

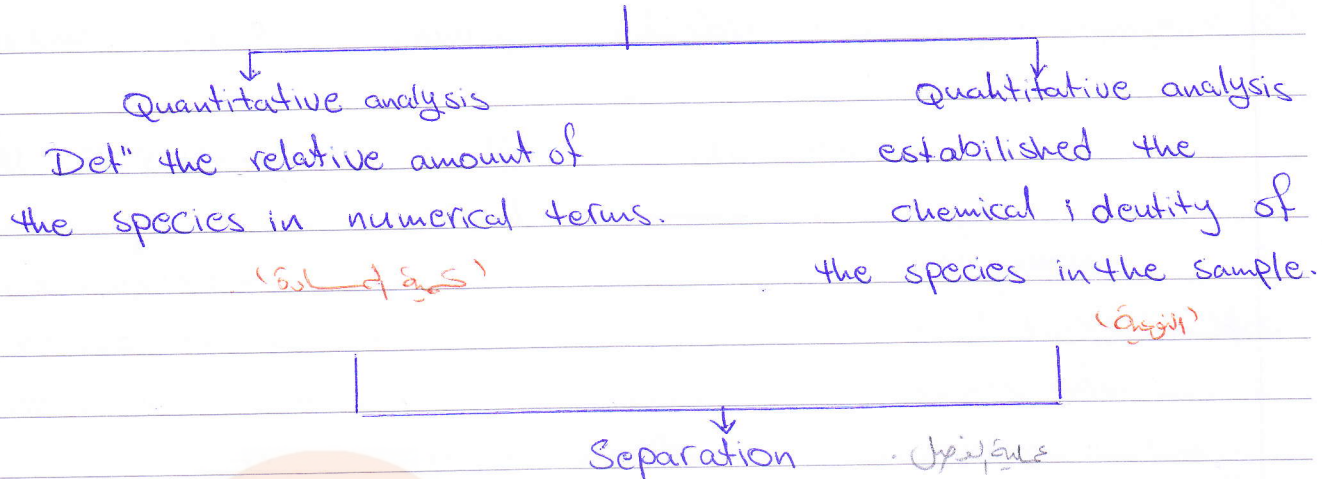
دفتري كيمياء تحليلية

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* Detⁿ → Determination.

The Nature of analytical chemistry.



* [IA] The role of analytical chemistry analytical chemistry applied in :- 'Industry, medicine, all sciences...etc'.

[IB] Quantitative analytical methods :-

① Gravimetric method → detⁿ the mass of the analyte.
(قياس الكتلة)

② Volumetric method :- measure the volume of solution containing reagents. (قياس الحجم)

③ Electroanalytical method → measure the electrical properties (resistance, current, potential...)

④ Spectroscopic method → measure the inter (Xn) between the electromagnetic radiation and the analyte. (التفاعل)

في جميع الحالات (Nuclear, etc) 'chemical, etc' يجب التعرف على العنصر.

* [IC] Typical Quantitative analysis: 9 steps:-

① choosing method.

depends on the accuracy I need, Cost, complexity of sample. (أدق، أقل، أبسط)

② Acquiring the Sample. (أخذ، جلب، جلبات)

Homogeneous

Can't be distinguish the components.

Heterogeneous.

We can distinguish the components.

- Sampling is collect sample. (أخذ عينة)

- Assay is The proces of determining how much a given sample is the material indicated by it's name.

③ Processing sample:-

[a] preparing samples:-

→ Solid: ↓ size then mix to ensure homogeneous, then stored. (لقد، سائل)

→ liquid: cover and stored.

We cover the liquid to avoid from evaporation.

[b] Defining replicate samples:- (أدق) 'Reliability' running the analysis in the same conditions.

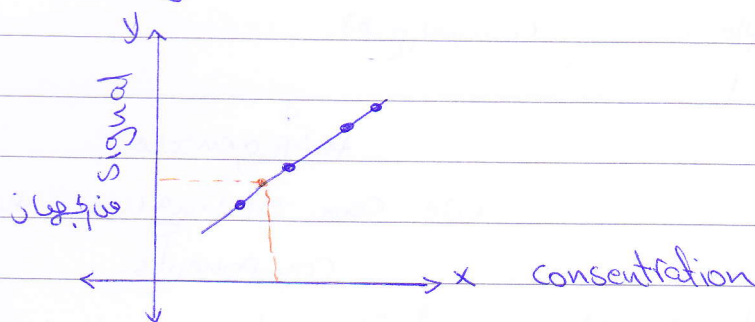
[c] preparing solutions:-

should be homogeneous by: * heating

* stirring. (التهريك) * Adding acids or bases.

- ④ Eliminate interferences :- إزالة التداخل
ex :- precipitate. الترسيب

- ⑤ Calibrating and measuring using standard material (known concentration). [C] :- Concentration



$$C_A = KX$$

C → concentration, K → constant.

- ⑥ Calculating results by computer.

- ⑦ Evaluating results :- by measuring the degree of uncertainty.
(تقدير الأخطاء)

* IID An integral chemical analysis :-
Role for

Feed back control system.

* ex :- Det^{نظام} the [glucose] in blood for diabetic patient?

soln :- ① Desired is blood glucose level < 95 mg/dL.

② Measure the glucose in blood level of your patient.

③ ↑ 95 mg/dL give the patient insulin.

④ Test again after x time.

⑤ "control" = Feedback . (cycle analysis) ^{نظام تحكم}

* Calculations Used in Analytical chemistry...

* [4A-1] :- Some important terms of measurements.

Table [4-1]

S I units

Quantity	unit	ab ↓
mass	kilogram	kg
length	meter	m

* [4A-2] :- The distinction between mass and weight.

- mass → measure of the amount of matter.

- weight → is the force of gravitational attraction between matter and Earth.

** $W = mg$

w: weight

m: mass

g: acceleration due to the gravity.

* [4A-3] :- Mole (M) :- The mass in gram of 1 mole of substance.

$$** \text{Mole} = \frac{\text{Mass (g)}}{\text{Molar Mass (g/mole)}}$$

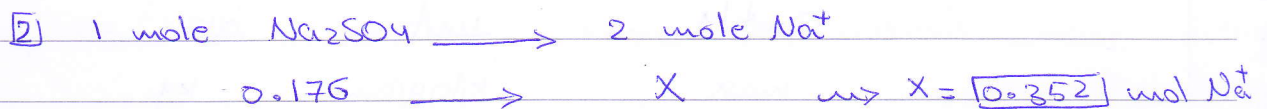
* e.x :- How many moles and ml moles of CH_3COOH (Acetic) are contained in (2)g ?

$$M = \frac{2}{(12 \times 2) + (1) + (2 \times 16)} = \frac{1}{30} \Rightarrow \# \text{ Moles} = [0.0333] \text{ mole}$$

$$= [33] \text{ ml mole.}$$

* How many grams of Na^+ (22.99 g/mol) are contained in (26)g Na_2SO_4 (142.0 g/mol) ??

Solu :- ① # mol $\text{Na}_2\text{SO}_4 = \frac{26 \text{ g}}{142 \text{ g/mole}} = \boxed{0.176}$ mole Na_2SO_4



$0.352 = \frac{X}{22.99} \longrightarrow X = \boxed{8.1}$ g Na^+ .

* [4B] :- Solutions and their [] :-

[4B-1] :- [] of solution.

** Molar concentration = $\frac{\# \text{ of mole}}{\text{Volume (L)}} = M$.

* e.x :- calculate the Molar concentration of ethanol in an aq. solution contain (2.3)g of $\text{C}_2\text{H}_5\text{OH}$ (46.07 g/mol) in 3.5 L solution ??

Solu :- ① [] = $\frac{\# \text{ mole}}{V} = \frac{(2.3 \text{ g})}{(46.07 \text{ g/mol})} \div 3.5 \text{ (L)}$
 $= \boxed{0.0143}$ M.

* Analytical molarity: The total # of moles of solute in 1L of solution. مقدار ذرات کل در یک لیتر

* Equilibrium molarity: The molar concentration of particular species in a solution at equilibrium. التركيز الجزيئي

* e.x:- Calculate the analytical and equilibrium [] of the solute species in a eq. solutions that contain (285 mg) of Cl_3CCOOH (163.4 g/mol) in (10 ml) the acetic acid is 73% ionized in H_2O ??

Solu:- ① $285 \text{ mg} = 0.285 \text{ g}$.

$M = 163.4 \text{ g/mol}$, $V = 0.01 \text{ L}$.

[A] Analytical [] = $\frac{\# \text{ mole}}{V(\text{L})} = \frac{(0.285)/(163.4)}{0.01}$

= $\boxed{0.1744} \text{ mol/L (M)}$.



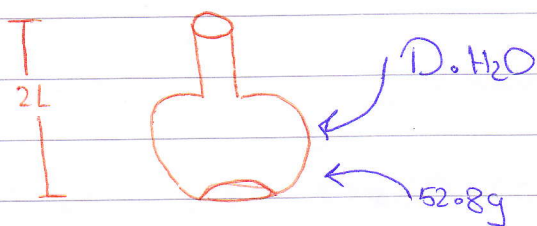
eq. [] = $0.1744 \times \frac{73}{100} = \boxed{0.127} \text{ mol/L} = [\text{A}^-] = [\text{H}^+]$.

* e.x:- Describe the preparation of 2.00L of 0.108 M of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (244.3 g/mol) ??

Solu:- ① $M = \frac{\# \text{ mol}}{V} \Rightarrow \# \text{ mol} = M \times V$

= $0.108 \times 2 = \boxed{0.216} \text{ mol}$

② $\# \text{ mol} = \frac{\text{mass}}{\text{molar mass}} \Rightarrow \text{mass} = 0.216 \times 244.3$
= $\boxed{52.8} \text{ g}$.



* J. Concentrations-

$$① \text{ w/w (weight \%)} = \frac{\text{mass solute}}{\text{mass solution}} * 100\%$$

$$② \text{ v/v (volume \%)} = \frac{\text{volume solute}}{\text{volume solution}} * 100\%$$

$$③ \text{ w/v (weight/volume)} = \frac{\text{Weight solute (g)}}{\text{Volume solution (ml)}} * 100\%$$

unitless

* Only weight depends on Temperature.

* ex:- 5% AgNO_3 w/v?يعني 5 g AgNO_3 dissolves in 100 ml H_2O .* ex:- 70% HNO_3 w/w?يعني 70 g HNO_3 dissolves in 100g Solution.

* part per million , part per billion :-
(ppm) , (ppb).

$$** \quad [] \text{ ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} * 10^6 \quad \rightarrow 1 \text{ ppm} = \frac{\text{mg}}{\text{L}} \quad \text{واحد غرام}$$

$$** \quad [] \text{ ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} * 10^9 \quad \rightarrow 1 \text{ ppb} = \frac{\mu\text{g}}{\text{L}} \quad \text{ميكرو غرام}$$

* e.x:- What is the molarity of K^+ in a solution that contain 63.3 ppm of $K_2Fe(CN)_6$ (329 g/mol)?

Solu:- ① $63.3 \text{ ppm} = \frac{63.3 \text{ mg}}{L} \rightarrow \frac{\text{mol}}{L} ?$

$$\frac{\text{mol}}{L} = \frac{\text{mass}}{L} / \text{molar mass} = \frac{0.0639}{329.3 \text{ g/mol}}$$

$$= [1.922 \times 10^{-4}] \text{ mol/L (M).}$$

② $[K^+] = 3 \times 1.922 \times 10^{-4} = [5.77 \times 10^{-4}] \text{ M.}$

* Solution - Diluent volume ration..

تخفيف المائيل

1:4 HCl $\rightarrow$ This mean 1 volume HCl in 4 volume H_2O .

1:4 سولوشن + 4 سولفانت = 5 سولوشن *
(Solvent) + (solute) = (solution)

* 0.5 = المائل

* p-Function or p-value:-

$$P_x = -\log [x]$$

* e.x:- Calculate the p value for each ion. in a solution contain $2.00 \times 10^{-3} \text{ M NaCl}$ and $5.4 \times 10^{-4} \text{ M HCl}$??

Solu:- $\left[\begin{array}{l} \text{NaCl} \rightarrow 2 \times 10^{-3} \\ \text{HCl} \rightarrow 5.4 \times 10^{-4} \end{array} \right.$

① Na^+, Cl^-, H^+, Cl^-

② $P_{Na} = -\log [Na^+] = -\log [2 \times 10^{-3}] = [2.699]$

$pH = -\log [H^+] = -\log [5.4 \times 10^{-4}] = [3.27]$

$[Cl^-]_1 + [Cl^-]_2 = (2 \times 10^{-3}) + (5.4 \times 10^{-4}) = [2.54 \times 10^{-3}] \text{ M}$

$P_{Cl} = -\log (2.54 \times 10^{-3}) = [2.595]$

* [413-2]: Density and specific gravity:-

* Density $\rightarrow$ mass of substance per unit volume.

* Specific gravity $\rightarrow$ The ratio of the mass of substance to the mass of an equal volume of H_2O at $4^\circ C$ (S.G.).

* Density $H_2O = 1$ *

* unit D : g/ml , kg/L.

* e.g:- Calculate the molar concentration of HNO_3 (63 g/mol) is a solution that has a specific gravity 1.42 and 70.5% HNO_3 (w/w)??

Solu:- * $M = \frac{\% \times 10 \times \text{Density}}{M.Wt.}$

$$M = \frac{70.5 \times 10 \times 1.42}{63 \text{ g/mol}} = 15.89 \approx \boxed{16} \text{ M}$$

* Dilution :- $M \times V_{\text{concentrated}} = M \times V_{\text{diluted}}$

* e.g:- How to prepare 100 ml of 6 M HCl from concentrated solution has S.G 1.18 and 37% (w/w) HCl (36.5 g/mol)?

Solu:- ① $M = \frac{37 \times 10 \times 1.18}{36.5} = \boxed{12.0} \text{ M}$

② $M \times V_{\text{conc}} = M \times V_{\text{dilu}}$

$$\frac{12 \times V}{12} = \frac{6 \times 100}{212} \rightarrow \frac{V}{\text{conc}} = \boxed{50} \text{ ml}$$

* [4C] :- Chemical stoichiometry :-

* [4C-1] :- Empirical formula and molecular formula :-

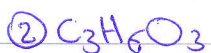
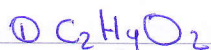
1] Empirical formula $\rightarrow$ Is the simplest whole # ratio of atom.

2] M. formula $\rightarrow$ specific the # of atom.

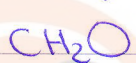
* c.x :-

فازلين

جولوز



} Molecular formula



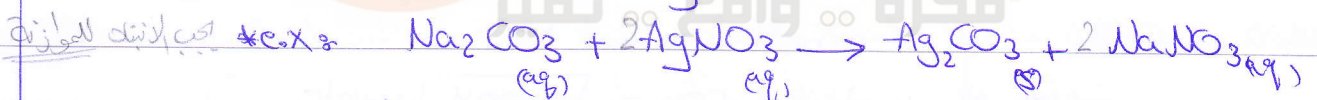
E. formula.

$\leftarrow$ (مؤثر)

3] Structural formula.

* [4C-2] :- Stoichiometry Calculation :-

* c.x :-



① Which mass of $AgNO_3$ (169.9 g/mol) is needed to convert 2.33 g of Na_2CO_3 (106 g/mol) to Ag_2CO_3 ?

Solus:- ① check the valence equation.

② # of mole $Na_2CO_3 = \frac{\text{mass}}{\text{M.mass}} = \frac{2.33 \text{ g}}{106 \text{ g/mol}} = \boxed{0.02198} \text{ mol}$



X = $\boxed{0.0439} \text{ mol } AgNO_3$.

④ mass $AgNO_3 = \text{M.mass} \times \text{\# mols}$

= 169.9 $\times$ 0.0439

= $\boxed{7.47} \text{ g}$.

[b] What mass of Ag_2CO_3 (275.7 g/mol) will be formed?

$$\begin{aligned} \text{mass} &= \text{M.Wt} \times \# \text{ mols} \\ &= 275.7 \times 0.02198 = \boxed{6.06} \text{ g } \text{Ag}_2\text{CO}_3. \end{aligned}$$

limiting
Reactant.

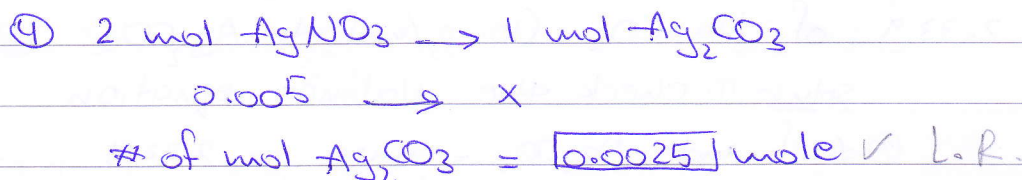
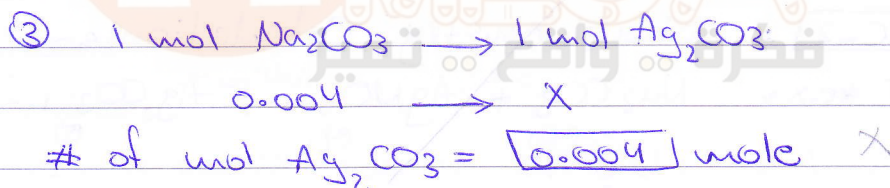
* ex: What mass of Ag_2CO_3 (275.7 g/mol) is formed when 25 ml of 0.2 M AgNO_3 mixed with 50 ml of 0.08 M Na_2CO_3 ??



Solu:

$$\begin{aligned} \textcircled{1} \# \text{ mole } \text{AgNO}_3 &= M \times V \\ &= 0.2 \times 25 \times 10^{-3} = \boxed{0.005} \text{ mol} \end{aligned}$$

$$\begin{aligned} \textcircled{2} \# \text{ mol } \text{Na}_2\text{CO}_3 &= 0.08 \times 50 \times 10^{-3} \\ &= \boxed{0.004} \text{ mol.} \end{aligned}$$



* limiting reactant AgNO_3 *

$$\begin{aligned} \textcircled{5} \text{ Mass } \text{Ag}_2\text{CO}_3 &= \# \text{ mol} \times \text{M.Wt.} \\ &= 0.0025 \times 275.7 \\ &= \boxed{0.689} \text{ g.} \end{aligned}$$

* Errors in Chemical Analysis:-

* mean $\equiv$ Average.

* Error $\rightarrow$ Difference between the mean value and the true value $\equiv$ Degree of uncertainty.

* [5-A] Some important terms:-

Run Always (2-5) 'Replicate' analysis في نفس الظروف

* Replicate $\rightarrow$ same conditions *

* [5A-1] The mean and the median:-

** mean ($\bar{x}$) = $\frac{\text{Summation of replicate measurement}}{\text{\# of measurement}} = \frac{\sum x_i}{N}$

* Median :- Is the middle result when replicate data are arranged $\uparrow$ و $\downarrow$ ترتيباً.

* في النتيجة المتوسطة بعد ترتيب القيم ترتيباً

* ex:- Calculate the mean and the median of:

19.4 19.5 19.8 19.6 20.1 20.3

Solve:-

$$\textcircled{1} \text{ mean} = \frac{\sum x_i}{N} = \frac{19.4 + 19.5 + 19.8 + 19.6 + 20.1 + 20.3}{6} = 19.78 \approx \boxed{19.8}$$

$$\textcircled{2} \text{ median} : \begin{array}{cccccc} 19.4 & 19.5 & 19.6 & 19.8 & 20.1 & 20.3 \\ & & \underline{19.6 + 19.8} & & & \\ & & 2 & & & \end{array} = \boxed{19.7}$$

→ If you have: 19.4 19.5 19.6 19.8 20.1
 $\therefore$ median = 19.6.

* 5A-2 precision:-

تعريف: How closeness of results run in the same conditions to each other.

* To express it:-

القياس عندها

1) Standard deviation. الفرق المعياري

2) Variance. مقياس التباين

3) coefficient of variation. معامل التباين

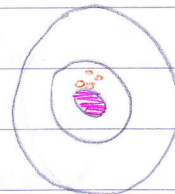
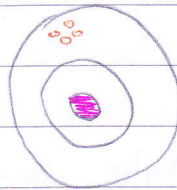
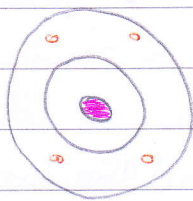
** deviation (d_i) = $|x_i - \bar{x}|$.

→ x_i :- القيمة التي تم حسابها. $\bar{x}$:- القيمة الوسطية

* 5A-3 Accuracy:-

def:- The closeness of the measurement to the true value.

*



true Value

No accuracy

X

✓

No precision

✓

✓

* To express accuracy:-

1) Absolute error (E)

الخطأ المطلق :-

$$E = x_i - x_t$$

→ x_t :- true value.

Q] Relative error (E_r):-

$$** E_r = \frac{x_i - x_t}{x_t} * 100\% \quad \begin{cases} +ve \\ -ve \end{cases} \text{ or } \textcircled{or}$$

* [5A-4] Types of error in experimental data:-

1] Random error (Indeterminate): affect the precision.

2] Systematic error (determined): affect accuracy.

3] Gross error (Human error): This leads to result that too high or too low from the true value.

4] Outlier: one result seems to be differ markedly from others.

* [5B] : Systematic errors:-

* [5B-1] : Sources of systematic error.

3 types of error:-

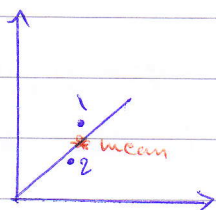
1] Instrumental :- from instrument.

2] Method error :- from chemical and physical analytical system.

3] personal error.

* Systematic error leads to bias:-

deviation from the mean (-ve, +ve).



(+ve) إيجابية

(-ve) سلبية

* 1] Instrumental error:-

→ From pipet, buret ... (volumetric flask).

→ Temp. change.

To eliminate the error comes from the instrument: make calibration.

[2] Method error:-

→ Decomposition of organic sample.

→ small excess in reagent.

[3] personal error:-

→ Comes from eyes error.

* [5B-2]:- The effect of systematic error on analytical result:-

* systematic error maybe ① constant ② proportional.

① constant doesn't depend on the size of sample.

→ serious:- when sample size ↓.

بعض الأخطاء منه ثابتة وبعضها متناسبة مع حجم العينة

التي هي خطأ

* e.x:- Titration.

خطأ القياس

② proportional error: ↑ or ↓ according to the size of sample.

→ comes from the interferences.

* [5B-3]:- Detection of systematic error.

* Instrument: correct by calibration.

* personal errors: pay attention.

note → Some errors (corrosion, mistreatment) ... by time

(sample) AS type

→ سوء استعمال

* [5B-4] : Detection of systematic method error:-

* [1] Standard reference material:- Sample with known concentration. (SRM).

* If there is a difference between SRM concentration you measured and the true concentration $\rightarrow$ error.

* إذا كان هناك فرق كبير $\therefore$ يوجد خطأ *

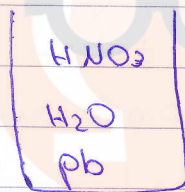
[2] Independent analysis:- When you don't have SRM $\rightarrow$ change method.

تغيير الطريقة إذا لم يوجد SRM

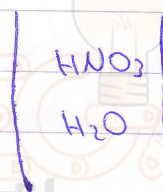
[3] Blank def:-

Blank:- contain all reagents in real sample except analyte.

* C.O.X:-



Sample [Pb] = 0.4



Blank [Pb] = 0

$$[Pb]_{\text{real}} = [Pb]_{\text{sample}} - [Pb]_{\text{Blank}}$$

* Sample matrix:- All the constituents in the sample.

كل شيء موجود بالعينية

[4] Variation is Sample Size:-

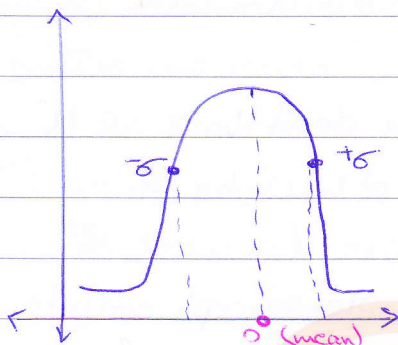
When size $\uparrow$ of measurement the effect of error $\downarrow$.

* Random errors in chemical analysis:

* [5A] The nature of random errors:

Random error exist in every measurement and cause uncertainty.

* [6A-1] Random error sources :



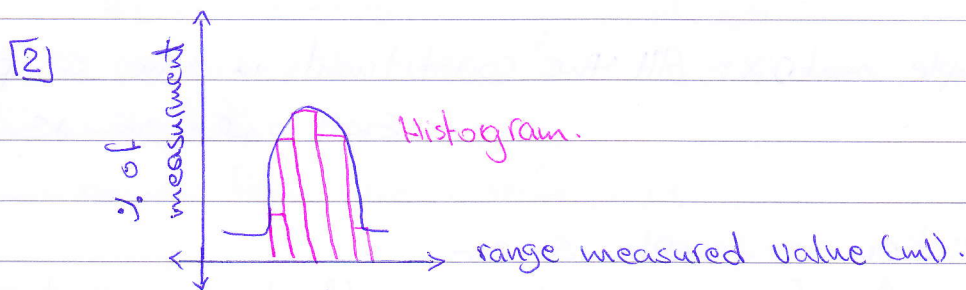
normal distribution (Gaussian distribution):
Curve shows symmetrical distribution data around mean.

→ σ : uncertainty : deviation from the mean.
 (الانحراف المعياري)

* [6A-2] Distribution of experimental data:

* e.g. We want to calibrate 10.0 ml Pipet. We run 50 trial.

Solu : [1] ① Mean ② median ③ Max, min
④ standard deviation. ⑤ spread (highest, lowest) results.



[3] Table.

Volume	# in range	% In range
9.69-9.971	3	6
:	:	:

نحوه 10 آند
نمودار في Pipet

عدد التجارب 50

100%

* Source of error :-

- ① visual judgment. ② Temp. ③ Balance reading.
④ Variation in the angle of pipet.

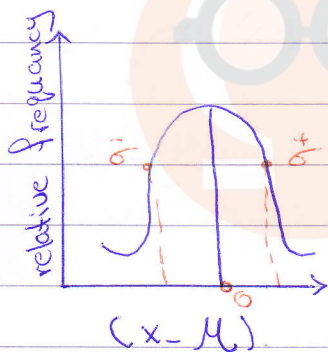
* [5B] Statistical treatment of random error:-
no new information will be created in statistical treatment.

* [5B-1] Sample and population:-

* population $\rightarrow$ collection of all measurement.

Sample $\rightarrow$ Subset (نمونه) of measurement.

* [5B-2] properties of Gaussian distribution curve:-



$\sigma \rightarrow$ Population standard deviation.

$\mu \rightarrow$ population mean.

$x \rightarrow$ data value.

$y \rightarrow \frac{e^{-(x-\mu)^2/2\sigma^2}}{\sigma\sqrt{2\pi}}$

(نمونه) جمع

* The population Mean (μ) and the Sample mean ($\bar{x}$):-

** Sample mean = $\frac{\sum x}{N} = (\bar{x}) \Rightarrow N$: number of measurement in Sample set.

** Population mean = (μ) = $\frac{\sum x_i}{N}$



N : # of measurement in the Population.

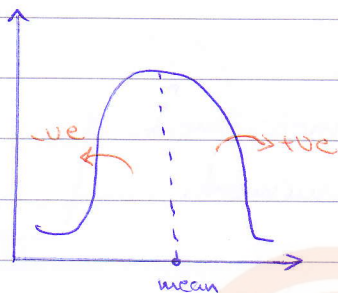
قاسم

* True value = mean

* The population standard deviation (σ):-

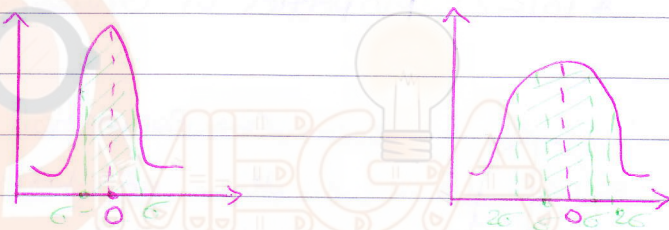
$$\sigma = \sqrt{\frac{\sum (x_i - \mu)^2}{N}}$$

* Note:-



The normal error curves:-

- ① Symmetrical around mean
- ② Mean is the central point. (اوسط)
- ③ When deviation $\uparrow$, frequency $\downarrow$.
- ④ Area under Gaussian Curve:-



$\rightarrow$ When area $\uparrow$, $\sigma \uparrow$.

* [B-3] The sample standard deviation, A measure of Precision:-

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}}$$

* $x_i - \bar{x}$ = deviation (error. انحراف و تباين)
 $N-1$ = degree of freedom. (درجات الحرية)

* Q:- Why use s ?? Why replace (N) by $(N-1)$?

Solu:- If $(N-1)$ not used (s) will be less than the true value.

* I.e :- (S) will have (-ve) bias. یعنی سب سے زیادہ

* S^2 = variance = square of standard deviation.

* Alternative expression for standard deviation (S.D):-

$$S = \sqrt{\frac{\sum x_i^2 - \left(\frac{\sum x_i}{N}\right)^2}{N-1}}$$

* ex:- 5 samples of Blood, got these results of pb:-
0.752, 0.756, 0.752, 0.751, 0.760 ppm, Calculate
the ① Mean + ② S.D ??

Solu:- ① Mean = $\frac{\sum x_i}{N} = \frac{0.752 + 0.756 + 0.752 + 0.751 + 0.760}{5}$

Mean = 0.754

② S.D = $\sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}} = 0.00377$
 $\approx$ 0.004

x_i	$(x_i - \bar{x})$	$(x_i - \bar{x})^2$
0.752	-2×10^{-3}	4×10^{-6}
0.756	2×10^{-3}	4×10^{-6}
0.752	-2×10^{-3}	4×10^{-6}
0.751	-3×10^{-3}	9×10^{-6}
0.760	6×10^{-3}	3.6×10^{-5}
0.754	1×10^{-3}	5.7×10^{-5}

* Note :- $N \rightarrow \infty$, then *

$\bar{x} = \mu$, $S = \sigma$.

یعنی جب N بڑھے تو

* Standard error of the mean:-

$$** S_m = \frac{S}{\sqrt{N}}$$

* e.x :- Mean = 3 , $S_m = 0.1$
 3 ± 0.1

استدلال * To ↑ precision by a factor 10 , require (100) times measurement.

* The coefficient of variation (CV), Relative standard deviation (RSD):-

$$** CV = \frac{S}{\bar{x}} * 100\%$$

* Reliability of (s) as a measure of precision:-
 $N \uparrow$, s becomes better estimator of σ .

* pooling data (combining data) to improve the reliability of (s).

* subset :- group of set.

Conditions:- ① same sources for all measurement.
 ② same analysis.

$$** S_{\text{pooling}} = \sqrt{\frac{\sum (x_i - \bar{x})^2 + (x_i - \bar{x})^2 + \dots}{N_1 + N_2 + \dots + N_r}}$$

* e.x :- Calculate Spooling ?

Solu:-

بجزيه الى اقسام
 على سبيل

Time	[Glucose] mg/L	mean	$\sum (x_i - \bar{x})^2$
month 1	1108, 1122, 1075, 1099, 1115, 1083, 1100.	1100.3.	1687.43
month 2	992, 975, 1022, 1001, 991.	996.2	1182.80
month 3	788, 805, 779, 822, 800.	798.8	1086.80
month 4	799, 745, 750, 774, 777, 800, 758.	771.9	2950.86

$$\rightarrow S_{\text{pooling}} = \sqrt{\frac{1687.43 + 1182.80 + 1086.80 + 2950.86}{24 - 4}}$$

(تقسیم کی (میانگین) کے لیے)

$$= 13.58 \approx 14 \text{ mg/L.}$$

* GB-5 Variance and other measurement of precision:

1] Variance (S^2):

$$** S^2 = \frac{\sum (x_i - \bar{x})^2}{N-1}$$

$$= \frac{\sum (d_i)^2}{N-1}$$

deviation.

S $\rightarrow$ Has the unit of the data.

S^2 $\rightarrow$ " " Square unit " " " " .

2] (RSD): Relative standard deviation.

$$** RSD = \frac{S}{\bar{x}}$$

$$** RSD \% = \frac{S}{\bar{X}} * 100\%$$

$$** RSD_{ppt} = \frac{S}{\bar{X}} * 1000.$$

[3] CV :- Correlation of variation:-

$$** CV = \frac{S}{\bar{X}} * 100\%$$

[4] spread (w):- الانتشار

spread $\rightarrow$ highest value - lowest value.

* e.g.:-

X_i	$X_i - \bar{X}$	$(X_i - \bar{X})^2$
0.752	-0.002	$4 * 10^{-6}$
0.756	0.002	$4 * 10^{-6}$
0.752	-0.002	$4 * 10^{-6}$
0.751	0.003	$9 * 10^{-6}$
0.760	0.006	$3.6 * 10^{-5}$
0.754		$5.7 * 10^{-5}$

Calculate :- ① Variance ? ② RSD_{ppt} ? ③ CV ? ④ w ??

Solu:- [1] Variance :-

$$S^2 = \frac{\sum (X_i - \bar{X})^2}{N-1} = \boxed{1.4 * 10^{-5}}$$

$$[2] RSD_{ppt} = \frac{S}{\bar{X}} * 1000 = \frac{\sqrt{1.4 * 10^{-5}}}{0.754} * 1000 = \boxed{4.96}$$

$$[3] \text{ CV} = \frac{\sqrt{1.4 \times 10^{-5}}}{6.754} * 100\% = \boxed{0.5\%}$$

$$[4] \text{ W} = 0.760 - 0.751 = \boxed{0.009}$$

* [5c] Standard deviation of calculate results-

[i] Standard deviation of sum or difference:-

$$Y = a(\pm S_a) + b(\pm S_b) - c(\pm S_c) \dots$$

$$** S_y = \sqrt{(S_a)^2 + (S_b)^2 + (S_c)^2}$$

$$* \text{e.g. } Y = 0.5(\pm 0.02) + 4.10(\pm 0.03) - 1.97(\pm 0.05)$$

calculate the standard deviation (S_y) = ?

$$\text{Solu:- } [1] 0.5 + 4.10 - 1.97 = \boxed{2.63}$$

$$[2] S_y = \sqrt{(0.02)^2 + (0.03)^2 + (0.05)^2} = \boxed{0.06}$$

$$[3] 2.63(\pm 0.06) \dots \text{حل نهائي}$$

Example * [SC-2] Standard deviation of product or quotient:-

$$y = \frac{a * b}{c}$$

$$** \frac{SY}{Y} = \sqrt{\left(\frac{Sa}{a}\right)^2 + \left(\frac{Sb}{b}\right)^2 + \left(\frac{Sc}{c}\right)^2}$$

*c.x:- Calculate the S.D of: $\frac{4.10(\pm 0.02) * 0.005(\pm 0.0001)}{1.97(\pm 0.04)}$?

Solu:- $\frac{4.10 * 0.005}{1.97} = 0.010406 (\pm ?)$

$$\frac{SY}{Y} = \sqrt{\left(\frac{0.02}{4.10}\right)^2 + \left(\frac{0.0001}{0.005}\right)^2 + \left(\frac{0.04}{1.97}\right)^2} \rightarrow \frac{SY}{Y} = \boxed{0.0289}$$

$$SY = 0.0289 * 0.010406 = \boxed{0.000301}$$

$$\Rightarrow 0.010406 (\pm 0.000301)$$

*[SC-3] in exponential calculation:-

$$y = a^x$$

$$** \frac{SY}{Y} = X \left(\frac{Sa}{a} \right)$$

*c.x:- $V = \frac{4}{3} \pi r^3$, if $d = 2.15 \text{ cm}$ (قطر) with $Sd = \pm 0.02 \text{ cm}$, What is the standard deviation of volume = ?

Solu:- ① $V = \frac{4}{3} \pi (2.15/2)^3 = \boxed{5.20} \text{ cm}^3 = V$

$$\textcircled{2} \frac{SY}{Y} = X \left(\frac{Sa}{a} \right) \rightarrow \frac{SY}{Y} = 3 * \left(\frac{0.02}{2.15} \right) = \boxed{0.0279}$$

$$S V = 0.0279 * 5.20 = \boxed{0.145}$$

$$\Rightarrow 5.2 (\pm 0.1)$$

* GC-4 S.D of logarithms and antilogarithms:-

** logarithms:- $S_y = 0.434 \frac{S_a}{a}$

** antilogarithms:- $\frac{S_y}{y} = 2.303 S_a$

* c.x:- Calculate S.D:-

$$y = \log [2.00 (\pm 0.02) \times 10^{-4}] \rightarrow y = -3.699 (\pm ?)$$

$$S_y = 0.434 \left(\frac{0.02}{2.00} \right) = \boxed{0.004}$$

$$\rightarrow y = -3.699 (0.004)$$

* 129 up to 1000 *

* GD-1 Reporting computed data:-

* you have to follow the S.F:-

* GD-2 S.F:-

1) Sum and difference:-

* c.x:- $3.4 + 0.020 + 7.31 = 10.730 \approx \boxed{10.7}$

في الجمع والفرق ←

2) product and Quotient:-

* c.x:- $\frac{24 \times 4.52}{100.0} = 1.084 \approx \boxed{1.08}$

في القسمة والجمع

* logarithms + antilogarithms:-

1) In log:- keep as many digits to the right of the (decimal) decimal point as there are in the original.

* e.x:- Round log $4.000 \times 10^{-5} = \boxed{-4.3979}$

الجواب يكون فيه 4 ارقام بعد الفاصلة . 4 s.f

2) Antilog:- keep as many digits as there are to the right of D.point in the original #.

* e.x:- Antilog $12.5 = \boxed{3 \times 10^{12}}$

ا. الجواب ليهنا فيه يكون مكون من رقم

واحد فقط (حسب عدد ارقام بعد الفاصلة)

* GD-3 Rounding Data:-

Always to the nearest even #.

* e.x:- Round $61.555 = \boxed{61.56}$

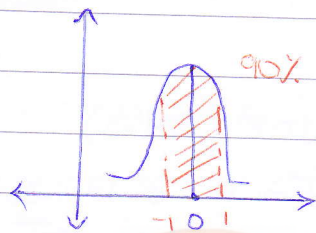
* GD-4 Expressing results of chemical computation:-
Always rounding off at the end.

* Statistical Data treatment and evaluation:-

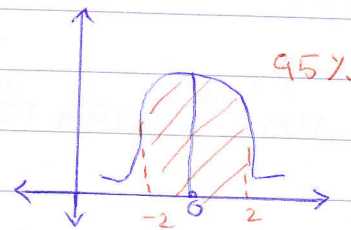
* [ZA] Confidence interval (C.I):-

Def:- The range of values within which the population mean (μ) is expected to lie within a certain probability.

* [ZA-1] Finding C.I when σ is known:-



$\pm 10\%$



$\pm 5\%$

* [ZA-2] Finding C.I when σ is unknown:-

* Confidence level (CL):-

Is the probability that the true mean lies within a certain interval.

* Significance level:-

The probability that a result is outside the C.I.

** $\boxed{CI \text{ for } \mu = \bar{x} \pm \sigma}$

** $\boxed{CI \text{ for } \mu = \bar{x} \pm z\sigma / \sqrt{N}}$

* e.g.:-

*e.x:- Determine the 80% and 95% CI for (a) 1108 mg/L • (b) the mean value 1100.3 of 7 measurement assume that $S=19$ is a good estimator of σ ?

Info z tabulated.

80%	95%
1.28	1.96

At 80% :-

(a) $z = 1.28$

CI = $1108 \pm 1.28 * 19 = (1108 \pm 24.3)$

أي نسبة (أو) بين (+) أو (-) في كل مرة.

(b) $CI = 1100.3 \pm \frac{1.28 * 19}{\sqrt{7}} = (1100.3 \pm 9.19)$

At 95% :-

(a) $z = 1.96$

CI = $1108 \pm 1.96 * 19 = (1108 \pm 37.24)$

(b) $CI = 1100.3 \pm \frac{1.96 * 19}{\sqrt{7}} = (1100.3 \pm 14.07)$

* [ZA-2] : Finding the C.I when σ is unknown -
t-statistics.

** $t = \frac{x - \mu}{s}$ For single measurement.

** $t = \frac{\bar{x} - \mu}{s/\sqrt{N}}$ For N measurement.

** CI for $\mu = \bar{x} \pm \frac{ts}{\sqrt{N}}$

* t values are tabulated at $(n-1) \equiv$ degree of freedom.

* e.x:- Analysis of Alcohol contained in sample:-
0.084, 0.089, 0.079. Calculate the 95% CI, $S=0.005\%$
is a good estimator for σ ?

Solu:- $CI = \bar{X} \pm \frac{ts}{\sqrt{N}}$

* $\bar{X} = \frac{0.089 + 0.084 + 0.079}{3} = [0.084]$

* $S = 0.005$

* at 95% look at t -value :- $t = 4.3$
 $N-1$

* $CI = 0.084 \pm \frac{4.3 * 0.005}{\sqrt{3}} = [0.012]$

Range = $(0.084 \pm 0.012) \rightarrow (0.072 \pm 0.096)$

* [7D] Detection of gross error:-

Out lies :- the result of an undetected gross error.

$\Rightarrow$ Decide :- IF we have to retain it or reject it.

* Apply Q-test:-

* Steps:-

① Arrange the data $\uparrow$.

رتب القيم تصاعدياً

② Calculate $Q_{exp} = \frac{|\text{suspected value} - \text{closest Value}|}{\text{Max. Value} - \text{min. Value}}$

الفرق بين القيمة المشكوك فيها والقيمة الأقرب إليها

③ At CI, Det" $Q_{critical}$ (tabulated).

④ IF $Q_{exp} > Q_{crit}$, reject the suspected value.

إذا تجاوزت القيمة المشكوك فيها القيمة الحرجة، نرفضها.

* Ex- Analysis of $\text{CaO}\%$ yield : 55.95 , 56.00 , 56.04 , 56.08 , 56.23 . The last value is questionable . Does it should be rejected or retained at 95% ?

Solu:-

① 55.95 , 56.00 , 56.04 , 56.08 , 56.23 .

$$\textcircled{2} Q_{\text{exp}} = \frac{|56.23 - 56.08|}{56.23 - 55.95} = \boxed{0.54} = Q_{\text{exp}}$$

③ at 95% from table, $n=5$, $Q_{\text{critical}} = \boxed{0.71}$

④ $Q_{\text{exp}} < Q_{\text{crit}}$, So keep the value .

* 7D-2 > Rules
7D-3

دراسة ذاتية (فردية)

فكرة .. واقع .. تميز

* Aqueous solutions and chemical (RXN):-

* [9A] Classifying solutions of electrolytes:-

* electrolytes:- Solute from ions when dissolves in H_2O and conduct electricity...

electrolytes 2 types

Strong electrolyte
Ionized completely

Weak electrolyte.
Ionized partially.

يكون إلكتروك با قاباه واحد (لفاعل)

يكون إلكتروك با قاباهين (غير مكمل)

* Table (9-1)

* ملاحظة

* [9A-2] :-

* Acids + Bases:-

Acid $\rightarrow$ proton donor .
Base $\rightarrow$ proton acceptor. } Bronsted.

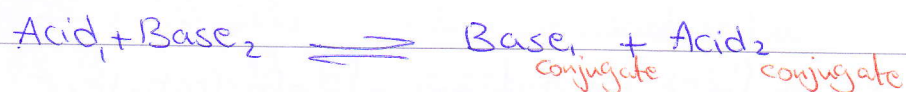
* Salt :- product from Acid + Base.

* Conjugate acid & conjugate base:-

Acid $\rightleftharpoons$ Base + proton
conjugate base.

Base + proton $\rightleftharpoons$ Acid
conjugate acid.

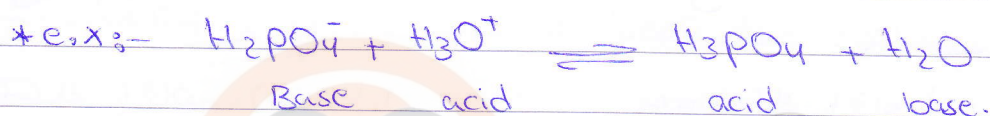
* Neutralization $RX.N_3^-$



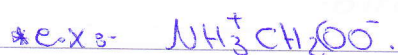
* لویں بقاعل باتہ واحد شیخ صالح + فاد *



* Q-3 :- Amphiprotic species :-
Species possess both acidic & basic properties.



فكرة ٠٠ واقع ٠٠ تمييز
Zwitterion :- Species bears both (-ve) and (+ve) charge. * عيالك سافين (٠) و (-)



*e.g. - Amphiprotic Solvents :- CH_3OH .

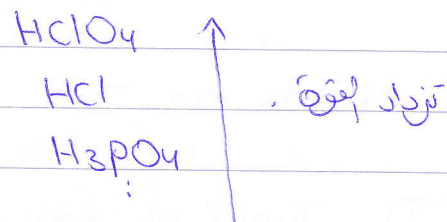
* QA-4 Autopyrolysis:- (Self Ionization):-

تفاعل مع نفسه لتكوين سكرية هو $\text{C}_6\text{H}_{12}\text{O}_6$ وأخرى سكرية *



* [9A-5] Strength of Acids & Bases :-

* Figure (9-2) :-



*** H.W :-

HClO_4 :- per chloric Acid.

H_2SO_4

ClO_4^- :- perchlorate :-

SO_4^{2-}

* [9B] :- Chemical equilibrium :-

Def" :- ratio [] of reactant & product.

* Equilibrium Constant expression :- Algebraic equation.

* [9B-1] The equilibrium state :-

principle of chatelier :- position of eq. always shift in such a direction as to relieve a stress to the system.

* [9B-2] Equilibrium Constant expression [K] :-



w, x, y, z :- # of moles.

$$** K = \frac{[Y]^y [Z]^z}{[W]^w [X]^x}.$$

* Notes:- ① If a species is:- pure liquid, solid or in excess no term of species appear.

* K depends on T , S and P .

② K Depends on T .

* [9B-3] Types of eq. Constant:-

① K_w :- dissociation of H_2O .

② K_{sp} :- Solubility.

③ K_a :- dissociation of Acid.

④ K_b :- dissociation of Base.

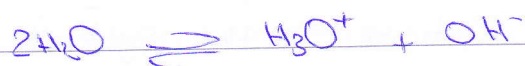
* [9B-4]:- Applying the ion product constant for H_2O :-



$$K_w = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$K_w = 1 \times 10^{-14} \text{ at } T = 25^\circ C.$$

* e.x:- Calculate the hydronium and hydroxide ion $[]$ of pure H_2O at $25^\circ C$, at $100^\circ C$?



$$\text{info } K_w \text{ at } 25^\circ = 1 \times 10^{-14} \\ \text{at } 100^\circ = 4.9 \times 10^{-13}$$

Solus:- At $25^\circ C$:-

$$\textcircled{1} K_w = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$\textcircled{2} [H_3O^+] = [OH^-]$$

$$K_w = \frac{[H_3O^+]^2}{[H_2O]^2}$$

pure liquid

1:1 ratio

$$\sqrt{1 \times 10^{-14}} = \sqrt{[H_3O^+]^2} \quad \rightarrow \quad [H_3O^+] = [OH^-] = \boxed{1 \times 10^{-7}}$$

At $100^\circ C$:-

$$K_w = [H_3O^+]^2 \quad \rightarrow \quad \sqrt{49 \times 10^{-14}} = \sqrt{[H_3O^+]^2}$$

$$[H_3O^+] = [OH^-] = \boxed{7 \times 10^{-7}}$$

* ex: Calculate $[H_3O^+]$ and $[OH^-]$ and pH, pOH of $0.200 M$ NaOH at $25^\circ C$, $K_w = 1 \times 10^{-14}$?

Solu: ① $[OH^-] = 0.200 + [H_3O^+]$ +200 مولات OH
NaOH هو مادة قلوية بالدرجة الأولى too small so cancel it.

$$\therefore [OH^-] \approx \boxed{0.200} M$$

$$pOH = -\log [OH^-] = -\log 0.2 = \boxed{0.699}$$

② $K_w = [OH^-][H_3O^+] =$ Since we have NaOH

$$\frac{K_w}{[OH^-]} = [H_3O^+] \quad \rightarrow \quad \frac{1 \times 10^{-14}}{0.2} = [H_3O^+]$$

$$\therefore [H_3O^+] = \boxed{5 \times 10^{-14}} M$$

$$pH = -\log [H_3O^+] = \boxed{13.301}$$

* [9B-5] Applying solubility product constant :-

[2] K_{sp} :-



$$K_{sp} = [Ba^{+2}][IO_3^-]^2$$

pure (s) لا يدخل في الحساب [Ba(IO₃)₂]

$$\therefore K_{sp} = [Ba^{+2}][IO_3^-]^2$$

* QB-5 Applying solubility-product constant:-
 $K_{sp} = [Ba^{2+}][IO_3^-]^2$

* e.x:- How many grams of $Ba(IO_3)_2$ (487 g/mol) can be dissolved in 500 ml of H_2O at $25^\circ C$?

info:- $K_{sp} = 1.57 \times 10^{-9}$ at $25^\circ C$?

Solu:- ① $Ba(IO_3)_2 \rightleftharpoons Ba^{2+} + 2 IO_3^-$

$$\textcircled{2} K_{sp} = [Ba^{2+}][IO_3^-]^2 = 1.57 \times 10^{-9} \dots \textcircled{a}$$

$$[IO_3^-] = 2[Ba^{2+}] \dots \textcircled{b}$$

Substitute $\textcircled{b}$ in $\textcircled{a}$:-

$$1.57 \times 10^{-9} = [Ba^{2+}] + (2[Ba^{2+}])^2$$

$$1.57 \times 10^{-9} = 4[Ba^{2+}]^2 \rightarrow [Ba^{2+}] = \boxed{7.32 \times 10^{-4}} M$$

$$\textcircled{3} [Ba^{2+}] = [Ba(IO_3)_2] = 7.32 \times 10^{-4}$$

$$\textcircled{4} M \times V = \frac{\text{mass}}{M.\text{mass}} \rightarrow 7.32 \times 10^{-4} \times 0.5 = \frac{\text{mass}}{487}$$

$$\therefore \text{mass} = \boxed{0.178} g$$

* The effect of the Common Ion on the solubility of ppt:-

* e.x:- Calculate the molar solubility of $Ba(IO_3)_2$ in a solution that is 0.02 M in $Ba(NO_3)_2$??

Solu:- ① Common ion Ba^{2+}

Common ion

$$[Ba^{2+}] \neq [Ba(IO_3)_2]$$

$$\text{so} \rightarrow \textcircled{2} [Ba^{2+}] = 0.02 + [Ba(IO_3)_2]$$

$$[Ba^{2+}] = 0.02 + \cancel{\frac{1}{2}[IO_3^-]}$$

في هذا السؤال

$$\therefore [\text{Ba}^{2+}] \approx 0.02$$

$$\textcircled{3} \quad K_{sp} = 1.57 \times 10^{-9} \quad \text{olpan}$$

$$1.57 \times 10^{-9} = [\text{Ba}^{2+}] [\text{IO}_3^-]^2$$

$$1.57 \times 10^{-9} = 0.02 [\text{IO}_3^-]^2 \rightarrow [\text{IO}_3^-] = \boxed{2.8 \times 10^{-4}} \text{ M.}$$

$$\textcircled{4} \quad [\text{Ba}(\text{IO}_3)_2] = \frac{1}{2} [\text{IO}_3^-] = \boxed{1.4 \times 10^{-4}} \text{ M.}$$

* 9B-5 Applying Acid-Base dissociation constant:-



** $\boxed{K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]}}$ Acid dissociation constant.



** $\boxed{K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]}}$ Base dissociation constant.

** $\boxed{K_w = K_a \times K_b}$ Dissociation constant for conjugate acid + Base.

* e.x:- What is K_b for:-



Solu:-

$$K_w = K_a \times K_b$$

$$1 \times 10^{-14} = 6.2 \times 10^{-10} \times K_b \rightarrow K_b = \boxed{1.61 \times 10^{-5}}.$$

* Hydronium ion $[H_3O^+]$ of solutions of weak Acid:-



$$* K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$\rightarrow [H_3O^+] \equiv [A^-] \dots ①$$

$$** C_{HA} = [A^-] + [HA] \dots ②$$

(تركيز الحمض) = (تركيز الأيونات) + (تركيز الحمض غير المتأين)

$$** C_{HA} = [H_3O^+] + [HA]$$

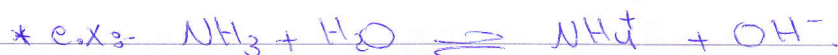
$$** [H_3O^+] = \sqrt{K_a \cdot C_{HA}}$$

* e.x:- Calculate $[H_3O^+]$ in 0.120 M nitric acid
 $K_a = 7.1 \times 10^{-4}$?

$$\text{Soln:- } [H_3O^+] = \sqrt{(7.1 \times 10^{-4})(0.12)} = [9.2 \times 10^{-3}] \text{ M.}$$

* كيف نعرف ان السؤال ينحل على هذا القانون ؟
 * لوطين $[HA]$ و K_a عندها يكون $[H_3O^+]$

* Hydronium ion $[H_3O^+]$ of solutions of weak Base:-



$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

* e.x: Calculate the hydroxide ion $[OH^-]$ of $0.0750 M$ NH_3 solution, $K_b = 1.75 \times 10^{-5}$?

Solu:- $1.75 \times 10^{-5} = \frac{[OH^-]^2}{0.0750} \rightarrow [OH^-] = \boxed{1.15 \times 10^{-3}} M.$

* 9C Buffer solution :-

def: resist any change in pH.

consist of conjugate acid/base pair. يكون من

* e.x: Acetic Acid / sodium acetate.

* 9C-1 Calculation of pH of Buffer:-

* $pH = -\log [H^+].$

** $[H_3O^+] = \frac{K_a [HA]}{[NaA]}$

تركيز $[H_3O^+]$ في حلول buffer من يعرف
قيمة pH

* e.x: What is pH of a solution that is $0.4 M$ in formic acid and $1 M$ in sodium formate?

* Solu:- ① $[H_3O^+] = \frac{K_a [\text{Formic Acid}]}{[\text{Sodium formate}]} = \frac{1.84 \times 10^{-4} \times 0.4}{1.00}$

$= \boxed{7.2 \times 10^{-5}} M.$

② $pH = -\log [7.2 \times 10^{-5}] = \boxed{4.14}$ Acid.

* 9C-2 properties of Buffer:-

* The effect of dilution:- No effect.

* لا يتأثر المحلول بالتحقيق من وجود buffer في أي كمية

قيمة pH للحلول *

* The effect of adding Acids + Bases:-

* e.x:- Calculate the pH Change that takes place when 100 ml of 0.05 M NaOH adding to 400 ml buffer solution (0.2) M NH_3 + (0.3) M NH_4Cl ?

Solu:- ① $[\text{NH}_3] = \frac{\text{\# of mole}}{V} = \frac{(400 \times 0.2) + (100 \times 0.5)}{500}$

$$[\text{NH}_3] = [0.17] \text{ M.}$$

$$\textcircled{2} [\text{NH}_4\text{Cl}] = \frac{(400 \times 0.3) - (100 \times 0.5)}{500} = [0.23] \text{ M.}$$

$$\textcircled{3} [\text{H}_3\text{O}^+] = \frac{K_a [\text{NH}_4\text{Cl}]}{[\text{NH}_3]} = \frac{5.7 \times 10^{-10} \times 0.23}{0.17} = [7.71 \times 10^{-10}] \text{ M.}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 7.71 \times 10^{-10} = [9.11] \text{ base.}$$

لأننا أضفنا قاعدة قوية.

* The composition of buffer solution as a function of pH :- α -Value.

$$C_T = C_{\text{HOAc}} + C_{\text{NaOAc}}$$

$C_T \rightarrow$ Total $[]$, $C_{\text{HOAc}} \rightarrow []$ of Acetic acid.
 $C_{\text{NaOAc}} \rightarrow$ Salt $[]$.

$$\alpha_0 = \frac{[\text{HOAc}]}{C_T} \quad \alpha_0 \rightarrow \text{The fraction of the total } [] \text{ of acid.}$$

$$\alpha_1 = \frac{[\text{OAc}^-]}{C_T} \quad , \quad \alpha_1 + \alpha_0 = 1.$$

* Buffer capacity :- Is the number of mole of strong acid or strong base that (1L) of the buffer can absorb without changing pH. $\Rightarrow$ Always (+ve).

* preparation a buffer :-

* e.x :- Describe how you prepare a buffer 500.0 ml, pH = 4.5 from 1.0 M acetic acid and Sodium Acetate?
 $K_a = 1.75 \times 10^{-5}$?



[H⁺] $\rightarrow$ solve ① $\text{pH} = -\log [\text{H}^+] \rightarrow [\text{H}^+] = 3.16 \times 10^{-5} \text{ M}$.

$$\text{② } K_a = \frac{[\text{H}^+][\text{OAc}^-]}{[\text{HOAc}]} \rightarrow [\text{OAc}^-] = 0.553 \text{ M} = [\text{NaOAc}]$$

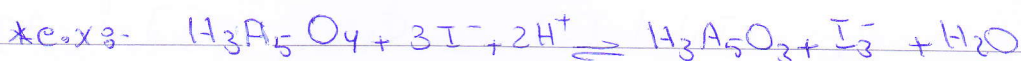
$$\rightarrow M \times V = \# \text{ of moles} = \frac{\text{mass}}{\text{molar mass}} \quad \text{mg } m = 0.553 \times 0.5 \times 82.034 = 22.7 \text{ g}$$

Report
 First

* Effect of electrolyte on chemical equilibrium:-

* [10A] The effect of electrolyte on chemical equilibrium:-

The position of most solution equilibrium depends on the [Electrolyte].



IF $\text{Ba}(\text{NO}_3)_2$ added, the color of triiodide becomes less intense, why??

Cause RXN shift to the left.

* Ba يفاعل مع I_3^- أي يقل تركيزه من قبله لونه (البنفسجي)

* تركيزه يفتقر

* Limiting Value :- عندما يصبح تركيزه بالحد الأدنى
When [] electrolyte reach zero.

* [10A-1] The effect of ionic charge on equilibrium:-
When adding ionic salt on the RXN, this will ↑ the charges.

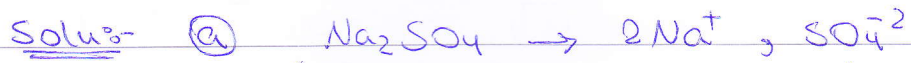
* [10A-2] The effect of ionic strength:-

~~Def~~ ** Ionic strength = $(M) = \frac{1}{2} ([A] Z_A^2 + [B] Z_B^2 + \dots)$.

$[A], [B] \rightarrow$ concentration of the species in molarity.

$Z_A, Z_B \rightarrow$ The charges.

* ex:- Calculate the ionic strength of:-
 (a) $0.1 \text{ M Na}_2\text{SO}_4$. (b) KNO_3 0.1 M ??



$$\mu = \frac{1}{2} (0.1 \times 2 \times (+1)^2 + 0.1 \times (-2)^2) = \boxed{0.3} \text{ M}$$

$\equiv$ Ionic strength.



$$\frac{1}{2} (0.1 \times (1)^2 + 0.1 \times (-1)^2) = \boxed{0.1} \text{ M.}$$

* Type of electrolyte	example	Ionic strength
1:1	NaCl	C
1:2	$\text{Ba}(\text{NO}_3)_2$	$3C$
1:3	$\text{Al}(\text{NO}_3)_3$	$6C$

$\rightarrow C$:- concentration.

فكرة .. واقع .. تغيير

* [10A-3] The Salt effect :-

When BaSO_4 in solution, the effect of Ba^{2+} ion and SO_4^{2-} becomes less as the ionic strength of medium $\uparrow$.

* [10-B] Activity coefficient :-

** $a_x = [x] \gamma_x$. $a_x \rightarrow$ activity , $x \rightarrow$ species
 $\gamma_x \rightarrow$ activity coefficient.

* Activity coefficient Always (+ve) above one*

** $K_{sp} = a_x^m \cdot a_y^n$.

** $K_{sp} = [x]^m [y]^n \cdot \gamma_x^m \gamma_y^n = K_{sp} \cdot \gamma_x^m \gamma_y^n$.

$K_{sp} \rightarrow$ Thermodynamic solubility product.

$K_{sp} \rightarrow$ [] Solubility product constant.

مايل في كونه صغير
 ك_b و ك_a الـ

* [10B-1] properties of activity coefficient :-

① At any ionic strength, the activity coefficient of ions of the same charge are equal.

② The activity coefficient of uncharged molecule = 1.

③ In two concentrated solution, activity coefficient depends on Ionic Strength.

④ $\gamma_x < 1$:-

Infinite solution.

نقصي اني خفت المحلول أكثر ما يمكن
 (لا يمكن تخفيفه أكثر)

*[10B-2] The Debye-Hückel equation :-

$$** \quad \boxed{-\log \gamma_x = \frac{0.51 (Z_x^2) \sqrt{\mu}}{1 + 3.3 \alpha_x \sqrt{\mu}}}$$

$\gamma_x \rightarrow$ Activity coefficient, $Z_x \rightarrow$ charge

$\mu \rightarrow$ Ionic strength, $\alpha_x \rightarrow$ effective diameter in (nm).

← معادلة حسب درجة الحرارة

*e.x:- Use equation of Debye to calculate the activity coefficient for Hg^{+2} in a solution of an ionic strength of 0.085 M. Use 0.5 nm for α ?

Solu:- ① $-\log \gamma_x = \frac{0.51 (Z_x^2) \sqrt{\mu}}{1 + 3.3 \sqrt{\mu} \alpha_x}$

$$-\log \gamma_x = \frac{0.51 * (+2)^2 * \sqrt{0.085}}{1 + 3.3 * (0.5) * \sqrt{0.085}} = \boxed{0.4016}$$

∴ $\gamma_{Hg^{+2}} = \boxed{0.4}$

فكرة .. واقع .. تمين

* [IOB-3] Equilibrium Calculation using activity coefficients-

*ex: Use the activity coefficient to calculate the hydronium ion concentration in 0.12 M HNO_2 that is 0.05 M in NaCl. What is the relative error by neglecting activity coefficient?

Solu: ①

أي μ لا استخراج قيمة γ من جدول

$$\mu = \frac{1}{2} [0.05 \times (1)^2 + 0.05 \times (1)^2] = \boxed{0.05} \text{ M} = \text{Ionic strength.}$$

② $\gamma_{\text{H}_3\text{O}^+} = 0.85$, $\gamma_{\text{NO}_2^-} = 0.81$, $\gamma_{\text{HNO}_2} = 1$ (لأنه ليس أيون)

③ $K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{K_a \cdot \gamma_{\text{HNO}_2}}{\gamma_{\text{H}_3\text{O}^+} \cdot \gamma_{\text{NO}_2^-}}$

$$= \frac{7.1 \times 10^{-4} \times 1}{0.85 \times 0.81} = \boxed{1.03 \times 10^{-3}}$$

④ $[\text{H}_3\text{O}^+] = \sqrt{K_a \cdot C_{\text{HA}}} = \sqrt{1.03 \times 10^{-3} \times 0.12} = \boxed{1.11 \times 10^{-2}} \text{ M}$

← القيمة التي أنا (مستحق)

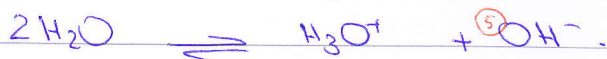
⑤ Relative error assuming $[\text{H}_3\text{O}^+] = 9.2 \times 10^{-3} \text{ M}$.

$$E = \frac{9.2 \times 10^{-3} - 1.11 \times 10^{-2}}{1.11 \times 10^{-2}} \times 100\% = \boxed{17\%}$$

$\boxed{\pm 0.17}$ يعني

* Solving problems for complex system:-

* IIA Solving problem by a systematic (منظم) method:-



* مكوّنات في flask و مادة متفاعلة (أي متبركة على سطحها)

→ There are (5) species, need to determine concentration

* IIA-1 Mass balance equation:-

def: Equilibrium [] of various species in a solution to one another and to the analytical [] of solutes.

* e.g. Write the mass balance expression for 0.01 M solution of HCl that is eq. with an excess of solid BaSO_4 ?

Solu:-



أول خطوة لكل نظام كيميائي (دائم)

التدوين يكون بالماء



منشك كيميائي لسائل و تفاعله

مع H_3O^+



دائمًا لهذا الجرد موجود لكل تفاعلات

$$\textcircled{2} [\text{Ba}^{+2}] = [\text{SO}_4^{-2}] + [\text{HSO}_4^-]$$

نوع تراكيز المواد المتفاعلة و الناتجة

و هي هنا Ba^{+2} و SO_4^{-2} و HSO_4^-

$$\textcircled{3} [\text{H}_3\text{O}^+] + [\text{HSO}_4^-] = C_{\text{HCl}} + [\text{OH}^-]$$

$$[\text{H}_3\text{O}^+] + [\text{HSO}_4^-] = 0.01 + [\text{OH}^-]$$

$$\hookrightarrow \text{Since } [\text{OH}^-] = [\text{H}_3\text{O}^+]$$

* IIA-2 charge - Balance equation:-

* Solution are neutral:-

** molar [] of (+ve) charge = molar [] of (-ve) charge.

** # of mole (+ve) charge = # of mole (-ve) charge.

*e.x:- How much charge is contributed by 1 mole of Na^+ , Mg^{+2} , Al^{+3} ??

Solu:-

[1] Na^+ :- molar [] of (+ve) charge Na^+ = $1[\text{Na}^+]$.

[2] Mg^{+2} :- " " " " " " Mg^{+2} = $2[\text{Mg}^{+2}]$.

[3] Al^{+3} :- " " " " " " Al^{+3} = $3[\text{Al}^{+3}]$.

*e.x:- How to write the charge - balance equation for 0.1 M solution of NaCl ??

Solu:- $\rightarrow$

* IIA-2 charge - balance equation:

Solu: $\text{NaCl} + \text{H}_2\text{O}$

(+ve) charges $[\text{Na}^+], [\text{H}^+] \rightarrow [\]$ of (+ve) charge = 0.1×10^{-7} .

(-ve) charges $[\text{Cl}^-], [\text{OH}^-] \rightarrow [\]$ of (-ve) charge = 0.1×10^{-7} .

المعادلة → $[\text{Na}^+] + [\text{H}_3\text{O}^+] = [\text{Cl}^-] + [\text{OH}^-] = (0.1 + 0.1) \times 10^{-7}$.

الأسئلة IIA-3 Steps of solving problems involving several equilibria:

- ① Write the balance equation.
- ② Set up quantity being in terms of $[\]_{\text{eq}}$.
- ③ Write the equ. constant relation (ratio).
- ④ Write the mass balance expressions.
- ⑤ Write the charge balance expressions.
- ⑥ Count the # of equations and # of unknowns.
- ↪ # of equations $\geq$ # of unknowns.
- ⑦ Make suitable approximation.
- ⑧ Solve equations.
- ⑨ Valid approximation.
- ⑩ problem solved.

* Computer programs can solve the problems:-

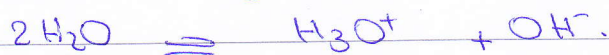
① Excel.

② Mathcad.

③ Mathematica.

* II B-1 Solubility of metal hydroxide :-

* e.x :- Calculate the molar solubility of $Mg(OH)_2$ in H_2O ??



② Solubility $[Mg(OH)_2] = [Mg^{+2}]$

③ قانون

$[Mg^{+2}][OH^-]^2 = 7.1 \times 10^{-12} \dots \text{A}$

$[H_3O^+][OH^-] = 1 \times 10^{-14} \dots \text{B}$

④ $[OH^-] = 2[Mg^{+2}] + [H_3O^+] \dots \text{C}$

⑤ $[OH^-] = 2[Mg^{+2}] + [H_3O^+]$

⑥ # of unknown :- $[Mg^{+2}], [OH^-], [H_3O^+]$

⑦ $[H_3O^+] \ll [OH^-]$

$\hookrightarrow$ equation C becomes

$[OH^-] = 2[Mg^{+2}]$

⑧ $2[Mg^{+2}] = [OH^-]^2 \dots \text{D}$ (9) + (8) subs,

$[Mg^{+2}] \times 4[Mg^{+2}]^2 = 7.1 \times 10^{-12}$

$[Mg^{+2}] = \boxed{1.2 \times 10^{-4}} M$

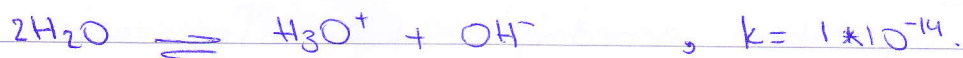
⑩ $[OH^-] = 2 \times 1.2 \times 10^{-4} = 2.42 \times 10^{-4}$

$\frac{K_w}{[OH^-]} = [H_3O^+] = \frac{1 \times 10^{-14}}{2.42 \times 10^{-4}} = \boxed{4.1 \times 10^{-11}} M$

* II B-2 The effect of pH solubility :-

* e.x :- Calculate the molar solubility of calcium oxalate in a solution that buffered with pH = 4 ? [H+] = 10⁻⁴





Solu:- ① $[\text{Ca}^{2+}] = [\text{C}_2\text{O}_4^{2-}] + [\text{HC}_2\text{O}_4^-] + [\text{H}_2\text{C}_2\text{O}_4]$

② $[\text{HC}_2\text{O}_4^-] = \frac{[\text{H}^+][\text{C}_2\text{O}_4^{2-}]}{K_2} = \frac{1 \times 10^{-4} \times [\text{C}_2\text{O}_4^{2-}]}{5.42 \times 10^{-5}}$

$$\therefore [\text{HC}_2\text{O}_4^-] = 1.85 \times [\text{C}_2\text{O}_4^{2-}] \quad \dots [1]$$

$$[\text{H}_2\text{C}_2\text{O}_4] = \frac{1.85 \times 10^{-4} \times [\text{C}_2\text{O}_4^{2-}]}{5.6 \times 10^{-2}}$$

$$\therefore [\text{H}_2\text{C}_2\text{O}_4] = 3.3 \times 10^{-3} \times [\text{C}_2\text{O}_4^{2-}] \quad \dots [2]$$

$\hookrightarrow$

$$[\text{Ca}^{2+}] = 3.3 \times 10^{-3} \times [\text{C}_2\text{O}_4^{2-}] + 1.85 \times [\text{C}_2\text{O}_4^{2-}]$$

$$\therefore [\text{Ca}^{2+}] = 2.85 \times [\text{C}_2\text{O}_4^{2-}]$$

* III-C-1 Separation of ions by control of the ppt agent:-

* Separation according to K_{sp} differences:-

* Ex-3- Can Fe^{+3} and Mg^{+2} be separated on hydroxide from a solution of $0.1 M$??

Info:- ① $K_{sp1} \ll K_{sp2}$

$$② [Fe^{+3}] [OH^{-}]^3 = 2 \times 10^{-39}$$

③ Assumption:-

$1 \times 10^{-4} = [Fe^{+3}] \Rightarrow$ one part in 1000 of ions.

$$\Rightarrow 1 \times 10^{-4} * [OH^{-}]^3 = 2 \times 10^{-39}$$

$$[OH^{-}] = \sqrt[3]{2 \times 10^{-35}} M.$$

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

$$7.1 \times 10^{-12} = 0.1 [OH^{-}]^2 \rightarrow [OH^{-}] = \sqrt{8.4 \times 10^{-8}} M.$$

⑤

$Fe(OH)_3$ can be separated if $[OH^{-}] > 3 \times 10^{-12} M.$

$Mg(OH)_2$ " " " " $[OH^{-}] > 8.4 \times 10^{-6} M.$

* III-C-2 Sulfide separations:-

sulfide forms (ppt) with heavy metals cations that K_{sp} (10^{-10} - 10^{-40}) or smaller.

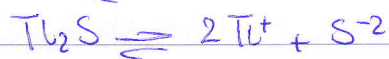
$$[H_3O^{+}]^2 = \frac{1.2 \times 10^{-22}}{[S^{2-}]}$$

* e.g. - (CdS) is less soluble than thallium sulfide
Find the condition under which (Cd²⁺) and (Tl⁺) can be separated with 0.1 M of H₂S?

Soluz. Write equation:



$$K_{sp} = 1 \times 10^{-27} = [\text{Cd}^{2+}][\text{S}^{2-}]$$



$$K_{sp} = 6 \times 10^{-22} = [\text{Tl}^{+}]^2[\text{S}^{2-}]$$

① 1 part of Cd in 1000 been removed.

$$1 \times 10^{-27} = 1 \times 10^{-4} [\text{S}^{2-}] \Rightarrow [\text{S}^{2-}] = \boxed{1 \times 10^{-23}} \text{ M.}$$

$$\textcircled{2} 6 \times 10^{-22} = [0.1]^2 [\text{S}^{2-}]$$

$$[\text{S}^{2-}] = \boxed{6 \times 10^{-20}} \text{ M.}$$

③ ppt (Cd²⁺) will happen $[\text{S}^{2-}] > 1 \times 10^{-23}$.

ppt (Tl⁺) will happen $[\text{S}^{2-}] > 6 \times 10^{-20}$.

$$\textcircled{4} [\text{H}_3\text{O}^{+}]^2 = \frac{1.2 \times 10^{-22}}{\boxed{6 \times 10^{-20}}} = 2.0 \times 10^{-3} \text{ M.}$$

فكرة واقع تميز
في كسب من التميز

$$\therefore [\text{H}_3\text{O}^{+}] = \boxed{0.045} \text{ M.}$$

* Gravimetric methods of Analysis :- قاله منو به قلعه
 defⁿ :- Based on mass measurement of a ppt. that filtered.

* [12A-1] properties of ppt and ppt agent :-

① Easily filtered and washed.

② low soluble.

ذائبه قليله

③ Unreactive with environment.

④ known composition.

در مقياس آتون عارضة كيميائي مناسب بهرجهت

* [12A-2] particle size and filter ability of ppt :-

* Factor affecting the particle size of ppt :-

① Temperature.

② Solubility.

③ concentration

④ Rate of mixing.

* Type of particles :-

① Colloidal suspension :-

الذره، منتشره، كيميائي (مثل كليب)

Tiny particles, invisible to naked eyes (10^{-7} - 10^{-4} cm d_I)

- Difficult to be filtered.

② Crystalline suspension :-

D_I $\geq$ 10 mm, easily filtered and settled down.

↓
نسيم

* Tyndall effect :- The path of beam through the solution can be seen by eyes.

* Super Saturation solution:- فوق المشبع
Solution contain high concentration for solute.

** Relative Super saturation = $\frac{Q - S}{S}$

$Q = [\text{solute}]$, $S = \text{equilibrium solubility}$. (مذاب)

* Mechanism of (ppt) formation:-

* Nucleation :- min # of atoms, ions join together to give a stable solid.

* ppt can form in 2 ways:-

① Nucleation.

نواة يتجمع حولها

② Particle growth.

نواة يتجمع عليها

Competition between additional nucleation and existing nuclei.

فكرة .. واقع .. تميز

* Experimental Control of Particle Size :- *تجارب حجم ذره ؟* *کنایه بی*

① $T \uparrow$, This will $\uparrow$ solubility.

② Good stirring. ③ $\downarrow [C]$. ④ Control pH.

* [12A-3] Colloidal precipitates :- *کنایه بی از بد حجم این به چه می رسد ؟*

* Coagulation of colloids (تخثر)

We coagulate the particles by:-

① Adding an electrolyte. ② Heating. ③ stirring.

* Adsorption :- Bonded to the surface.

→ See figure 12-1 & P 318.

* Ions (-ve) or (+ve) retained on the surface of colloidal particles, their kinds depends on σ - $[C]$ of ion.

(در هر نوعی تراکوبه یون را می بیند)

* particle treatment of colloidal ppt :-

Use an acid, "digestion".

تغذیه با اسید (مهم)

Digestion → A process in which ppt heated in the solution from which it was formed.

* [12A-4] Crystalline ppt :-

Methods of improving particle size :-

1] Use ppt agent.

2] Adjust pH.

3] Adding hot solution.

4] Use dilute solution.

* [12A-5] Coprecipitation:

آمیختن دو ماده در یک محلول و ترسیب یکنواخت آن‌ها

Proces in which soluble compound are carried out of solution by ppt. I.e (soluble compounds are removed from solution).

یعنی املاح محلول را با ترسیب از محلول خارج می‌کنند.

* There are 4 types of coppt:-

- ① Surface adsorption.
- ② mixed crystal formation.
- ③ Occlusion. ④ entrapment.

* Surface adsorption:-

⇒ see figure 12-4 ; p 321.



It's Cause of contamination in coagulated colloide, but not crystalline ppt.

سبب آلودگی در رسوبات کلوئیدی، اما نه در رسوبات بلورین

Surface adsorption به بیرون از بلورین

* Minimize adsorbed impurities on colbides:-

- ① Washing with a solution contain volatile electrolyte.

← ترسیب با محلول الکترولیت فرار.

- ② Digestion.

* Reprecipitation:-

- ① The filtered solid redissolved.
- ② The first ppt solid carryout contamination, so the second layer is the core. (به ترسیب اولی، به بیرون بردن آلودگی و رسوب دوم را در هسته قرار دادن)

* Mixed crystall formation:-
Defn:- Type of coppt in which a contaminat ion replace an ion in the crystal.

* Occlusion and mechanical entrapement:-
Type of Coppt in which a Cpd is trapped within a pocket formed.

* Coprecipitate errors:-
Might be (+ve) or (-ve).

* e.g. When colloidal AgCl adsorbs AgNO_3 during chloride analysis, (+ve).



* [12A-6] ppt from homogeneous solutions.

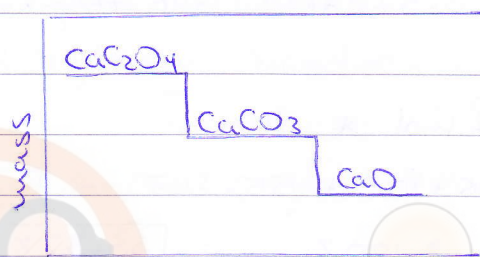
Homogeneous ppt:- when the ppt formed by slow generation of ppt agent homo. through out of solution.

* [12A-7] Drying and ^{سخت کردن} ignition ppt:-

After filtration, ppt is heated to remove solvent and volatile compound.

* Some ppt ignited to decompose the solid.

* e.g:-



← مسبقه، پخت، سخت کردن

* Thermogravimetric → تجزیه

* [12B] Calculation of results from Gravimetric data:-

* e.g:- Ca in 200 ml H_2O was determined by ppt the cation CaC_2O_4 . The ppt filtered, washed and ignited in crucible of mass = 26.6002 g. The mass of crucible and CaO = 56.077 g was 26.7134 g Calculate $[Ca]$ (40.078 g/mol)?

Solve:- ① mass CaO =

$$[(\text{mass crucible} + CaO) - \text{mass crucible}] \\ = 26.7134 \text{ g} - 26.6002 \text{ g} = \underline{0.1132 \text{ g}}$$

$$\textcircled{2} CaO \quad 1:1 \Rightarrow \# \text{ mols } Ca = \# \text{ mols } CaO = \frac{0.1132}{56.077} = \underline{2.018 \times 10^{-3}}$$

$$\textcircled{3} \# \text{ mols } Ca = M \times V \Rightarrow \frac{2.018 \times 10^{-3}}{0.2 \text{ L}} = \underline{0.01009 \text{ M}}$$

$$\textcircled{4} \text{ Concentration g/L} = M \times M.w \\ = 0.01009 \frac{\text{mol}}{\text{L}} \times 40.078 \frac{\text{g}}{\text{mol}} = \underline{0.404 \frac{\text{g}}{\text{L}}}$$

* e.x:- Iron was analyzed by dissolving 1.1324 g Sample in HCl . The solution was diluted in H_2O . Fe(III) was precipitate as $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ by adding NH_3 . After filtration, washing, the residue ignited to give 0.5394 g of Fe_2O_3 (159.69 g/mol). Calculate % Fe (55.847) in the sample ??

Solu:- ① # of mol $\text{Fe}_2\text{O}_3 = \frac{0.5394}{159.69} = [3.378 \times 10^{-3}]$ mol

② In Fe_2O_3 , we have 2 mole Fe

$\therefore$ # mole Fe = $2 \times 3.378 \times 10^{-3} = [6.7556 \times 10^{-3}]$ mole Fe.

③ Mass Fe = # of mol * Mw.

$= 6.7556 \times 10^{-3} \times 55.847 = [0.3773]$ g

④ % Fe = $\frac{0.3773}{1.1324} \times 100\% = [33.32\%]$.

* [12C] Application of Gravimetric methods:-

* ① Inorganic precipitating agents:-

* e.x:- H_2SO_4 , AgNO_3 , HNO_3 , ... Table (12-2).

② Reducing agent.

* e.x:- $\text{H}_2\text{C}_2\text{O}_4$.

... (12-2) ...

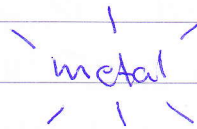
③ Organic precipitating agents:-
12 types.

↓
form slightly soluble
nonionic product
coordination compound.

↓
form products that are
largely ionic.

* Note 3-

Organic reagents yield low soluble compounds contain 2 functional group, each group capable to bond with a cation.



⇒ This reagent called: chelating agent
The product called: chelates.

مركب

أولاً * Metal chelate: non polar, low soluble in H_2O , but high soluble in organic liquid.

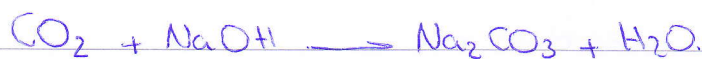
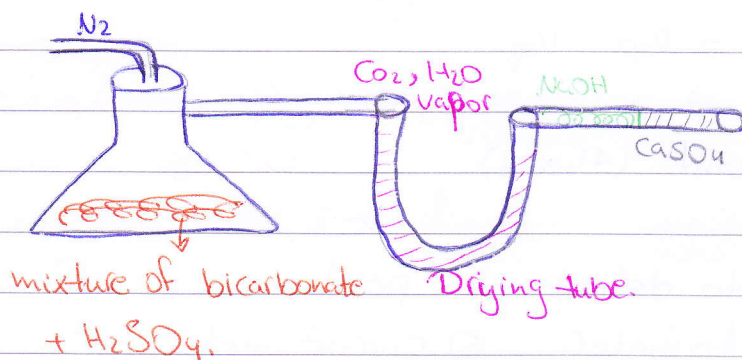
* ex- ① 8-hydroxy quinoline (Oxine) ... low soluble chelate.

② Dimethyl glyoxime: Organic ppt agent $Ni(II)$.

← لنيل فقط

③ Sodium tetrakis phenyl Borate: Special for Na and ammonium ions.

ثانياً * Volatilization Gravimetry: To detⁿ H_2O , CO_2 .



* Titrimetric methods, precipitation titrimetry:-
def:- Analytical methods based on det' the quantity of reagent of known [] that required to react completely with the analyte.

* Volumetric titrimetry:-
Measure the volume of standard reagent.

26/11 * 13-A Some terms used in volumetric titrimetry:-

* Standard solution:- reagent with known [].

* Titration:- process in which a standard reagent is added to solution of analyte until the rxn between analyte and reagent complete.

* Back titration:- The excess of a standard solution used to consume an analyte is det' with a second standard solution.

* Equivalence point:- # of mole Acid = # of mole base. ← *نقطة التكافؤ*

* End point:- The point when we see the color change. ← *نقطة التغير اللون*

* E_t = titration error = $V_{ep} - V_{eq}$.

→ V_{ep} = end point (exp) *من التجربة*

→ V_{eq} = equivalence point (theor). *من الحساب*

* 13-B Instrument used to detect end point:-

- ① Voltmeter. ② Refractometer. ③ Current meter.

* 13A-2 Primary standard:-

- ① High purity. ② Stable. ③ Absence of hydrate (*غير مائي*)
- ④ Reasonable solubility. ⑤ Large molar mass.

* [13B] Standard Solution:-

- ① Stable. ② react rapidly with analyte. ③ selective reaction.

الهدف من التحليل هو الحصول على نتائج دقيقة

* To obtain [] in titration:-

II Direct method:- weight quantity of primary standard then dissolve it in a solvent then dilute.

II] Standardization:-

The titrant (المادة التي تضاف) used to titrate:-

- ① weight quantity of primary standard.
 ② " " " Secondary " "
 ③ Measured volume of standard solution.

$$\Rightarrow \# \text{ mol } 1 = \# \text{ mole } 2$$

$$M_1 V_1 = M_2 V_2$$



* [13C] Volumetric Calculations:-

$$** \text{ Molarity} = \frac{\# \text{ mol}}{V(L)}$$

$$** \text{ Normality} = \frac{\# \text{ of equivalence}}{\text{volume}}$$

الهدف من التحليل هو الحصول على نتائج دقيقة

$$** M \times V = \# \text{ of moles} = \frac{\text{mass}}{\text{molar mass}}$$

~~~~~>



\* e.x:- How you prepare 2.0 L of 0.05 M  $\text{AgNO}_3$  (169.87 g/mol)??

Soluz:- ① # of mole =  $M \times V = 0.05 \times 2 = \boxed{0.1}$  Mole

② # of mole =  $\frac{\text{mass}}{M.wt.} \rightarrow \text{mass} = 0.1 \times 169.87 = \boxed{16.987}$  g.

\* e.x:- Standard 0.01 M solution of  $\text{Na}^+$  is required to Calibrate method to det' metal. How 500 ml of the solution can be prepared from standard  $\text{Na}_2\text{CO}_3$  (105.99 g/mol)?

Soluz:- ① # mole =  $M \times V$

# mole  $\text{Na} = 0.01 \times 0.5 \text{ L} = \boxed{0.005}$  mol.

② You have 2  $\text{Na}^+$ .

$\rightarrow$  # of mol  $\text{Na} = \frac{0.005}{2} = \boxed{0.0025}$  mol.

③ mass = # of mol  $\times$  M.wt  
 $= 0.0025 \times 105.99 = \boxed{0.265}$  g.

\* e.x:- How would you prepare 50.0 ml of standard solution that is 0.005 M from 0.01 M?

Soluz:-

$$M_i V_i = M_f V_f$$

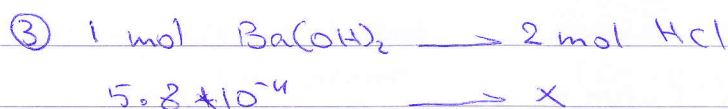
$$\frac{0.01}{0.01} \times V_i = \frac{50.0 \times 0.005}{0.01} \rightarrow V_i = \boxed{25} \text{ ml}$$

\* 13C-3 Treating titration data:-

\* e.x:- 50 ml portion of HCl required 29.71 ml of 0.01963 M Ba(OH)<sub>2</sub> to reach the end point. Calculate M of HCl?

Solus:- ①  $2\text{HCl} + \text{Ba(OH)}_2 \rightarrow \text{BaCl}_2 + 2\text{H}_2\text{O}$ . استعملوا المعادلة وبنوا عليها

$$\textcircled{2} \text{ \# of mols Ba(OH)}_2 = M \times V = 29.71 \times 10^{-3} \times 0.01963 = \boxed{5.9 \times 10^{-4}} \text{ mol.}$$



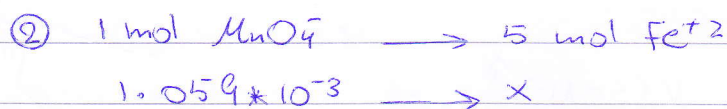
$$\text{\# of mol HCl} = \boxed{1.166 \times 10^{-3}} \text{ mol.}$$

$$\textcircled{4} \text{ \# mol HCl} = M \times V(L) \Rightarrow M = \frac{1.166 \times 10^{-3}}{0.05} = \boxed{0.0233} \text{ M}$$

\* e.x:- 0.804 g sample of Fe dissolved in Acid the Iron reduced to Fe<sup>2+</sup> with 47.22 ml of 0.02242 M KMnO<sub>4</sub>. Calculate the results of the analysis in % Fe (55.847 g/mol)??



$$\text{\underline{Solus:-}} \textcircled{1} \text{ \# mol KMnO}_4 = M \times V = 0.04722 \times 0.02242 = \boxed{1.059 \times 10^{-3}} \text{ mol.}$$



$$x = \boxed{5.29 \times 10^{-3}} \text{ mol Fe}^{2+}$$

$$\textcircled{3} \begin{aligned} \text{mass} &= \text{\# of mol} \times M_{\text{wt}} \\ &= 5.29 \times 10^{-3} \times 55.847 = \boxed{0.295} \text{ g} \end{aligned}$$

$$\textcircled{4} \% \text{ Fe in sample} = \frac{0.295}{0.804} \times 100\% = \boxed{36.77 \%}$$

\* ليس نستخدم KMnO<sub>4</sub> في هذا المثال \*



\* 13D Gravimetric titrimetry:-

سحب، وزن

To det<sup>n</sup> the mass.

الوزن  $\rightarrow$  weight molarity =  $\frac{\# \text{ mole solute}}{\text{kg solution}}$   
 (الوزن)

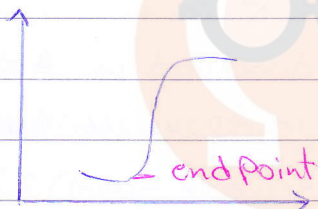
## \* Advantages of weight molarity:-

- ① No calibration needed.
- ② Accuracy & precision is higher.
- ③ Automated.

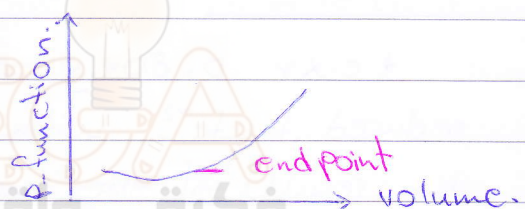
\* 13E Titration Curve:-

## \* Types:-

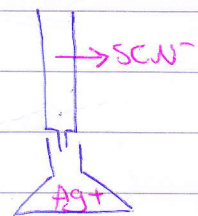
① Sigmoidal.



② linear.



\*  $[Ag^+] \downarrow$ ,  $V(SCN^-) \uparrow$

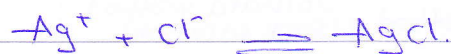
\* 13F ppt titrimetry:-

الوزن، السحب، التبريد

(Argentometric method) :- The ppt reagent is  $AgNO_3$ .

$\rightarrow$  Used for ppt  $CN^-$ , halids,  $SCN^-$ .

\* e.x : perform calculation needed to generate titration curve for 50 ml of 0.05 M NaCl with 0.1 AgNO<sub>3</sub> for AgCl ( $K_{sp} = 1.82 \times 10^{-10}$ )?



[1] If 10 ml AgNO<sub>3</sub> added? (pre equ. point)

مقدار الفضة  
المضافة

$$M \times V = M \times V \rightarrow 0.05 \times 50 = 0.1 \times V \rightarrow V = 25 \text{ ml}$$

$$\rightarrow \text{original of mole NaCl} = M \times V = 0.05 \times 0.05 (L) = \boxed{0.0025} \text{ mol NaCl}$$

$$\rightarrow \# \text{ of mol AgNO}_3 = M \times V = 0.1 \times 0.01 = \boxed{0.001} \text{ mol.}$$

$$\rightarrow [NaCl] = \frac{\text{original} - \text{Added}}{\text{Total volume}} = \frac{0.0025 - 0.001}{(50 + 10) \times 10^{-3}} = \boxed{0.025} M$$

$$\rightarrow [Cl^-] = \boxed{0.025} M.$$

$$K_{sp} \approx [Ag^+] \rightarrow K_{sp} = 1.82 \times 10^{-10} = [Ag^+] (0.025) = \boxed{7.28 \times 10^{-9}} M.$$

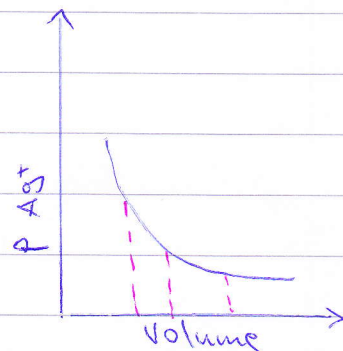
$$p[Ag^+] = -\log [Ag^+] = \boxed{8.14}$$

[2] At equ. point

$$Ag^+ = Cl^- \rightarrow K_{sp} = [Ag^+]^2 = 1.82 \times 10^{-10}$$

$$[Ag^+] = \boxed{1.34 \times 10^{-5}} M.$$

$$p[Ag^+] = \boxed{4.87}$$



مقدار الفضة  
المضافة

[3] post-equivalence:-

At 26 ml AgNO<sub>3</sub>? Ag excess.

$$** [Ag^+] = \frac{\text{excess} - \text{original}}{\text{Volume}} = \frac{(26 \times 0.1 \times 10^{-3}) - (0.0025)}{(50 - 26) \times 10^{-3}} = \boxed{4.167 \times 10^{-3}} M$$

$$p = \boxed{2.4}$$

المقدار المتبقى بعد التفاعل

excess  $\rightarrow$  # of mol for excess

original  $\rightarrow$  # of mol for original.

Volume  $\rightarrow$  not the total volume. لأنني في لحظة من حجم المحلول حول التوازن.

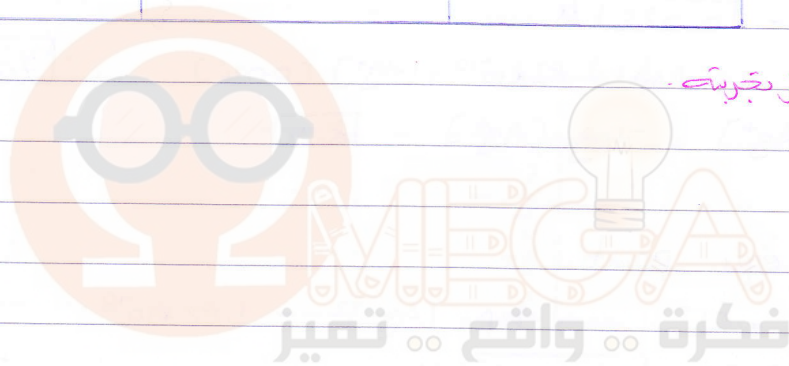


## \* Indicators for Argentimetric titrations:-

| Mohr's method                         | Fajon's method | Volhard method<br>(Back titration) |
|---------------------------------------|----------------|------------------------------------|
| * Indicators<br>chromate ion          | fluorescein    | Iron (III)                         |
| * pH:- 7-10                           | أقرب المقاب    | Acidic medium                      |
| * To det <sup>n</sup> halides, $Cl^-$ | نفس السيترا    | نفس السيترا                        |
| * color:- Red                         | Red            | Red                                |

use thiocyanate ion.

السيترا الذي يميز بجريته



\* principles of Neutrization titrations:

\* Neutrization rxn :- Acid - Base rxn.

\* [14A-1] Standard solution :- solution with known  $[ ]$ .

\* Standard solution of Acids :- prepared by diluting.

HCl, sulfuric Acid, perchloric  $??$  strong Acids since the react  
(تفاعل كامل) completely with analyte.

\* Standard solution of Base, prepared by solid

NaOH, KOH, Ba(OH)<sub>2</sub>.

\* [14A-2] Acid-Base indicators:-

Weak organic Acid or base.

\* e.g:-



$\Rightarrow HIn$  :- Acid indicator.



$\Rightarrow In^-$  :- Base indicator.

$$K_a = \frac{[In^-][H_3O^+]}{[HIn]} \Rightarrow [H_3O^+] = \frac{K_a [HIn]}{[In^-]}$$

$\Rightarrow$  Note :- if  $\frac{[HIn]}{[In^-]} \gg 10$

acid color. (لون أحمر)

$$\Rightarrow [H_3O^+] = 10 K_a$$

if  $\frac{[HIn]}{[In^-]} \ll \frac{1}{10}$

Base color.  $[H_3O^+] = 0.1 K_a$ .

$$** \boxed{PH = pK_a \pm 1}$$



\* Titration errors with Acids / Base indicators.

① Determinate error ; occur when pH at which the indicator changes color differs from pH at eq. point.  
→ make correction using blank k.

② Indeterminate error :- from eyes.

\* The errors depend on :-

1] [Indicator].

2] Sensitivity of eyes reading.

3] Change of pH.

\* Variables influence the behavior of indicators :-

① Temperature.      ② presence of organic solvent.

③  $\mu$  of the medium  $\leftarrow \rightarrow$  (pH) من الوسط

فكرة .. واقع .. تميز

\* Titration of strong acids and strong bases:

$$[H_3O^+] = C_{\text{strong acid}} + [OH^-] \approx C_{\text{strong acid}}$$

$$[OH^-] = C_{\text{strong base}} + [H^+] \approx C_{\text{strong base}}$$

\* [14B-1] Titrating a strong acid with strong bases:

$$pK_w = pH + pOH$$

$$-\log 10^{-14} = 14$$

\* ex- Generate a hypothetical titration curve for titration of 50.0 ml of 0.05 M HCl with 0.1 M NaOH?

① After the addition of 10 ml reagent?

Soln:  $M \times V = M \times V$

$$0.05 \times 50 = 0.1 \times V \rightarrow V_{\text{NaOH}} = 25 \text{ ml}$$

$$\textcircled{a} C_{\text{HCl}} = \frac{\text{Original \# mol HCl} - \text{\# mol NaOH added}}{\text{Total Volume}}$$

$$C_{\text{HCl}} = \frac{(0.05 \times 50 \times 10^{-3}) - (0.1 \times 10 \times 10^{-3})}{(0.05 + 0.01) \text{ L}} = 2.5 \times 10^{-2} \text{ M} = [H_3O^+]$$

$$pH = -\log [H_3O^+] = 1.60$$

② After the addition of 25.0 ml reagent?

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}$$

$$pH = 7$$

③ After the addition of 25.10 ml reagent.

$$C_{\text{NaOH}} = \frac{\text{\# mol NaOH added} - \text{\# mol original HCl}}{\text{Total Volume}} = \frac{(0.0251 \times 0.1) - (0.05 \times 0.05)}{(0.05 + 0.0251)}$$

$$= 1.33 \times 10^{-4}$$

$$pOH = 3.88 \rightarrow \text{so } pH = 14 - 3.88 = 10.12$$



\* Choosing an indicator:

Bromothymol is the best with the lowest error, low [ ].

\* [14B-2] Titrating a strong base with a strong acid:-

\* e.g:- Calculate the pH during titration of 50 ml of 0.05 M NaOH with 0.1 M HCl after the addition of 24.5 ml?

Ⓐ 25 ml ? Ⓒ 25.5 ml ?

Solus:-

$$\textcircled{1} \quad M \times V_{\text{acid}} = M \times V_{\text{base}}$$

$$0.1 \times V = 0.05 \times 50 \rightarrow V = \boxed{25} \text{ ml} \quad \text{end point}$$

Ⓐ At 24.5 ml ? (before end point).

$$C_{\text{NaOH}} = \frac{\# \text{ mole original of NaOH} - \# \text{ mole HCl added}}{\text{Total Volume.}}$$

$$= \frac{(0.05 \times 50 \times 10^{-3}) - (0.1 \times 24.5 \times 10^{-3})}{(0.05 + 0.0245)} = \boxed{6.71 \times 10^{-4}}$$

$$\text{pOH} = -\log(6.71 \times 10^{-4}) = 3.17$$

$$\text{pH} = 14 - 3.17 = \boxed{10.83}.$$

Ⓑ At 25 ml ? (pH = 7 At end point).

Ⓒ At 25.5 ml ?

$$C_{\text{H}_3\text{O}^+} = \frac{\# \text{ mol HCl Added} - \# \text{ mol original}}{\text{Total Volume}}$$

$$= \frac{(0.025 \times 0.1) - (0.05 \times 50 \times 10^{-3})}{(0.05 + 0.0255)} = \boxed{6.62 \times 10^{-4}} \text{ M}$$

$$\text{pH} = \boxed{3.18}$$

\* [14C] Titration curve for weak acids:

\* Ex: Generate a curve for titration of 50 ml of 0.1 M Acetic Acid with 0.1 M NaOH? Calculate Initial pH,  $K_a = 1.75 \times 10^{-5}$  ?  
 1- After the addition of 5 ml? 2- After the addition of 25 ml?  
 3- At the equivalence point? 4- After addition of 50 ml?

Solu:-

$$[H^+] = \sqrt{K_a C_{HOAc}} = \sqrt{1.75 \times 10^{-5} \times 0.1} = [1.32 \times 10^{-3}] M$$

$$pH = [2.88]$$

$$① C_{HOAc} = \frac{\# \text{ mol HOAc Original} - \# \text{ mol NaOH added}}{\text{Total volume}}$$

$$= \frac{(0.05 \times 0.1) - (0.005 \times 0.1)}{(50 + 5) \times 10^{-3}} = [0.0818]$$

$$C_{NaOAc} = \frac{0.005 \times 0.1}{0.055} = [9.1 \times 10^{-3}] M.$$

$$K_a = [H^+] \times 9.1 \times 10^{-3} = 1.75 \times 10^{-5}$$

$$[H^+] = [1.58 \times 10^{-4}] M \quad \Rightarrow \quad pH = [3.80]$$

$$② C_{NaOAc} = \frac{0.025 \times 0.1}{(0.05 + 0.025)} = [0.033] M.$$

$$K_a = 1.75 \times 10^{-5} = [H^+] \times 0.033$$

$$[H^+] = 5.3 \times 10^{-4} M. \quad \Rightarrow \quad pH = [3.28]$$

$$③ \frac{K_w}{K_a} = K_b \quad \Rightarrow \quad \frac{1 \times 10^{-14}}{1.75 \times 10^{-5}} \quad \Rightarrow \quad K_b = [5.71 \times 10^{-10}]$$

$$[OH^-] = \sqrt{K_b \times C_{NaOH}^{0.1}}$$

$$pH = [8.73]$$

\* إذا كان المحلول يحتوي على buffer لـ 13.1

\*  $H_2O$  لا تتأثر قيمة pH

\* عند اختيار indicator يجب أن يكون  $K_a$



\* Complexation rxn and titration:-

\* [17A] The formation of Complexes:-

Most metal ions react with  $\bar{e}$  pair donor to form compounds  
= Complexes.

\* e.x:- Ammonia, halides,  $H_2O \Rightarrow$  (in organic ligand).

يكون أن يحتوي على زوج  $\bar{e}$  غير رابط.

\* Ligand:- Ion or molecule that forms a covalent bond with a cation.

\* e.x:-  $Cu(II) \xrightarrow{H_2O} Cu(H_2O)_4^{+2}$

اللياندر لينتقلية تكون مركبات معقدة.

\* The # of covalent bond the cation forms:-

(2, 4, 6)  $\Rightarrow$  2, 4, 6 أزواج زوجية

\* Note:- Complex might be (-ve) or (+ve) or neutral.

\* Complexometric method:-

Titrimetric based on complex formation.

\* Chelate:- produced when metal ion coordinates with two or more donor groups of single ligand.

\* Macrocycle:- metal ion + cyclic organic compounds.

\* Unidentate:- ligand has a single donor group.

\* e.x:- Ammonia.

\* [17A-1] Complexation equilibrium:-

\* Equilibrium constant:-



$$K_1 = \beta_1 = \frac{[ML]}{[L][M]}$$



$$k_1 k_2 = \beta_2 = \frac{[ML_2]}{[L]^2 [M]}$$



$$k_1 k_2 k_3 = \beta_3 = \frac{[ML_3]}{[L]^3 [M]}$$

\* **Alpha Value**:- Fraction of total metal concentration existing in the form.

$$** \alpha_M = \frac{1}{1 + \beta_1 [L] + \beta_2 [L]^2 + \dots + \beta_n [L]^n}$$

$$** \alpha_{ML} = \frac{\beta_1 [L]}{1 + \beta_1 [L] + \beta_2 [L]^2 + \dots + \beta_n [L]^n}$$

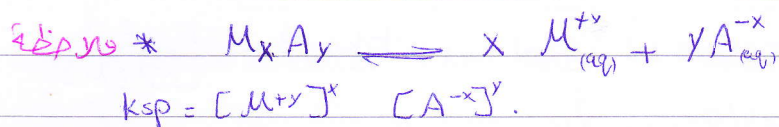
\* **[7A-2]** The formation of insoluble species:-

The complexes formed are soluble in solution, but addition of ligand to metal ion results in insoluble:-



Adding large excess of  $Cl^-$ , produce soluble species, such as:-  $AgCl_2^-$ ,  $AgCl_3^{2-}$ ...





\* [17A-3] Ligand that can protonate:-  
 When they are weak Acid.

\* complexation with protonated ligands:-



adding acid to a solution containing  $M$  and  $L$ , will reduce  $[L]$  of free  $L$ .

\* ex: oxalate  $H_2Ox$ .

DiP \*\*  $C_T = [H_2Ox] + [HOx^-] + [Ox^{2-}]$

charge balance equ.

$$\alpha_0 = \frac{[H_2Ox]}{C_T} = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\alpha_1 = \frac{[HOx^-]}{C_T} = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\alpha_2 = \frac{K_{a1} + K_{a2}}{C_T}$$

DiP \*\*  $[Ox^{2-}] = C_T \alpha_2 \rightarrow$  (قيمة  $\alpha_2$  موزون  $H$  لا  $OH$ )

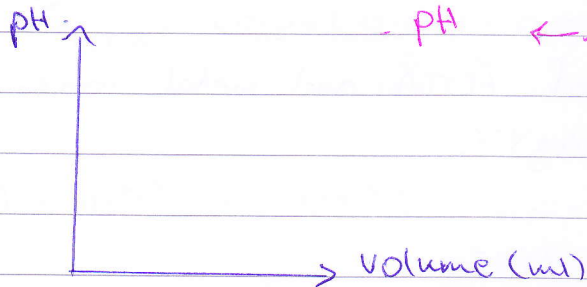
\* Additional Formations Constants:-

pH-constant :- Constant depends on pH.

DiP \*\*  $k_i = k_1 \alpha$  (قيمة  $k_i$  موزون  $H$  لا  $OH$  const. لا يكون)

\* [17B] Titration with inorganic complexing agent:-

Volume ml ← x وازدادت  
- pH ← y وازدادت



\* [17C] Organic complexing agent:-

They are used to:-

① To convert metal Ions into forms that can be extracted from  $H_2O$  into immisible phase.

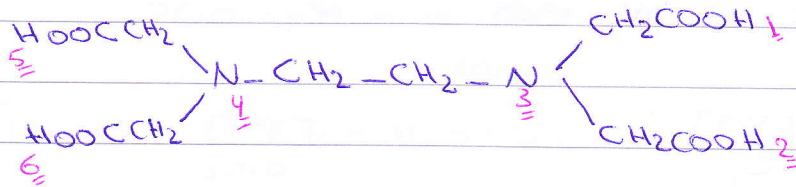
نضع مادة في محلول نجمع عليها  
مادة المادتين وتبقى الأخرى.

② They are used as masking agent.

لتخليق مادة (مادة معدنية بالمحلول) عزلها عن المواد الأخرى.

(29/12) \* [17D] Amino carboxylic acid titration:-

\* [17D-1] Ethylenediamic tetraacetic acid (EDTA) :-  $(H_4Y)$  ويرمز له  
6 sites for bonding metal Ion.

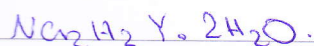


مواقع ارتباط فلزات.

EDTA :- has 4 ka values.

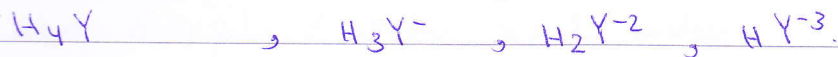
حسب عدد الـ  $(COOH)$ .

\* Reagents for (EDTA):-

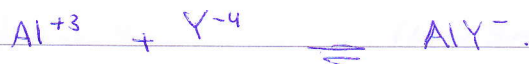
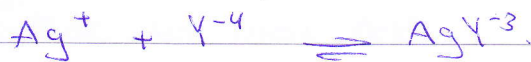




→ 4  $K_a$  values:-



\* [17D-2] :- Complexes of EDTA and metal ions:-



\* [17D-3] Equilibrium Calculation involving EDTA:-

$$** C_{T \text{ EDTA}} = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^{-}] + [H_4Y].$$

$$** \alpha_4 = \frac{[Y^{4-}]}{C_T} = \frac{K_1 K_2 K_3 K_4}{D}$$

\* ينبغي الاستحسان  
أسي

من كل قيم  $\alpha$  مذبذبة

\* ex:- Calculate the  $[Y^{4-}]$  in 0.02 M EDTA solution buffered to pH = 10.00?

أعطاني قيمة pH من استقر قيمة  $\alpha$  مذبذبة

Soln:-

$$\alpha_4 \text{ at pH} = 10.0 \rightarrow \alpha_4 = 0.35.$$

$$\alpha_4 = \frac{[Y^{4-}]}{C_T} \rightarrow 0.35 = \frac{[Y^{4-}]}{0.02} \rightarrow \therefore [Y^{4-}] = [7 \times 10^{-3}] M$$

\* ex:- Calculate  $[Ni^{+2}]$  in a solution prepared by mixing 50.0 ml of 0.03 M  $Ni^{+2}$  with 50.0 ml of 0.05 M EDTA pH = 3?

Soln:-

$$\textcircled{1} \quad C_{\text{NiY}^{2-}} = \frac{M \times V}{\text{Total Volume}} = \frac{50.0 \text{ ml} \times 0.03}{100 \text{ ml}} = \boxed{0.015} \text{ M}$$

$$\textcircled{2} \quad C_{\text{EDTA}} = \frac{(0.05 \text{ L} \times 0.05) - 0.015 \text{ M}}{0.1 \text{ L}} = \boxed{0.01} \text{ M}$$

← تركيز EDTA يوجد داخل complex

$$\textcircled{3} \quad [\text{Ni}^{+2}] \ll [\text{NiY}^{2-}] \longrightarrow [\text{NiY}^{2-}] = \boxed{0.015}$$

لأنه في معادلة  $[\text{Ni}^{+2}]$  لدينا في المعادلة لم نجد

$$C_{\text{EDTA}} = 0.01 \text{ M}$$

$$\alpha_4 K = K'$$

بعد اشتقاق نموذج لفا تون

$$** \quad \boxed{[\text{Ni}^{+2}] = \frac{C_{\text{NiY}^{2-}}}{\alpha_4 * C_{\text{EDTA}}}}$$

$$\alpha_4 \text{ at } \text{pH} = 3 \text{ is } 1.05 * 10^{-8}$$

$$\therefore [\text{Ni}^{+2}] = \frac{0.015}{1.05 * 10^{-8} * 0.01} = \boxed{1.4 * 10^{-8}} \text{ M}$$



\* [17D-7] Titration methods employing EDTA:-

\* Direct titration:-

① Methods based on indicators for the analyte.

40 metal can be det<sup>n</sup> - with EDTA.

② Methods based on indicators for an added metal ion.  
Eriochrome Black T.

\* Spectrophometric methods:-

2 Types :- ① Back titration available for Cr III, Co III.

② Displacement method:-



الدمج

\* Masking agent:- A complexing agent that react selectively with Component by prevent that component from rxn.

\* (EDTA) أشهر تفاعلات

The det<sup>n</sup> of H<sub>2</sub>O hardness:-

عسر الماء

(سبب عسر الماء في الماء)

Water hardness:- Contain Ca, Mg and heavy metal ions that form ppt with Soap.