Experiment Title (4):

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PURPOSE:

Determination of Ksp at room temperature for calcium sulfate by measuring the solubility of this salt in sodium chloride solution of various ionic strengths & derivation some of the relation.

INTRODUCTION:

Effect of Ionic Strength: The effect of added electrolyte on equilibrium is independent of the chemical nature of the electrolyte but depends on ionic strength, μ, of the electrolyte.

$$\mu = \frac{1}{2}([A]Z_A^2 + [B]Z_B^2 + [C]Z_C^2 + \ldots)$$

where [A], [B], [C]… represent the molar concentrations of the species in solution, and Z corresponds to their respective charges. At ionic strengths of 0.1 or less, the effect of added electrolyte on solubility is independent of the electrolyte ionic species.

Source of the Salt (Electrolyte) Effect: Each dissociated reactant ion is surrounded by a solvent sheath containing both positive and negative ions, but a slight excess of the counter charge; thus slightly decreasing the charge of the dissociated ion, decreasing the attraction of the dissociated ions, and increasing solubility. The effective molar concentration of equilibrium ions is less as the ionic strength increases. The effective concentration decreases, so the actual concentration (solubility) can increase.

Activity Coefficients: The activity, *a*, of a species, *X*, is a measure of its effective concentration as determined by the lowering of the freezing point of water or by electrical conductivity. It is a function of concentration and its activity coefficient (which is a function of ionic strength).

$$a_X = \gamma_X[X]$$

γ_X is the dimensionless activity coefficient for the species X. It is dependent upon ionic strength and approaches 1 as ionic strength approaches 0. Activity coefficients vary with ionic strength in such a way that when activities are replaced into the equilibrium constant expressions, the thermodynamic solubility constant is freed of ionic strength dependence (it is a constant). For X_mY_n

$$K_{sp} = a_X^m a_Y^n = \gamma_X^m \gamma_Y^n [X]^m [Y]^n = \gamma_X^m \gamma_Y^n K_{sp}^{'}$$

Properties of Activity Coefficients

i. The activity coefficient of a species is a measure of the effectiveness with which that species influences an equilibrium in which it is a participant. Effectiveness often decreases as the ionic strength increases up to ~0.1 M. At ionic strengths above 0.1 M the activity coefficients sometimes increase above unity. This phenomenon is complex and will not be addressed.

ii. In solutions that are not too concentrated (< 0.1 M ionic strength), the activity coefficient for a given species is independent of the nature of the electrolyte and dependent only on the ionic strength.
iii. At a given ionic strength, the activity coefficient of an ion departs farther from unity as the charge on the species increases. Activity of a neutral species is unaffected by ionic strength.
iv. At any given ionic strength of < 0.1 M, the activity coefficients on ions of the same charge are approximately equal.
v. The activity coefficient of a given ion describes its effective behavior in all equilibrium in which it participates.

The Debye-Hückel Equation: An equation used to calculate activity coefficients from their average size and charge.

$$-\log \gamma_X = \frac{0.51 Z_X^2 \sqrt{\mu}}{1 + 3.3\alpha_X \sqrt{\mu}}$$

where Z_X is the charge on X and α_X is the effective diameter of the hydrated ion X in nanometers (often 0.5 nm is assumed, since at <0.01 M the error is minimal). The constants 0.51 and 3.3 are only applicable in water at 25˚C. 0.3 nm for univalent ions (denominator becomes $1 + \sqrt{\mu}$ or 1) and as high as 1.0 nm for multivalent. The constants are applicable only at 25 ˚C. Unfortunately, there can be considerable uncertainty in α_X, however uncertainties are of little significance at *ionic strengths of less than 0.01* (based on equation). Works well only up to 0.1 ionic strength.

Mean Activity Coefficients: It is impossible to measure the properties of individual ions in the presence of counter ions of opposite charge and solvent molecules. Experimental methods give only a mean activity coefficient for the positively and negatively charged ions in solution, however, experimental and theoretical values correspond well. For electrolyte A_mB_n

$$\gamma_\pm = (\gamma_A^m \gamma_B^n)^{1/(m+n)}$$

This can be experimentally determined by taking two solubility measurements (one very dilute with unit values for activity coefficients and another at a higher ionic strength). The experimental determination of individual activity coefficients is impossible.

Equilibrium Calculations Employing Activity Coefficients: Equilibrium calculations with activities yield values in better agreement with experimental results. Calculations can be done showing the relative error in not using activity coefficients or changes in solubility in solvents containing electrolytes of non-common ions.

References:

http://www.udel.edu/pchem/C445/C445f06/Exp3.pdf

www.wikipedia.com

www.answers.com

THEORY:

In a saturated solution of a sparingly soluble salt (MA) the solubility, S, is equal to the concentration of either M^+ or A^- provided the salt is fully dissociated.
The solubility product (Ks) is defined as the following:

$$K_{sp} = a_1 * a_2 = (c_1\ c_2)\ (f_1\ f_2) = S^2\ f^2_{\pm}$$

Where:
The subscripts 1 & 2 refer to the ions M^+ or A^- respectively.
$f^2_{\pm}$ is the mean ionic activity coefficient.

For the particular salt, K_{sp} is the solubility constant and dependent only on the temperature. One way of eliminating the activity coefficient is by using an extended form of the Debye-Huckel equation:

$$\text{Log } f\pm = -A\ z_1\ z_2\ I^{1/2} + BI$$

Where z is the valency of the ion, B an unknown constant, and A is a known constant, And I is the ionic strength.

The ionic strength (I) for a solution contains the species 1,2,3 …ect the consist of which are z_1, z_2, z_3, ect. And their concentration is c_1, c_2, c_3 then the ionic species can be calculated as follows:

$$I = ½\ (c_1z_1^2 + c_2\ z_2^{2+} + c_3z_3^2\ )$$

Or simply the Ionic strength may be expressed as:

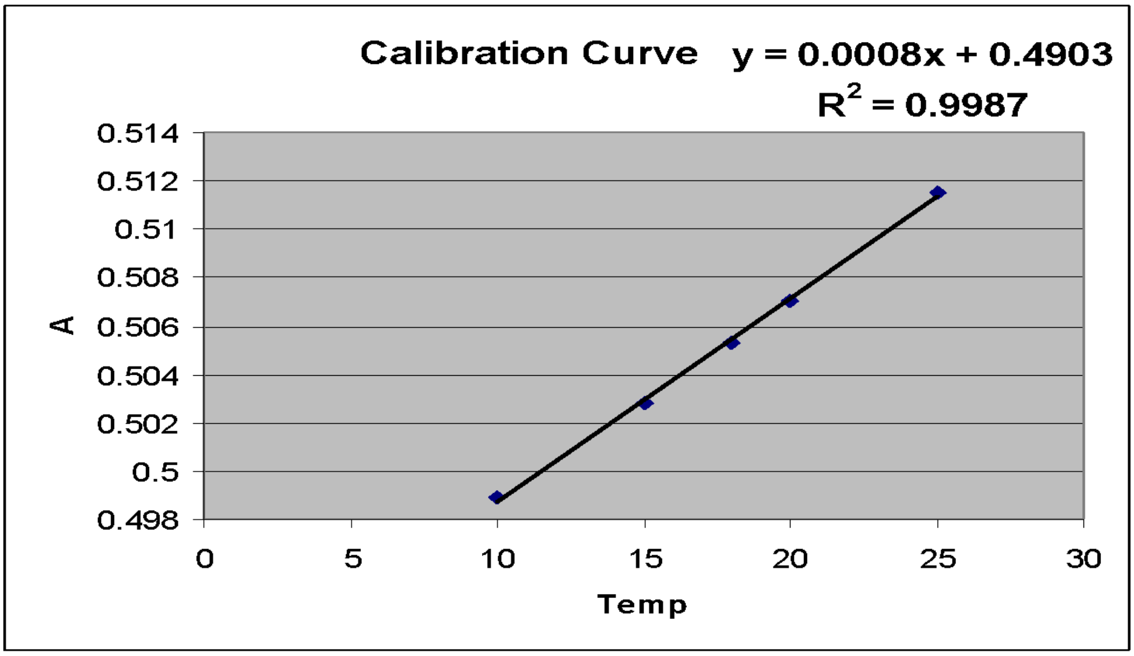
$$I = \frac{1}{2}\Sigma\, c_i z_i^2$$

DATA:

The values of the constant A at various temperatures as the following:

Temp(°C)	10	15	18	20	25
A	0.4989	0.5028	0.5053	0.5070	0.5115

The graph is the following:



From the above graph that shows that:

Y=0.0008X+0.4903 ⟶ But the temp is 23ºC then:

Y=0.0008(23)+0.4903

Y=0.5087.

at 23 C° the A constant value = 0.5087

CALCULATION:

Standardization of EDTA solution with $ZnSO_4$:

Wt. of $ZnSO_{4.}7\ H_2O$ = 0.03 g , V_{EDTA} = 11.5 mL
$(M*V)_{EDTA}$ = # of moles $ZnSO_4$
$(0.01\times11.5\times10^{-3})$ = mass / MM
(0.01×0.0115) = mass / 287.54
Mass = 0.033 g of $ZnSO^{-4}$

For the first solution:

$$CaSO \rightleftharpoons Ca^{+2}+SO_4^{-2}$$

[NaCl] = 0.01M , V_{EDTA} = 12.6 ml

$(M*V)_{CaSO4} = (M*V)_{EDTA}$
$(M*10) = (0.01*12.6)$
M =[$CaSO_4$] =$S_{CaSO4 =}$ 0.0126 mol/L

I=[NaCl] + 4 S_{CaSO4}
I= 0.01+4 (0.0126) = 0.0604 M

$b=A\ |\ z_1\ |\ |z_2\ |\ (\ I\ )^{1/2}$
$b=0.5087\ (2)\ (2)\ (0.0604)^{1/2}=0.5$

For the second solution:

[NaCl] = 0.02 M , V_{EDTA} = 13.4 ml

$(M*V)_{CaSO4} = (M*V)_{EDTA}$
$(M*10) = (0.01*13.4)$
M =[$CaSO_4$] =S_{CaSO4} = 0.0134 mol/L

I=[NaCl] + 4 S_{CaSO4}
I= 0.02+4 (0.0134) = 0.0736 M

$b=A\ |\ z_1\ |\ |z_2\ |\ (\ I\ )^{1/2}$
$b=0.5087\ (2)\ (2)\ (0.0736)^{1/2} = 0.5520$

For the third solution:

$[NaCl] = 0.03$ M , $V_{EDTA} = 15.3$ ml

$(M*V)_{CaSO4} = (M*V)_{EDTA}$
$(M*10) = (0.01*15.3)$
$M = [CaSO_4] = S_{CaSO4} = 0.0153$ mol/L

$I = [NaCl] + 4\ S_{CaSO4}$
$I = 0.03 + 4\ (0.0153) = 0.0912$ M

$b = A\ |\ z_1\ |\ |z_2\ |\ (\ I\ )^{1/2}$
$b = 0.5087\ (2)\ (2)\ (0.0912)^{1/2} = 0.6145$

For the fourth solution:

$[NaCl] = 0.04$ M , $V_{EDTA} = 15.7$ ml

$(M*V)_{CaSO4} = (M*V)_{EDTA}$
$(M*10) = (0.01*15.7)$
$M = [CaSO_4] = S_{CaSO4} = 0.0157$ mol/L

$I = [NaCl] + 4\ S_{CaSO4}$
$I = 0.04 + 4\ (0.0157) = 0.1028$ M

$b = A\ |\ z_1\ |\ |z_2\ |\ (\ I\ )^{1/2}$
$b = 0.5087\ (2)\ (2)\ (0.1028)^{1/2} = 0.6524$

For the fifth solution:

$[NaCl] = 0.05$ M , $V_{EDTA} = 16.0$ ml

$(M*V)_{CaSO4} = (M*V)_{EDTA}$
$(M*10) = (0.01*16.0)$
$M = [CaSO_4] = S_{CaSO4\ =}\ 0.016$ mol/L

$I = [NaCl] + 4\ S_{CaSO4}$
$I = 0.05 + 4\ (0.016) = 0.114$ M

$b = A\ |\ z_1\ |\ |z_2\ |\ (\ I\ )^{1/2}$
$b = 0.5087\ (2)\ (2)\ (0.114)^{1/2} = 0.6870$

For the sixth solution:

$[NaCl] = 0.10$ M , $V_{EDTA} = 18.5$ ml

$(M*V)_{CaSO4} = (M*V)_{EDTA}$
$(M*10) = (0.01*18.5)$
$M = [CaSO_4] = S_{CaSO4} = 0.0185$ **mol/L**

$I = [NaCl] + 4\ S_{CaSO4}$
$I = 0.10 + 4\ (0.0185) = 0.174$ **M**

$b = A\ |z_1|\ |z_2|\ (I)^{1/2}$
$b = 0.5087\ (2)\ (2)\ (0.174)^{1/2} = 0.8488$

For the seventh solution:

$[NaCl] = 0.20$ **M** , $V_{EDTA} = 19.6$ **ml**

$(M*V)_{CaSO4} = (M*V)_{EDTA}$
$(M*10) = (0.01*19.6)$
$M = [\ CaSO_4] = S_{CaSO4} = 0.0196$ **mol/L**

$I = [NaCl] + 4\ S_{CaSO4}$
$I = 0.20 + 4\ (0.0196) = 0.2784$ **M**

$b = A\ |z_1|\ |z_2|\ (I)^{1/2}$
$b = 0.5087\ (2)\ (2)\ (0.2784)^{1/2} = 1.0736$

For the eighth solution:

$[NaCl] = 0.30$ **M** , $V_{EDTA} = 22.5$ **ml**

$(M*V)_{CaSO4} = (M*V)_{EDTA}$
$(M*10) = (0.01*22.5)$
$M = [CaSO_4] = S_{CaSO4} = 0.0225$ **mol/L**

$I = [NaCl] + 4\ S_{CaSO4}$
$I = 0.30 + 4\ (0.0225) = 0.39$ **M**

$b = A\ |z_1|\ |z_2|\ (I)^{1/2}$
$b = 0.5087\ (2)\ (2)\ (0.39)^{1/2} = 1.2707$

For the ninth solution:

$[NaCl] = 0.50$ **M** , $V_{EDTA} = 25.5$ **ml**

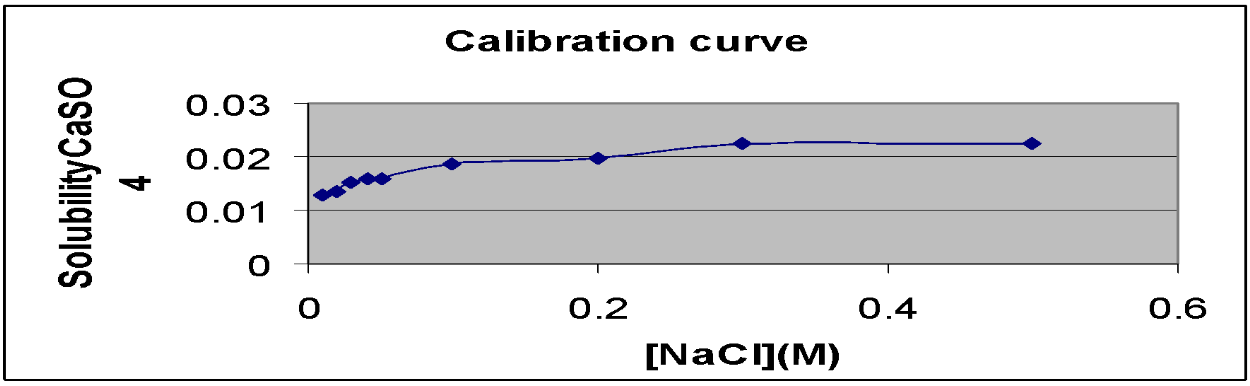
$(M*V)_{CaSO4} = (M*V)_{EDTA}$

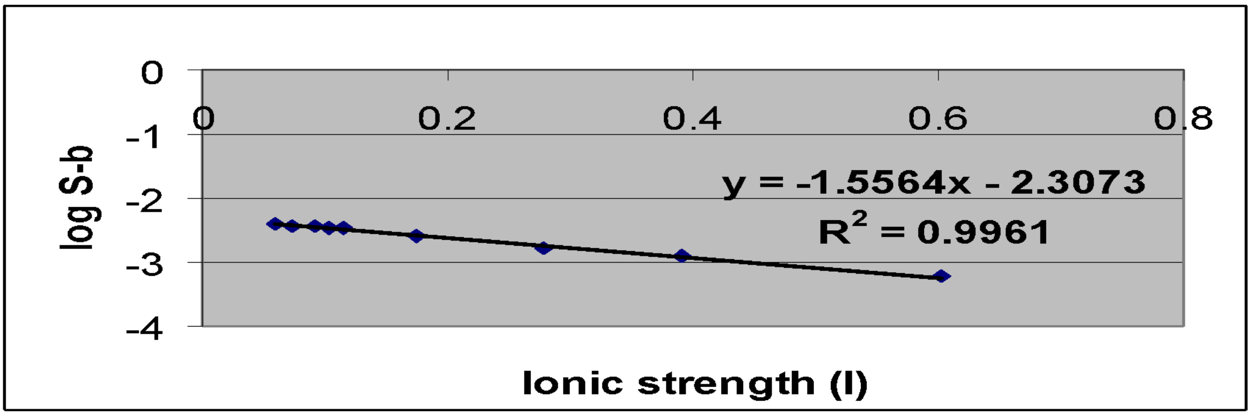
(M*10) =(0.01*25.5)
M = CaSO$_4$] =S$_{CaSO4}$ = 0.0255 mol/L

I=[NaCl] + 4 S$_{CaSO4}$
I= 0.50+4 (0.0255) = 0.602

b=A | z$_1$ | |z$_2$ | (I)$^{1/2}$
b=0.5087 (2) (2) (0.602)$^{1/2}$ =1.5788

[NaCl](M)	V $_{EDTA}$(mL)	SolubilityCaSO$_4$	Ionic strength (I)	b	log S	log S-b
0.01	12.6	0.0126	0.0604	0.5	-1.899629455	-2.39962945
0.02	13.4	0.0134	0.0736	0.552	-1.872895202	-2.4248952
0.03	15.3	0.0153	0.0912	0.615	-1.815308569	-2.42980857
0.04	15.7	0.0157	0.1028	0.652	-1.804100348	-2.45650035
0.05	16	0.016	0.114	0.687	-1.795880017	-2.48288002
0.1	18.5	0.0185	0.174	0.849	-1.732828272	-2.58162827
0.2	19.6	0.0196	0.2784	1.074	-1.707743929	-2.78134393
0.3	22.5	0.0225	0.39	1.271	-1.647817482	-2.91851748
0.5	25.5	0.0225	0.602	1.579	-1.647817482	-3.22661748




0
-1
-2
-3
-4
0
0.2
0.4
0.6
0.8
log S-b
y = -1.5564x - 2.3073
R² = 0.9961
Ionic strength (I)

DERINATION OF THE RELATION:

$$CaSO_4 \rightleftharpoons Ca^{+2} + SO_4^{-2}$$

$$Cf_+ \quad Cf_-$$

$K_{sp} = [\ Ca^{+2}\ ]\ f_+\ \ [\ SO_4^{-2}\ ]\ f_-$ ---------------(1)

But $f_\pm = f_+ * f_-$ substituted in to equation (1) to give:

$K_{sp} = [\ Ca^{+2}\ ]\ [\ SO_4^{-2}\ ]\ f_\pm^2$---------(2)

but $[\ Ca^{+2}\ ] = [\ SO_4^{-2}\ ] = S$ then substituted in equation (2) to get the following:

$K_{sp} = S^2\ \ f_\pm^2$ ----------------(3)

Take square roots for equation (3) to get the following:

$\sqrt{Ksp} = S \ \ f_\pm$

take log value for equation (3) to get the following:

$\log \sqrt{Ksp} = \log S + \log f_\pm$ ----------(4)

By make rearrangement for equation (4) we get:

$\text{Log } S = \log\sqrt{ksp} - \log f_\pm$ -----------(5)

but $\log f_\pm = -A\ z_1\ z_2 \sqrt{I} + BI$, substituted in equation (5) to get the following:

$\log S = \log \sqrt{Ksp} + A\ z_1\ z_2 \sqrt{I} - BI$ -----------(6)

But $b = A\ z_1\ z_2 \sqrt{I}$ substituted in to equation (6) to get the following:

$\log S = \log\sqrt{Ksp} + b - BI$ -------------(7)

By make rearrangement for equation (7) we get:

$\log\sqrt{Ksp} = \log s - b + BI$

$\log S - b = \log \sqrt{K_{sp}} - BI$

$\log S - b = 1/2 \log K_{sp} - BI$ ##

When plot log S - b vs. I the equation of the graph as:

$y = -1.5564x - 2.3073$

$\log S - b = 1/2 \log K_{sp} - BI$

$1/2 \log Ksp = -2.3073$

$\log Ksp = 2\ (\ -2.3073\ ) = -4.6146$

take inverse log then:

$K_{sp} = 2.4288 \times 10^{-5}\ mol^2\ L^{-2}$

Also –B Unknown constant = -1.5564

then B=1.5564

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$CaSO_4 \rightleftharpoons Ca^{+2} + SO_4^{-2}$

$Cf_+ \quad cf_-$

$K_{sp} = [\ Ca^{+2}\ ]\ f_+\ \ [\ SO_4^{-2}\ ]\ f_-$ ---------------(1)

But $f_\pm = f_+ * f_-$, substituted in to equation (1) to give:

$K_{sp} = [\ Ca^{+2}\ ]\ [\ SO_4^{-2}\ ]\ f_\pm^2$---------(2)

but $[\ Ca^{+2}\ ] = [\ SO_4^{-2}\ ] = S$, then substituted in equation (2) to get the following:

$K_{sp} = S^2\ \ f_\pm^2$ ----------------(3)

Take square roots for equation (3) to get the following:

$\sqrt{Ksp} = S \ \ f_\pm$

take log value for equation (3) to get the following:

$\log \sqrt{Ksp} = \log S + \log f_\pm$ ----------(4)

By make rearrangement for equation (4) we get the desired derivation:

$\text{Log } S = \log\sqrt{ksp} - \log f_\pm$

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$$I = \frac{1}{2} \sum c_i z_i^2$$

But we have 4 ions there are: Na^+; Cl^-; Ca^{+2}; SO_4^{-2} then we can write the following:

$I = 1/2\ [\ c_{Na+}\ z_{Na+}^2 + c_{Cl-}\ z_{Cl-}^2 + c_{Ca+2}\ \ z_{Ca+2}^{\ 2} + c_{SO4-2}\ \ z_{SO4-2}^2\ ]$

$I = 1/2\ [\ \ c_{Na+}\ (\ 1\ )^2 + c_{Cl-}\ (\ 1\ )^2 + c_{Ca+2}\ (\ 2\ )^2 + c_{SO4-2}\ (\ 2\ )^2\ ]$

But $c_{Na+} = c_{Cl-} = C$

$c_{Ca+2} = c_{SO4-2} = S$

$I = 1/2\ (C + C + 4S + 4S\ )$

$I = 1/2\ (\ 2C + 8S\ )$

$I = \ C + 4S$

DISUSSION:

- **The solution must be saturated with NaCl salt to calculate Ksp value for $CaSO_4$.**

- **We must be care in take the volume of saturated $CaSO_4$ to not get any solid in pipette, because it will decrease the volume taken, so have error value for the solubility of $CaSO_4$ salts.**

- **Not clean well the pipette used will and rains it with acetone, gives error because may be contain of last concentration of $CaSO_4$ used entered to the concentration used, it will increase the concentration for each times and give error value for the solubility.**

- **Deviation from Debye - Hukle Limiting low is result from higher concentration, because Debye - Hukle Limiting low is found to apply satisfactory only at extremely low concentration.**

- **Using buffer solution because the $CaSO_4$ – EDTA complex is stable in basic media, and will dissociate in acidic media so resist any change in PH.**

- **Increase the indicator quantity used gives errors volume taken, because it's effecting on the sharp end point, which can be present.**

- **Errors in the volume taken of saturated solution or the volume of EDTA, which present from error in a point the color, change reading.**

- **As the ionic strength increase then the $f_{\pm}$ will be increase and the solubility will be decreased.**

- **At higher ionic strength , f± rises as I increase, and [Ca+2] [SO4-2] therefore diminishes . thus there is a decrease in solubility .**

- **At low ionic strengths I ↑ → f± ↓ → S ↑**
  At higher ionic strength I ↑ → f± ↑ → S ↓

- **The solution must be saturated with NaCl salt to calculate Ksp value for CaSO4.**

- **We must be care in take the volume of saturated CaSO4 to not get any solid in pipette, because it will decrease the volume taken, so have error value for the solubility of CaSO4 salts.**