

## Solubility of sparingly soluble salts, PbSO<sub>4</sub> and BaSO<sub>4</sub> by conductivity measurement and direct titration

**Aim:** to determine solubility of lead (II) sulphate and barium sulphate in water at 25°C by measuring conductivity of their saturated solutions.

**Abstract:** the experiment was design to determine solubility product of lead sulphate and barium sulphate using conductivity measurement and direct titration. by conductivity measurement the solubilities of PbSO<sub>4</sub> and BaSO<sub>4</sub> were  $1.3430 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$  and  $1.2589 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$  respectively at 25°C with percentage errors 10.56% and 18.76% respectively.

**Theory:** for a saturated solution of a sparingly soluble salt the molar conductance can be assumed to be the limiting value at infinite dilution given by the sum of the molar ionic conductance.

$$\Lambda_0 = \Lambda_{0+} + \Lambda_{0-}$$

Where C is the concentration of ions. The specific conductivity K of the solution the concentration can be obtained from the equation.

$$\Lambda_C = \Lambda_0 = K \cdot 1000 / C$$

Where C is concentration of the salt in mol l<sup>-1</sup>

Since the conductivity is low due to low concentration of ions, K of water must be measured and subtracted from measured conductivity of saturated solution.

These concentrations can be determined via conductivity measurements. In this practical PbSO<sub>4</sub> is used.



Assume concentration of solid is a constant.

Concentration of Pb<sup>2+</sup> = concentration of SO<sub>4</sub><sup>2-</sup> = C

$$K_{sp} = [\text{Pb}^{2+}_{aq}] [\text{SO}_4^{2-}_{aq}]$$

$$K_{sp} = C^2$$

The measurement of the specific conductivity, K of the saturated solution leads to a value of the concentration.

i.e.  $C = K / \Lambda_0$

As,  $K_{sp} = C^2$

$$K_{sp} = (K / \Lambda_0)^2$$

$\Lambda_0$  for  $\text{PbSO}_4 = 3.02 \times 10^{-2} \text{ m}^2\text{Smol}^{-1}$   
 $\Lambda_0$  = Molar conductivity at infinite dilution

## Procedure

### *Preparation of saturated solutions.*

Some lead sulphate was placed in a conical flask and washed repeatedly with deionized water by shaking then decanted. This was repeated.

Finally deionized water (100ml) was added to the sample and boiled. The hot solution was filtered into clean dry 250ml conical flask and placed in the thermostat bath to equilibrate.

This procedure was repeated with to make solution of barium sulphate.

### *Conductivity measurements.*

The cell constant was determined using 0.02M potassium chloride solution at temperature of the thermostat.

The cell was washed with CO<sub>2</sub> free deionized water and water (20ml) placed in the cell and its conductivity measured.

The cell was rinsed with acetone and dried.

Saturated lead sulphate solution (10ml) was transferred to the conductivity cell using pipette and its conductivity measured.

This procedure was repeated with saturated solution of barium sulphate and temperature of measurements recorded.

### *Determination of Pb<sup>2+</sup> titration*

10ml Standard 0.02M EDTA was diluted to 1 litre flask and mixed well using deionized water.

Saturated lead sulphate solution (25ml) was pipetted into clean 250ml conical flask using a glass wool filter on the pipette. Ammonium buffer (2ml) and 3 drops of Eriochrome black T was added.

This was titrated against by EDTA solution from the burette until sharp colour changed from violet to blue i.e. end point.

The titration was repeated using fresh sample of lead sulphate solution and the results tabulated.

## Treatment of results

Conductivity measurements

Temperature = 25°C

	Conductivity ( $\mu\text{S}/\text{cm}$ )	Corrected conductivity( $\mu\text{S}/\text{cm}$ )
HO <sub>2</sub>	4.20	
PbSO <sub>4</sub>	39.20	35.00
BaSO <sub>4</sub>	36.40	32.20

$$K \text{ of PbSO}_4 \text{ in S/m} = 35.00/100$$

$$= 0.35\text{S/m}$$

$$(\Lambda_0) \text{ Of PbSO}_4 = 146.0 + 159.6 = 305.6 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

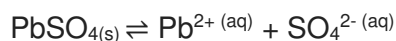
$$= 0.03056 \text{ m}^2\text{Smol}^{-1}$$

$$C = k / \Lambda_0$$

$$= (0.35) / (0.03056)$$

$$= 11.589/100 = 0.11589\text{molm}^{-3}$$

$$= 0.00011589\text{mol dm}^{-3}$$



$$K_{sp} = [\text{Pb}^{2+}_{aq}] [\text{SO}_4^{2-}_{aq}]$$

$$K_{sp} = C^2$$

$$= (0.11589 \times 10^{-3} \text{ mol dm}^{-3})^2$$

$$= 1.3430 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$$

RFM of PbSO<sub>4</sub> = 302g

$$K_{sp} = (303 \times 1.3430 \times 10^{-8}) = 4.0693 \times 10^{-6} \text{ g/L}$$

$$K \text{ of BaSO}_4 \text{ in S/m} = 32.2/100$$

$$= 0.322 \text{ S/m}$$

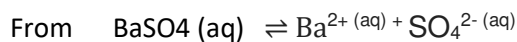
$$(\Lambda_0) \text{ of BaSO}_4 = 127.3 + 159.6 = 286.9 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

$$= 0.02869 \text{ m}^2\text{Smol}^{-1}$$

$$C = k / \Lambda_0$$

$$= 0.322/0.02869 = 11.2234/100 = 0.112234\text{molm}^{-3}$$

$$= 0.0001122\text{mol dm}^{-3}$$



$$K_{sp} = [\text{Ba}^{2+} (\text{aq})] [\text{SO}_4^{2-} (\text{aq})]$$

$$= C^2$$

$$= (0.1122 \times 10^{-3} \text{ mol dm}^{-3})^2$$

$$= 1.2589 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$$

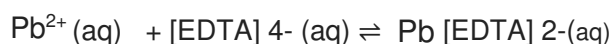
$$\text{RFM of BaSO}_4 = 233 \text{ g}$$

$$K_{sp} = (233 \times 1.2589 \times 10^{-8}) = 2.9332 \times 10^{-6} \text{ g}$$

### PbSO<sub>4</sub> - EDTA titration results

Volume of pipette used = 25.0ml

		Trial	1	2	3
Burette readings (0.02M EDTA)/ml	Final		14.00	27.50	40.90
	Initial		0.00	14.00	27.50
Volume of EDTA used/ml			14.00	13.50	13.40
Average volume/ml	13.45				



$$\text{Moles of EDTA in 10ml} = (0.02 \times 10) / 1000$$

$$= 0.0002$$

Moles of EDTA that reacted with Pb<sup>2+</sup>

$$= (0.0002 \times 13.45) / 1000$$

$$= 2.68 \times 10^{-6}$$

Reaction ratio Pb<sup>2+</sup>: EDTA = 1:1

$$\text{Moles of Pb}^{2+} \text{ that reacted} = 2.68 \times 10^{-6} \times 10^3 \times 25$$

$$= 1.076 \times 10^{-4} \text{ M}$$

$$K_{sp} = [\text{Pb}^{2+} (\text{aq})] [\text{SO}_4^{2-} (\text{aq})]$$

$$= C^2$$

$$= (1.076 \times 10^{-4})^2$$

$$=1.156 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$$

## Comparing

The K<sub>sp</sub> of lead sulphate by direct titration is lower than that of conductivity measurement and it approximate to the true K<sub>sp</sub>. the deviation is may be due to some errors e.g.

Impurities leftover impurities in the sample.

Failure to maintain the temperature of the saturated solution to that of thermostat.

## Discussion

The precipitate was washed in order to remove impurities that may affect the results. It should be washed several times to obtain a well- washed precipitate. During this process, precipitate can be also removed. Therefore all amount of the sample wouldn't be left.

When maintaining the temperature of 25<sup>o</sup>C, the thermostat bath was kept at a temperature about 24<sup>o</sup>C. This is because we measure the temperature of the thermostat bath assuming the temperature inside the reagent bottle is at 25<sup>o</sup>C. But actually the temperature of the solution inside would be slightly higher than the temperature of the water bath as the glass of the reagent bottle separates both. Therefore the temperature of the thermostat bath was kept at lower temperature to obtain the required temperature for the solution.

Reagent bottle should be shaken time to time when it was kept in the water bath. This is to increase the dissociation and reach the equilibrium. If not, we might have not measured the conductivity at the equilibrium and that will alter the true K<sub>sp</sub> value.

The calculated K<sub>sp</sub> value is slightly smaller than the exact given K<sub>sp</sub> value due to errors occurred during the experiment. Mainly the personal errors. Such as temperature maintaining errors, measuring errors and personal carelessness.

When preparing the solutions, the distilled water was added. Distilled water also contains ions itself. Therefore additional conductivity from the distilled water would be raised in the solution. For this reason the conductivity of the solution is corrected by deducting the conductivity of water.

## Conclusion

Exact given K<sub>sp</sub> at 25<sup>o</sup>C for PbSO<sub>4</sub> is  $1.06 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$ . Practically obtained K<sub>sp</sub> at 25<sup>o</sup>C is  $1.3430 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$

As the both values are closer we can use conductivity measurements in order to calculated K<sub>sp</sub>.

## References

Grey, James .R handbook (2004) conductivity analyser and their applications (pp. 491-510)

Acta chim. S (2006) modern advances in electrical conductivity measurement of solutions (pp. 53, 391-395)