B.Sc Sem-5 US05CCHE24 Analytical Chemistry
Unit-4 Solvent Extraction Methods Lecture-3,4,5,6

By

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- *Example 1 : 100 cm^3 of an aqueous solution containing 5M HCL and 0.5 M $FeCl_3$ are shaken with 10 cm^3 of ether, The distribution coefficient is 17.6 Find the number of consecutive extractions required for reducing the Fe^{+3} concentration in the aqueous phase to 10^{-4} M.*
- Solution : We have,
- p = $\frac{logm_0 - logm_1}{\log(V_1 + DV_2) - logV_1}$
- p = $\frac{log0.5 - log10^{-4}}{\log(100 + 17.6x10) - log100}$ = 8.4 = 9 extractions.
- The percentage of extraction or degree of extraction E is another important characteristic of an extraction process. It represents the part of solute that is transferred into the organic phase.

- E%= $\frac{100}{1+(V_1/DV_2)}$
- *Example 2 :Determine whether nickeldimethylglyoxime will be extracted completely or not from 10 cm^3 of an aqueous solution at pH 8 after shaking twice with 5 cm^3 of chloroform. The distribution coefficient is 410.*
- Solution: E%= $\frac{100}{1+(V_1/DV_2)}$ = $\frac{100}{1+(\frac{50}{5x410x5})}$ = 98.5%
- Thus nickel dimethylglyoxime will be extracted nearly completely. A more effective extraction of a desired component can be accomplished by using a mixture of solvents.
- In analytical practice extraction is typically achieved in separatory funnel (Fractional extraction).

- A mixture of two solvents and a substance being extracted is shaken, the phases after complete separation into layers are separately withdrawn.
- The unknown substance is removed from the extract thus obtained by evaporation, dryıng, distillation, and crystallisation.
- Coloured extracts are directly evaluated photometrically.
- Commercially extraction is carried out in perforated tray tower and automatic extractions.

- ***LIQUID LIQUID EXTRACTION :***
- The most important application of distribution law is in the process of extraction which is of great importance both in the laboratory as well as in industry. In the laboratory, often substances dissolved in water have to be separated by means of organic solvents like, ether, carbon tetrachloride, chloroform, benzene etc.
- In these separations, the advantage is taken of the fact that the distribution ratio of most inorganic substances is in the favour of water, while those of organic compounds is in favour of organic solvents.

- This is due to the fact that organic compounds are generally more soluble in organic solvents like benzene, ether, chloroform etc. than in water and these solvents are immiscible with water.
- Organic compounds are then easily separated from the mixture with inorganic compounds in aqueous medium by adding benzene, chloroform, ether etc.
- Because organic compounds have their distribution ratio largely in favour of organic solvent, more of them would pass into non-aqueous layer. Finally, this non-aqueous layer is removed and distilled to obtain the purified compound. Sometimes, the distribution ratio can also be increased in the desired direction by adding another compound which decreases the solubility of the substance being extracted in the original solvent.

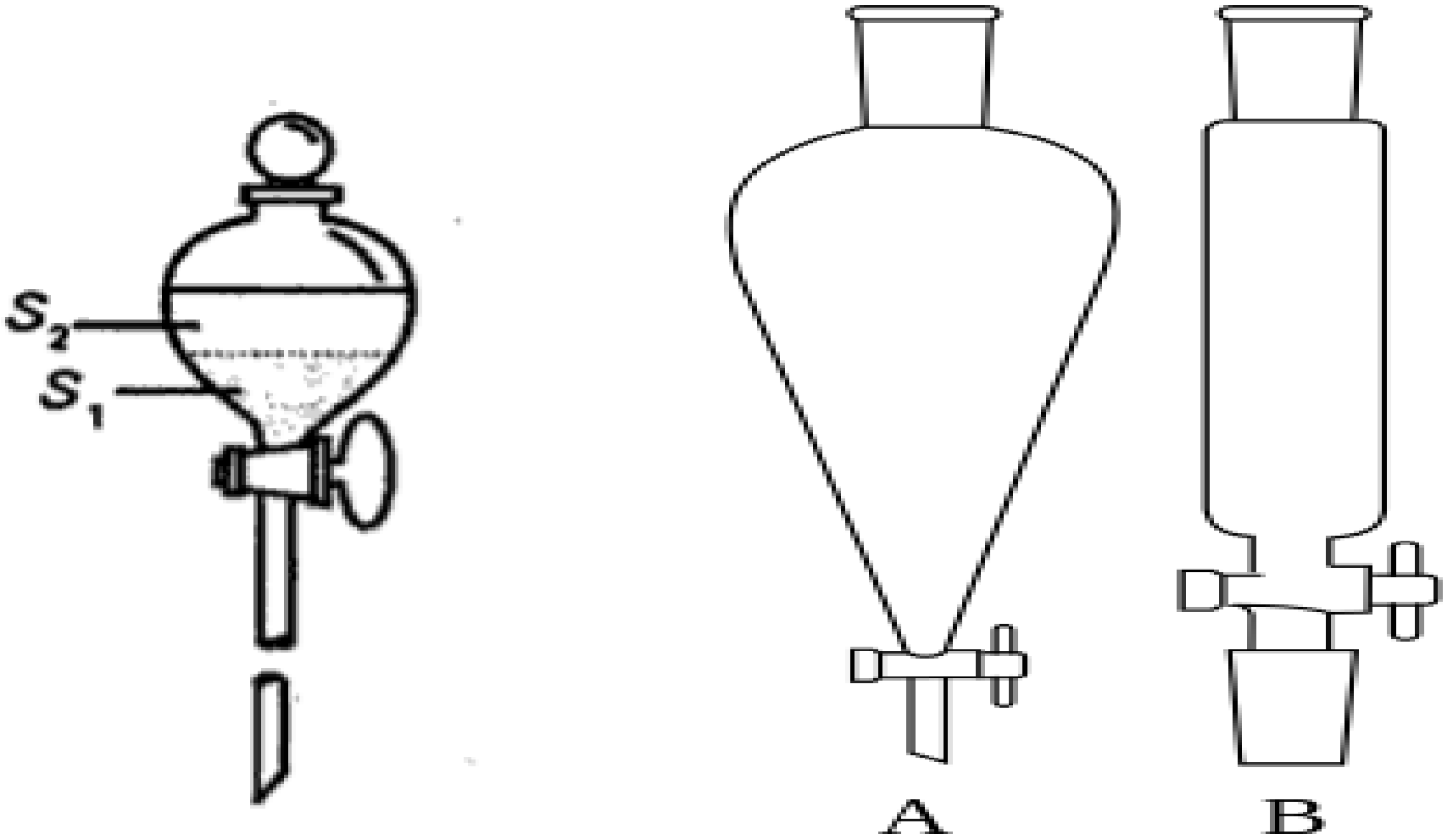


Fig. 2.1 *Separating funnel with solute A distributed in two immiscible solvents S_1 (water) and S_2 (diethyl ether)*

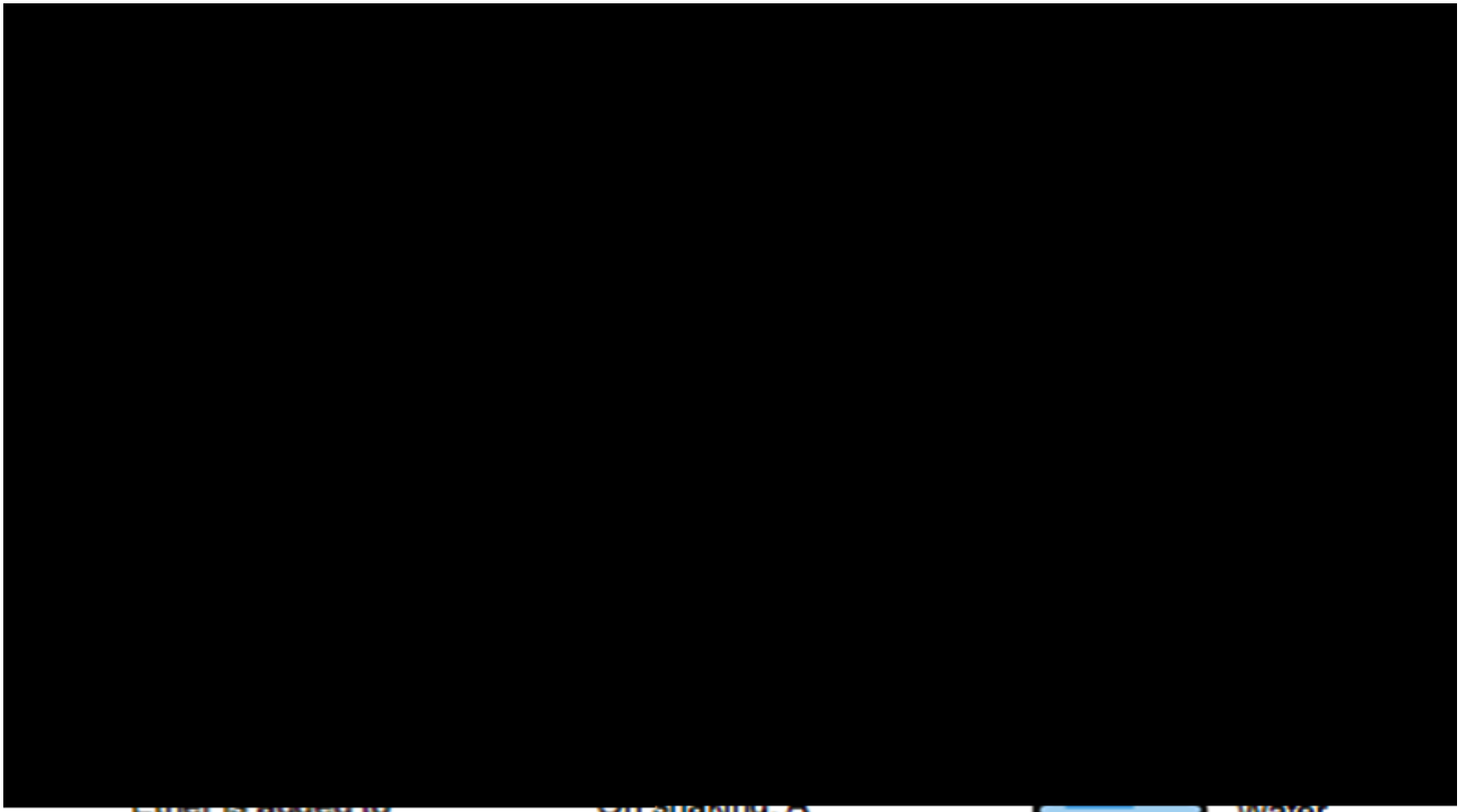
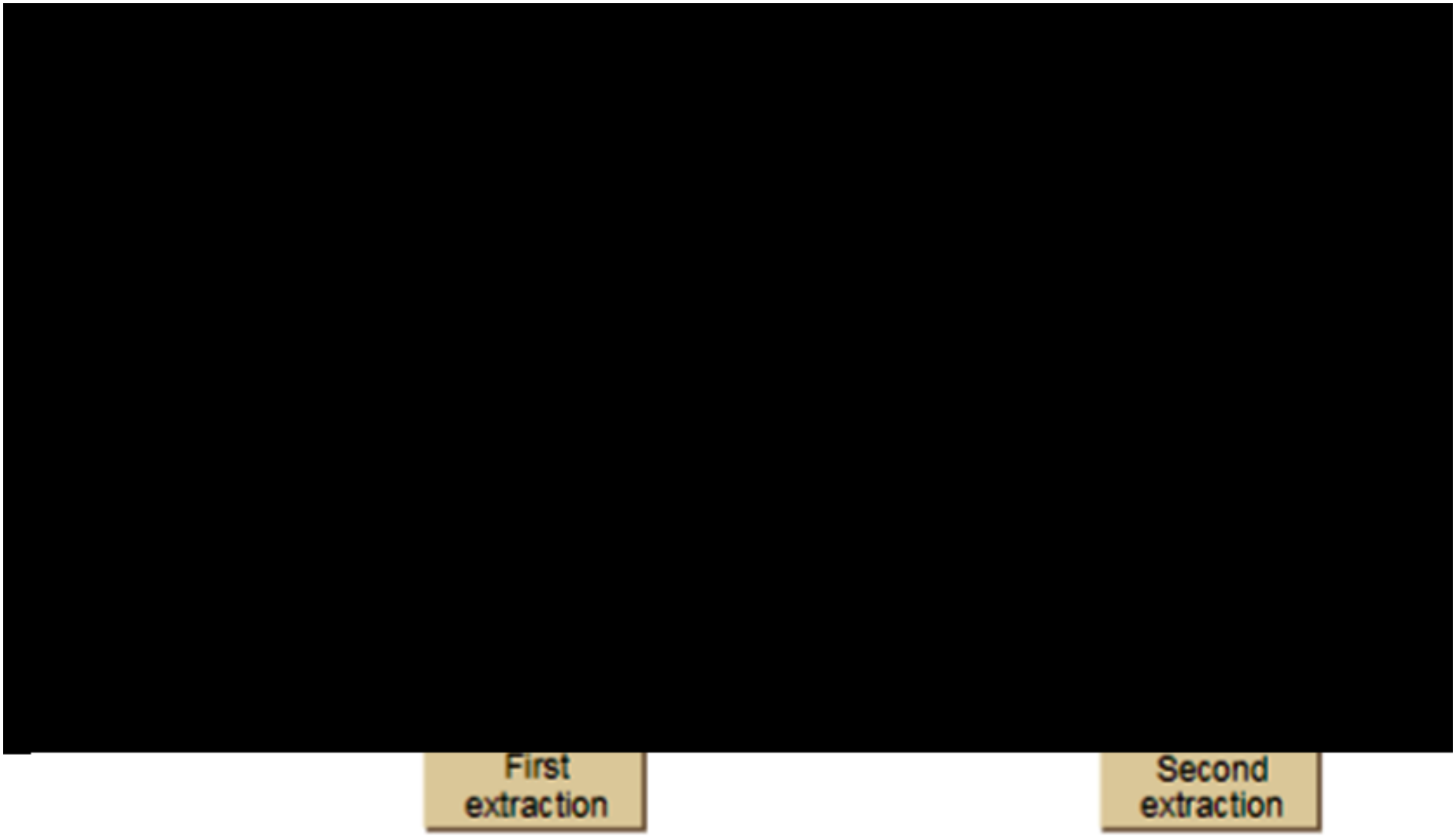


Figure
Extraction in a separatory funnel.



Figure

Illustration of Multiple extraction. The given solvent (ether) is used in two successive portions of 50 ml each.

- For example the extraction of organic acid from water will be more economical after the addition of HCl, a strong acid, because the latter reduces the solubility of organic acid in water.
- Similarly, an organic base can be extracted more effectively from ether after addition of a strong base, such as NaOH.
- Also in industry, extraction process is used to remove the impurities from the product.

- The type of extractions discussed above are known as liquid extractions.
- The liquid extraction. (which used in so many analytical separations and procedures) is a technique in which a substance dissolved n one phase (usually an aqueous solution) is more or less completely transferred to the second phase, essentially immiscible with the first, i.e., an organic liquid such as benzene, chloroform, carbon tetrachloride etc.
- The separations that can be performed are simple, clean, rapid and convenient.

- It is not clear when, and by whom this technique was first introduced into preparative organic chemistry on the laboratory scale, but there is no doubt that its use from the earliest times in technology. (e.g. the preparation of perfumes, essential oils, drugs and dyestuffs), anticipated the rise of modern chemistry.
- The technique is equally applicable to trace level and large amount of materials. In this chapter we are mainly concerned with samples in aq. solutions, and the production of chelate and of ion association extraction systems.

- In liquid system it is very essential to know how much solvent and how many treatments are necessary accomplish a particular degree of separation.
- It may also be asked frequently whether it is more economical to extract with all the solvent available in one operation, or to use it in several operations, separating each time.
- It is very easy to show that with a given volume of extracting solvent available, the reaction is more complete, if it is used in several operations (i.e, in several instalments) that if it is used all in one operation. This may be made clear from the following illustration.

- Suppose we require to extract some (say A gms.) of succinic acid from aqueous solution with ether, We have one litre of ether at our disposal. Let the distribution ratio of succinic acid between ether water be 2. If all the ether is used in one operation, the amount a of the succinic acid that passes ethereal layer, will be given by,
- $\frac{[\frac{a}{1000}]}{[\frac{A-a}{1000}]} = 2$ or a = $\frac{2A}{3}$
- In other words 2/3, i.e.,66.7% succinic acid will be extracted.

- Now suppose the extraction is carried in two instalments, each of 500 ml of ether. Then the amount extracted (a_1) in the first operation will be given by,
- $\frac{[\frac{a_1}{500}]}{[\frac{A-a_1}{1000}]} = 2$ or $a_1 = \frac{A}{2}$
- Thus 50% of the solute will be extracted in one operation. The amount a_2 extracted in the second operation will be,
- $\frac{[\frac{a_2}{500}]}{[\frac{A/2-a_2}{1000}]} = 2$ or $a_2 = \frac{A}{4}$
- i.e.,25% of the solute will be extracted in the second operation. Thus in two operations, the amount of succinic acid extracted will be

- 50 + 25= 75 percent. Similarly, the amount extracted 80.2% if the extraction is carried out in four operations and it will be 83.8%, if the extraction is carried out in 10 operations. In other words, the process of extraction is more economical if it is carried out in several operations.
- As another example, consider a solute A present in 100 mL water and suppose that 100 mL of ether is used for its extraction and suppose that the distribution coefficient of the solute A between ether and water is 4. Thus,
- $K = D = \frac{\text{Concentration of A in ether}}{\text{Concentration of A in water}} = 4$
- When whole of 100 ml ether is used at a time for extraction, suppose w_e grams of solute pass into ether layer and w_a gram left in the aqueous layer. Thus,

- $\frac{w_e/100}{w_a/100} = 4$ or $\frac{w_e}{w_a} = 4$ or $\frac{w_e}{w_e+w_a} = \frac{4}{5}$
- This shows that 100 mL ether has separated 4/5th or 80% of the solute originally present.
- Now, when we use 100 mL of ether in two successive extractions using 50 mL each time. Then the first extraction, we have,
- $\frac{w_e/50}{w_a/100} = 4$ or $\frac{w_e}{w_a} = 2$ or $\frac{w_e}{w_e+w_a} = \frac{2}{3}$
- That is, in the first extraction 2/3rd (66.7%) solute is extracted and 1/3rd of the original amount is left behind in the aqueous medium.

- In the second extraction using 50 mL ether again, we shall further extract 2/3rd of 1/3rd i.e, 2/9th of the original amount.
- In other words, in two extraction using the same 100 mL ether we can separate 213 + 29 = 8/9 (88.9%) of the original amount of the solute. This again shows that a two stage extraction is more economical and efficient. If the same 100 mL ether is used 4 or 5 instalments, a still greater amount of the solute can be extracted. Hence, in solvent extraction it advantageous to use a given volume of the extracting solvent in small amounts in successive stages rather than in one whole at a time.

- We are now in a position to derive a general formula from which the amount of solute that is left unextracted after a given number of operations can be easily calculated.
- ***Que- Derive an equation for amount of solute unextracted after 'n' no. of extractions. 2014, 2019***
- Suppose we have a solution containing m gms of a substance in V ml of solution. This solution is repeatedly extracted using every time v ml of another solvent which is immiscible with the first.
- Suppose m_1 be the amount of solute that remains contracted at the end of first operation. Then the distribution coefficient may be written as,

- $\frac{[\frac{m_1}{V}]}{[\frac{m-m_1}{v}]}$ = K.....(1) or $m_1 = m\,[\frac{KV}{KV+v}]$.....(2)
- Exactly in the similar manner, amount m_2 that remains unextracted at the end of second extraction.
- $m_2 = m_1 \frac{KV}{KV+v}$ .....(3) or $m_2 = m\,[\frac{KV}{KV+v}]^2$ .....(4)
- Therefore, the weight that remains in extracted at the end of operations will be given by,
- $m_n = m\,[\frac{KV}{KV+v}]^n$ .....(5)
- and the weight extracted in n operations will be given by,
- $m - m_n = m\left[1 - [\frac{KV}{KV+v}]^2\right]$ .....(6)
- If the entire amount of the extracting solvent be used in one instalment, then amount extracted is given by
- $x' = m\,[\frac{KV}{KV+nv}]$.....(7)

- Since the quantity within the parantheses is less than unity, m_n < x' and m_x will be smaller the greater the value of n.
- It is well evident from this equation that a greater efficiency can be obtained by using small amounts of solvent v in a number of times than to use total volume of the solvent at one time.
- In other words, the efficiency of extraction increases by increasing the number of operations using only a small quantity of the extracting liquid at each time.
- The same argument holds good for washing of precipitates In washing the precipitate, whereby the impurities distribute between the liquid and the precipitate, it is more effective to use a small amount of washing liquid at a time and to repeat the process a number of times.
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- The principle of solvent extraction is made use of in desilverisation of lead by Parke's process. Silver is more soluble in zinc than in lead. Molten lead is immiscible with molten zinc. Thus when zinc is added to argentiferrous lead, a large amount of silver passes readily into solution with zinc leaving little silver in the lead.
- This is due to the fact that the distribution ratio between zinc and lead is 300 at 800°C Zinc containing silver forms the upper layer. By repeating the process three or four times, almost the entire amount of silver passes into zinc .

THANK YOU