1:5 dilution of HCl, this refers to 1 vol HCl + 4 vol water

Exercise: How many litres of concentrated 12.1N HCl are required to prepare 0.5L of 3.0M HCl?

$$12.1M \times V1 = 3.0M \times 0.5L$$
$$V1 = 0.1L$$

To try on own… The content of Ni(II) is to be determined in an unknown sample. 160mL of the sample solution are treated with 0.5210g KCN to form $Ni(CN)_4^{2-}$. Calculate the molarity of the Ni(II) solution.

CHAPTER 3 ANALYTICAL ERROR

- A reflection of uncertainty associated with the measurement

Types of Error

I. Systematic Error:
- Reproducible and can be corrected.
- Anything you can classify as hyman error
- Fixed deviation from a true value
- Not easy to find, normally second pair of eyes are required;
  - ie. Badly degraded standard, addition of too much/little reagent, incorrectly calibrated instrument

Remedies:

- *Analyze for a known sample*
- *CRM (certified reference material)*
- *Use alternative method*
- *Use a different analyst*
- *analyze a blank*
- *Round Robin testing*

II. Random Error:

- Cannot be controlled and cannot be fixed
- Random variation within your results i.e.. goes either way too high or too low
- In order to treat data using s tats it must be random error
  - ie. Readings from a scale, electronic noise

Precision and Accuracy

- With only one measurement there is no precision or accuracy.
- One way to calculate precision and accuracy is taking the distances away from the true value — the standard deviation

Absolute Uncertainty

Definition: Margin associated with the measurement.

ie. Buret:

$$\pm 0.02 mL$$

Relative Uncertainty

Definition: the absolute uncertainty divided by the magnitude of the measurement multiple by 100.

$$\frac{Absolute}{Magniture} \times 100 = \_\_\_\_\_ \%$$

Series of Operations —> Total Error

Absolute total error:

$$E_T = \sqrt{E_1^{\,2} + E_2^{\,2} + ... + E_n^{\,2}}$$

Use when we have formal which consists of addition and subtraction. ie. weighing, dissolving, diluting, measuring.

Relative Error:

$$\%E_T = \sqrt{\%E_1^{\,2} + \%E_2^{\,2} + ... + \%E_n^{\,2}}$$

Use with formal consisting od multiplications and division.

Exercise: A solution is prepared by dissolving a 0.2222 +/- 0.0002g KIO_3 with a formula weight 214.0010 +/- 0.0009g/mol, in 50.00 +/- 0.05mL water. Find the molarity and uncertainty.

$$Molarity: \frac{0.2222}{214.0010} \times \frac{1}{0.05L} = 0.0207M$$
$$E_1 = \frac{0.0002}{0.2222} \times 100 = 0.096\%$$
$$E_2 = \frac{0.0009}{214.0010} \times 100 = 0.00042\%$$
$$E_3 = \frac{0.05}{50} \times 100 = 0.1\%$$
$$\%E_T = \sqrt{(0.096)^2 + (0.00042)^2 + (0.1)^2} = 0.135\%$$
$$E_T = 0.00003M$$

Therefore the molarity is 0.0207 +/- 0.00003M.

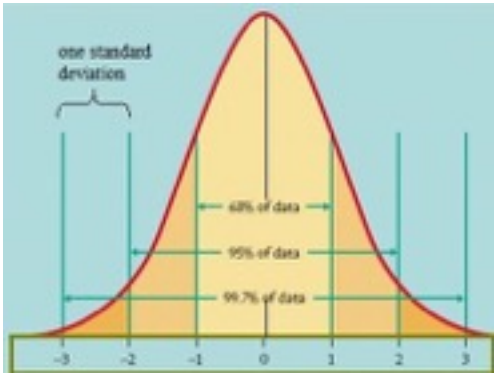
r^2= correlation coefficent

LOD= limit of detection

Aliquot= defined amount being taken out of a larger sample, assuming the sample is homogenous

CHAPTER 4 STATISTICS

- Only with random error present we can assume a normal (Gaussian) distribution.



- Greek lettering is used for population σ vs. s, and latin is used for a sample.
- Choosing a representative sample is important because you're looking to find an average.
- Typically the samples we choose to make conclusions about the population for are an underestimate of the real distribution.

$$\mu = x_{Bar} \pm \frac{ts}{\sqrt{n}}$$

μ is the estimation of the true value, X bar is the average, t is the safety factor, s is the standard deviation, and n is the number of measurements.

- The larger n is the closer s converges to σ and the smaller the safety factor (t) becomes.
- The confidence interval is defined:

$$\frac{ts}{\sqrt{n}}$$

- The degrees of freedom is defined:

$$DOF = n - 1$$

- Gaussian distributions work best with large values of data.

- To approximate the underlying data, it needs to be free of systematic error.

- Recall: The difference between population and a sample, a population includes all elements while a sample is just selected from the population. May or may not be representative of the population. As chemists we always use samples never populations.
  - Populations use greek letters σ, μ
  - Sample's we use $\bar{x}$ and S to denote the Gaussian distribution respectively.
- Samples should be representative of the population

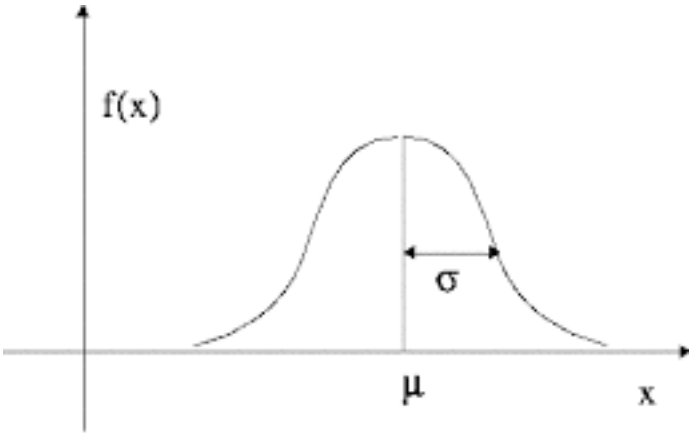


Figure 7. Gaussian (Normal) Probability Distribution Function

- Factors change with respect to the type of population.
- Also note when the samples become very large S become σ

Confidence Interval:

$$\mu = \bar{x} (\pm) ts / \sqrt{n}$$

- Confidence levels are found in the students table, these are correction factors, and denoted with the variable t.
- "ts / √n," together is the confidence interval.
- The larger n, the sample size is, the closer s converges to σ, and the smaller t becomes.

- s is the standard deviation (equation found on equation sheet.)
- Degrees of Freedom is almost the number of measurements. To use the t tables we must be able to find the DOF—> n-1

What Can we do with t-values?

- Is there a significant difference between data sets? ie. one method vs. another?
- Between data and the certified true value

Methods to Determine if the t Values are the same:

1. Comparing the measured $\bar{x}$ with the "true" certified value

$$t_{calc} = (|\bar{x} - \mu| / s)\sqrt{n}$$

- If t_{calc} is larger than $t_{table:}$ Values of $\bar{x}$ and μ are significantly different.
- The t value or the level of confidence (usually 95%) will be given so you can obtain the t value from the table.
- DOF= n-1
- 2. Comparison of measured $\bar{x}$
- Rather than comparing to the true value of t, we are comparing to the mean.

$$t_{calc} = (|\bar{x}_1 - \bar{x}_2| / s_{pooled})\sqrt{n_1 n_2 / n_1 + n_2}$$

S-pooled is a weighted standard deviation:

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

- DOF= n_1+n_2 -2
- If t-calc is larger than t-table than the two results are significantly different.

3. Comparison of Individual Differences

- Two methods, single measurements of different samples (no duplicates)

Do the methods give identical answers?

- Always when reading a problem if there are duplicates use method 2, if very little sample was available for measurements its a case 3— aka this method.
- Compute differences for two methods for one sample
- Compute mean difference (đ) from all n sample differences:

$$Sđ = \sqrt{\Sigma(di-đ)^2/n-1}$$

To find the value of t:

$$t_{calc} = đ/sd\ (\sqrt{n})$$

- DOF= n-1
- If t-calc is greater than t-table then results are significantly different.

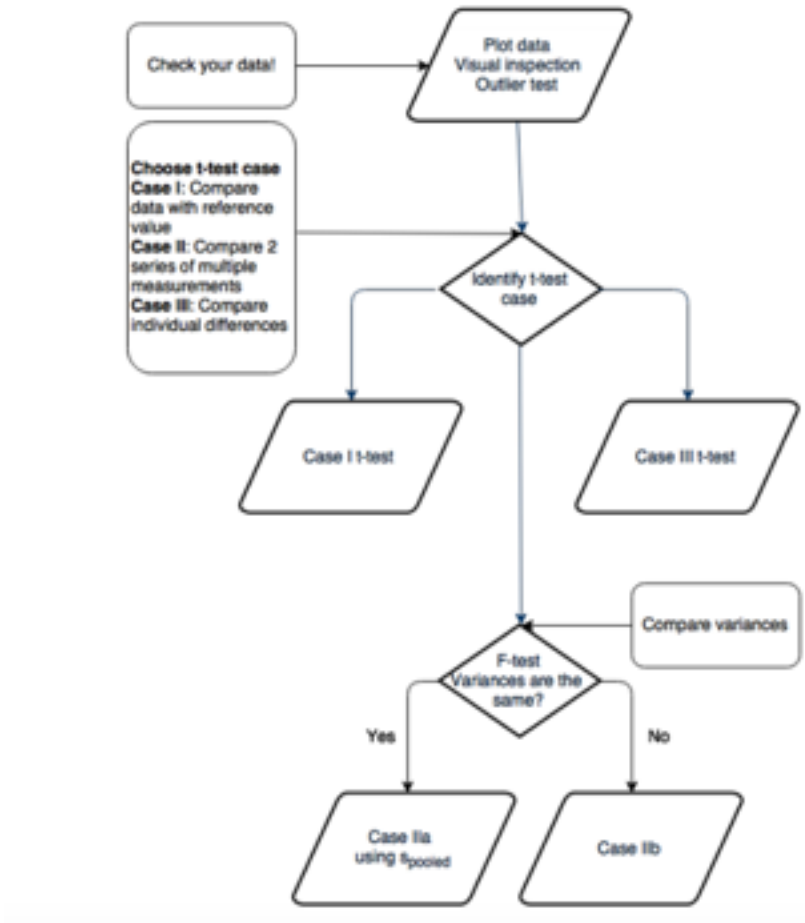
Data Assessment:

i. Visualization

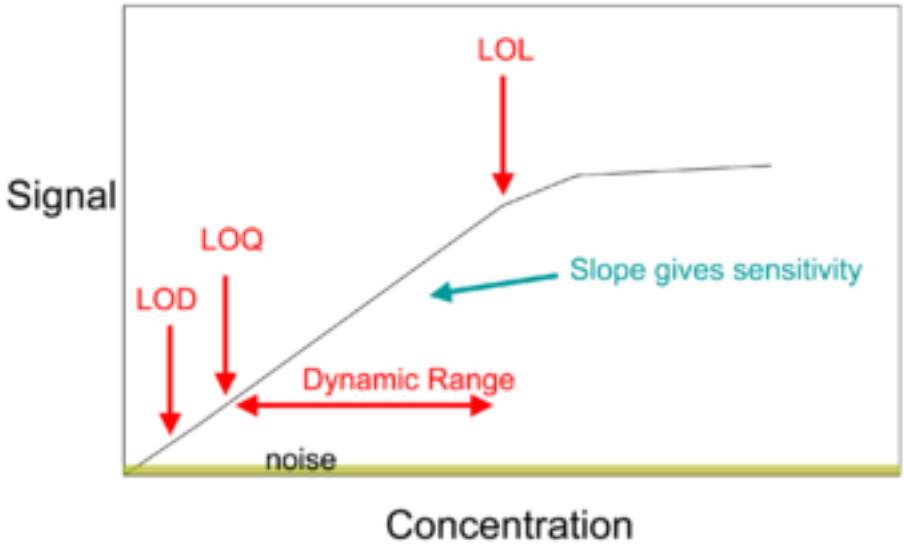
ii. Q-test for bad data

- Q test, tests for outliers, arrange data in numerical order and then look for any outrageous points. If the Q-calc is significant than you may take out the bad data point. You can find these numbers in the equation sheet or in the textbook.

iii. Calculate Q-calc— — — gap/range



CHAPTER 5 CALIBRATION METHODS



Above is a calibration curve. The sensitivity in a calibration curve drops as we approach saturation. That is why there is a visible change in slope.

Dynamic Range:

Definition: observing a signal with a change of concentration. Sensitivity changes

Linear Range:

Definition: typically we use this part of the curve y=mx+b, fixed slope range. Always work in the linear range from lowest-highest standard. We typically solve for x, and unknown concentration

Sensitivity:

Definition: slope of calibration curve, change in signal = change in analyze concentration

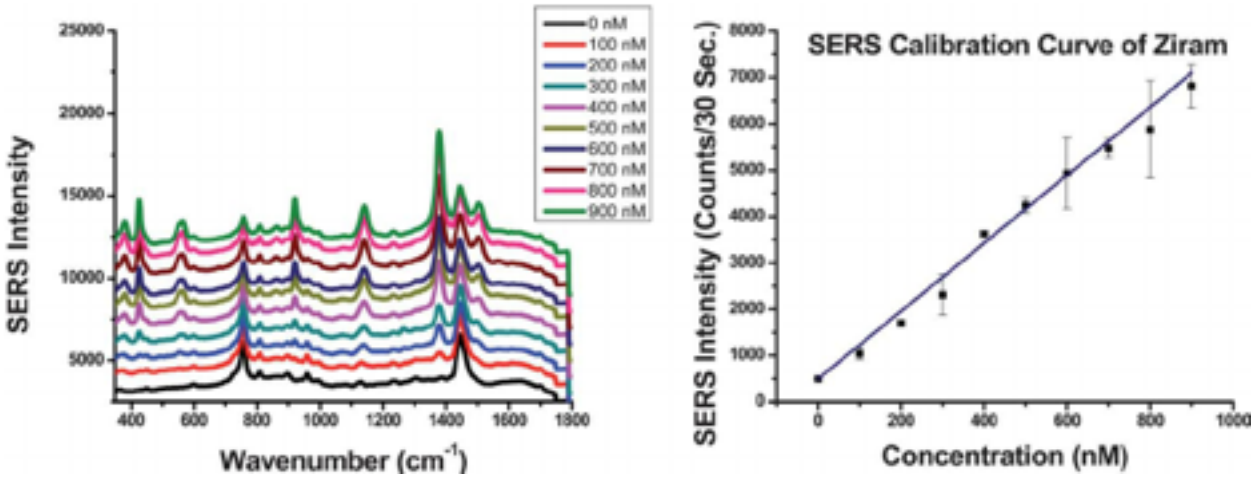
Matrix:

Definition: refers to everything in the sample other than analyte.

Spike:

Definition: also called a fortification, is known quantity of analyte added to the samples to test whether the response to the spike is the same that expected from a calibration curve.

Representing Error:



Here we have a calibration curve which represents error via error bars on the curve. We are making the assumption that the concentration error is less than the measurement error.

Detection Limit:

Definition: the concentration of analyte that gives a signal equal to three times the standard deviation of a signal from a blank.

$$DetectionLimit = \frac{3s}{m}$$

Linear Regression:

Definition: Minimizing the squared distances between the calculated average of the measurements and the estimate by the calibration line.

Standard deviation about Regression:

$$Sr = \sqrt{\sum_i \frac{(y_i - (b + mx_i))^2}{n-2}}$$

Standard deviation of Calculated Result:

$$Sc = \frac{Sr}{m}\sqrt{\frac{1}{M} + \frac{1}{N} + \frac{\overline{Y}_c - \overline{Y}}{m^2 S_{xx}}}$$

Where,

m= slope of regression line

Sr= standard deviation about regression

M= number of unknown measurements

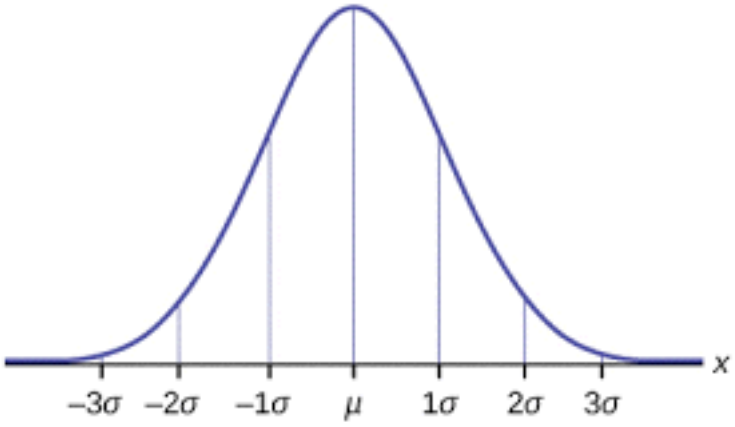
N= number of standard measurements

Ybar,c=Average signal of the unknown

Ybar= average signaal of calibration standards

Sxx=(individual concentration -average concentration)^2

Limit of Detection and Limit of Quantification



If you get a signal outside the range, signal blank +3σ_{blank} you can be 99.5% sure its an analytic.

Therefore, the limit of detection can be defined:

$$LOD = signal_{blank} + 3\sigma_{blank}$$

Using the calibration line:

$$Con'c = \frac{signal - signal_{blank}}{slope}$$

This is the same as 3σ/slope.

Limit of Quantification

$$Con'c_{LOQ} = \frac{10\sigma_{blank}}{slope}$$

These characterize lower end of linear range of the calibration curve.

Standard Addition Calibration:

Definition: used to deal with matrix effects which lead to signal enhancement or signal depression. Adds known amount of standard into sample, and re-analyzes.

There is a dilution factor associated with more volume being added

$$[S_i] * \frac{V_a}{V_o}$$

Where Va is volume added of known standard, and Vo is the sample volume.

Internal Standard Method:

Definition: Used to compensate for fluctuations beyond control in the instrument.

1. Add a known amount of non-analyte into sample, blanks and standard.
2. Internal standard must be structurally similar to analyte.
3. Ratio my analyte signal to internal standard signal.

CHAPTER 6 CHEMICAL EQUILIBRIUM

All biochemical processes are in equilibrium.

Recall,

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

and,

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The reaction is favour din K> 1 in the direction as written.

- titration reactions usually have large K values
- In nature, the K values are typically small.

For an Acid Reaction:

$$HA \rightleftharpoons H^+ + A^- \qquad\qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

Concentrations instead of Activities:

- For dilute solutions
- K is unitless
- If were in aqueous solution, the concentration units are Mol/L
- Gases are measured in bar
- Pure solids, liquids, ect. are set to 1, meaning there omitted from the equation.
- This pertains tot he face that there are minimal interactions, an thus for the sake of calculating K we only include the concentrations for dilute aqueous solutions.

Reactions Added Together:

$$K_3 = K_1 \times K_2 = \beta$$

Where Beta is the cumulative equilibrium constant.

- The quotient of unreached equilibrium is denoted Q.
  - Amount of product is still increasing, some reactants are still left, we would use Q here.
- We are assuming thermodynamic equilibrium, note taking into account kinetics (time)
  - Favoured far to the right does not entail the speed of the reaction.

Exercise:

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4{}^{2+}(aq)$$

In the case of a salt which dissolves very little,

$$K = \frac{[Ca^{2+}][SO_4{}^{2+}]}{1} = 2.4 \times 10^{-5}$$

At, K the solubility product (Ksp) has been reached. Everything else will remain undissolved at the bottom of the beaker.

Exercise: How many grams of PbI_2 will dissolve in 0.5L of a) water and b) 0.0634 M NaI?

$$PbI_2(s) \rightleftharpoons Pb^{2+} + 2I^-$$

$$Ksp = 7.9 \times 10^{-9}$$

a)

$$Ksp = 7.9 \times 10^{-9} = [Pb^{2+}][I^-]^2$$
$$Ksp = 7.9 \times 10^{-9} = x \times (2x)^2$$
$$x = 1.3 \times 10^{-3} M$$

Moles in 0.5L (half)

$$= 6.5 \times 10^{-4} mol$$
$$= 0.29 g$$

b)

$$Ksp = 7.9 \times 10^{-9} = [Pb^{2+}] \times (0.0634)^2$$
$$[Pb^{2+}] = 1.97 \times 10^{-6} M$$

Moles in 0.5

$$= 9.83 \times 10^{-7} mol$$
$$= 4.5 \times 10^{-4} g$$

Exercise: Is it possible to separate 99.90% of 0.020M Mg^{2+} from 0.10M Ca^{2+} without co-precipitation of $Ca(OH)_2$ by addition of NaOH?

$$Ksp(Ca(OH)_2) = 6.5 \times 10^{-6}$$
$$Ksp(Mg(OH)_2) = 7.1 \times 10^{-12}$$

0.1% of 0.020:

$$= 2.0 \times 10^{-5}$$

$$[Mg^{2+}][OH^-]^2 = 7.1 \times 10^{-12}$$
$$2.0 \times 10^{-5}[OH^-]^2 = 7.1 \times 10^{-12}$$
$$[OH^-] = 5.96 \times 10^{-4} M$$

Is this concentration enough to trigger precipitation of $Ca(OH)_2$?

$$Q = 0.1(5.96 \times 10^{-4})^2$$
$$= 3.55 \times 10^{-8} < 6.5 \times 10^{-6}$$

Therefore Calcium will not precipitate, and it is possible to separate 99.9% without co-precipitation.

Acids and Bases

- Acids are proton donors
- Bases are proton acceptors.
- The result of reacting an acid and a base is salt and water.
- Salts always dissolve into their ions.
- Water is autoprotolyic meaning it can act as both an acid an a base.

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$Kw = [H^+][OH^-] = 1.0 \times 10^{-14}$$

- Free H+ is a measure of the acidity in a solution.
  - Knowing the pH is essential

$$pH = -\log_{10}[H^+]$$

- For a neutral conditions:
- pH=7 $$[H^+] = [OH^-]$$

- For a concentrated strong acid you cannot calculate Ka because the concentration of the reactant/ acid is zero, and the Ka becomes very large and undefined.

Strong Acids	Strong Bases
HCl	NaOH
HBr	LiOH
HNO_3	KOH
HI	RbOH
$HClO_4$	CsOH
H_2SO_4	NH_4OH

HF because Flourine is the most electronegative element fully dissolves, but immediately forms an ion pair (adduct) making it look or act like a weak acid.

- We can normally neglect waters contribution to acids and bases since its contribution of H+ is so little.
- This is mostly true when working with strong acids and bases since water can also act was a weak acid or base.

$$pKw = pH + pOH$$

Exercise: if [OH-] = 1.0 x 10^{-9}M what is the pH?

$$14 - 9 = 5$$
$$\frac{10^{-14}}{10^{-9}} = 10^{-5}$$

(A) Strong Acids — Strong Electrolytes

$$HBr \rightleftharpoons H^+ + Br^-$$

If 0.1M of HBr is used, 0.1M of H+ and 0.1M of Br- will be the product
This is because strong acids dissociate completely.

(B) Weak Acids— Weak Electrolytes

$$HAc \rightleftharpoons H^+ + Ac^-$$

Here there is only ~5% dissociation of H+ which is the only contributor to the pH.

$$Ka = \frac{[H^+][Ac^-]}{[HAc]}$$
$$Ka = \frac{x^2}{F - x}$$

Larger the Ka value is the smaller reactant volume is which means more dissociation which results in the equilibrium favoured to the right.
The smaller Ka means the equilibrium is favoured to the left.

If F> 100 Ka then,

$$Ka = \frac{x^2}{F}$$

We can neglect the x in the denominator because it is not significant.

pH Calculations:

(A) Strong Acids/Bases

—> pH of 0.1M HBr

$$[H+] = 0.1M = 10^{-1}M$$
$$pH = 1$$

—>pH of 0.1M KOH

$$pOH = 1$$
$$pH = 14 - 1 = 13$$

—> [KOH]= 0.0000001M

$$[OH-] = 10^{-8}M$$
$$pOH = 8$$
$$pH = 14 - 8 = 6$$

Bases cannot be acidic? Apply systematic treatment of equilibrium

i. Charge balance

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

ii. Mass balance

$$[K+] = 10^{-8}M$$

iii. Equilibrium equations

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

$$[H+] = x$$
$$[OH-] = [K+] + [H+] = 1.0 \times 10^{-8}$$
$$Kw = x(1.0 \times 10^{-8} + x)$$
$$10^{-14} = 1 \times 10^{-8} x + x^2$$
$$x^2 + (1 \times 10^{-8})(x) - 10^{-14} = 0$$

Solve quadratic equation,

$$x_1 = 9.6 \times 10^{-9}$$

And disregard negative root that arose from quadratic equation.

$$[H+] = 9.6 \times 10^{-9}$$
$$pH = 7.02$$