

Advanced Chemical Thermodynamics & Kinetics
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Lecture – 43
Equilibrium constant using partition method

Hello, in today experiment, we will be determining the equilibrium constant of the reaction $\text{KI} + \text{I}_2 \rightleftharpoons \text{KI}_3$. Now this reaction is a reversible reaction. So, we need to determine the equilibrium constant for this reaction. But since, all the species present in this reaction are in combined form, we cannot directly measure the concentration of each individual species. So, we do this measurement by using a technique known as partition method.

So, in partition method, we need to perform a different set of experiment through, which we will determine the partition coefficient of the reaction or partition coefficient of iodine dissolved in the 2 layers. So, first of all we need to know; what is partition coefficient. Now partition coefficient is usually, the amount or ratio of concentration of a compound, which is which is distributed in 2 immiscible solvents at a given temperature. Now this indirectly gives us the solubility of any solute in 2 different solvent. So, the partition coefficient for any solvent pair will be constant at a given temperature and it will be same irrespective of the amount of solvent taken or solute taken.

So, in this experiment we will perform 2 sets of experiment, in which first we will determine, the partition coefficient of iodine in CCl_4 and aqueous layers. And then a second method, we will use this partition coefficient to determine, the equilibrium constant for the reaction, which we told.

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Introduction

The ratio of concentrations of a compound in two immiscible phases at equilibrium is called as **partition coefficient**.

In this experiment, we have a system of distribution of iodine between aqueous and CCl₄ layer with KI present in the aqueous layer. Iodine (I₂) is sparingly soluble in water but dissolves readily in water on addition of KI due to the presence of following equilibrium:

$$\text{KI} + \text{I}_2 \rightleftharpoons \text{KI}_3$$

The equilibrium constant of the above reaction is given as:

$$k_{eq} = \frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]}$$

In this two-phase system, two equilibria occur simultaneously which compete for I₂. The concentration of all the species present at equilibrium can be determined by titrating the solutions with sodium thiosulphate and the equilibrium constant for the formation of KI₃ can be calculated. Titrating the aqueous layer gives the total iodine present in the aqueous layer i.e.

$$\text{I}_3^- + 2\text{S}_2\text{O}_3^{2-} \rightleftharpoons 3\text{I}^- + \text{S}_4\text{O}_6^{2-}$$
$$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightleftharpoons 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$$


In today's experiment, we will be doing 2 things, the first one that will be doing is the calculation of partition coefficient and the second one, which will be doing is the calculation of equilibrium constant. So, partition coefficient is defined as the ratio of concentration of a compound in 2 immiscible phases at equilibrium. And the second part is calculation of equilibrium constant and the reaction that will be studying is KI plus I₂ gives KI₃, which is a reversible reaction. So, the equilibrium constant for this reaction is given by K equilibrium is equal to I₃⁻ divided by the concentration of I₂ and the concentration of I⁻.

So in this reaction, we have a system of distribution of I₂ between an aqueous layer and an organic layer which is CCl₄ here. So, and KI is present in aqueous layer. So, in KI iodine, which is present in the form of I₃⁻ after combining with KI reacts with sodium thiosulphate to give 3 I⁻ and S₄O₆²⁻ and iodine, which is present in this form as I₂ also combines with sodium thiosulphate to give 2 I⁻ and S₄O₆²⁻.

Now, we will be preparing the solutions that, we require for this experiment.

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First of all, we will be weighing sodium thiosulphate pentahydrate, in order to prepare n by 50 solution and will be weighing 0.49 grams.

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Now, we will be transferring this amount that we weighed to this volumetric flask. We will stir the contents.

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After the sodium thiosulphate has dissolved, will make up the volume to 100 ml; in a similar way, we will be preparing n by 200 of sodium thiosulphate solution by weighing 0.12 grams.

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Now, we will be preparing n by 10 of potassium iodide solution by weighing 3.32 grams and making up the volume to 200 ml.

Now, we well be preparing saturated solution of iodine in CCL 4 by dissolving maximum amount of iodine, which can be dissolved in this given volume of CCL 4.

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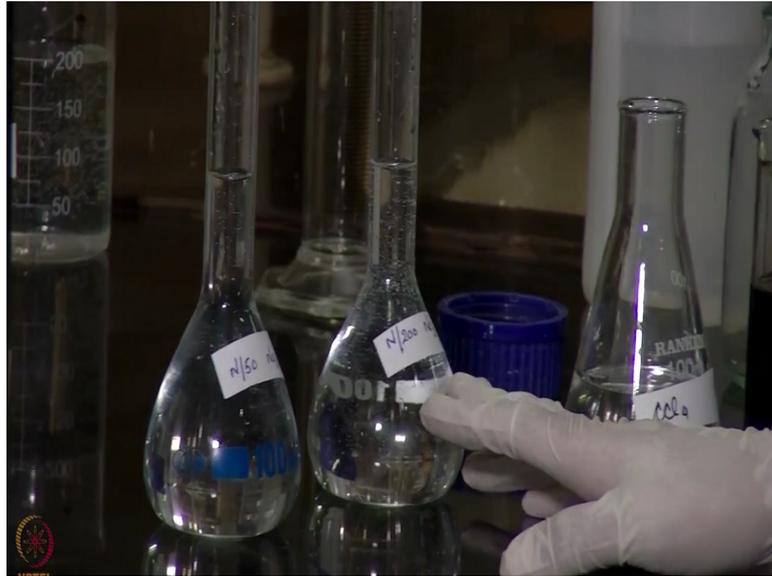


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This is the saturated solution of iodine and CCL_4 that we have prepared; now that we have prepared all the solutions, will now proceed with our experiment. Now the first experiment that we will be performing is to determine the partition coefficient of the reaction.

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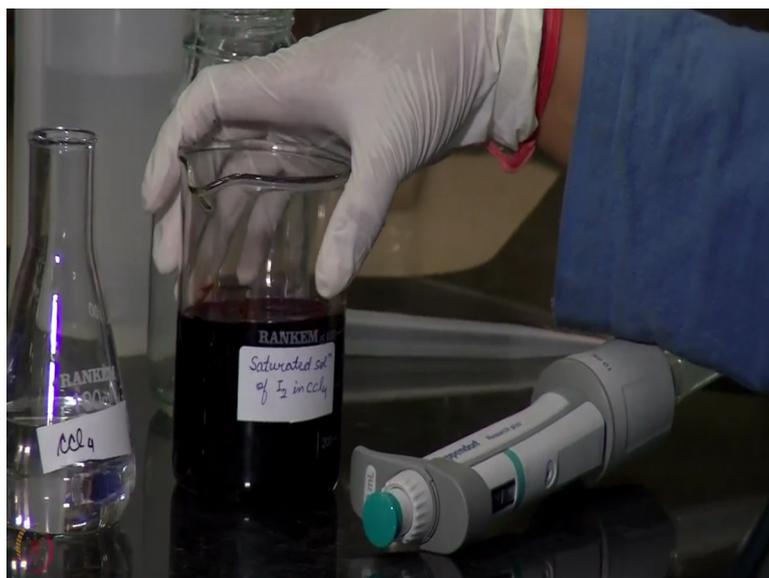
So, these are the solutions that we have prepared. We have an n by 50 sodium thiosulphate solution, we have an n by 200 sodium thiosulphate solution.

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A CCL 4.

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And a saturated solution of iodine in CCL 4.

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Now, we will be taking out some fixed amounts from these solutions and adding those to this stoppered bottle.

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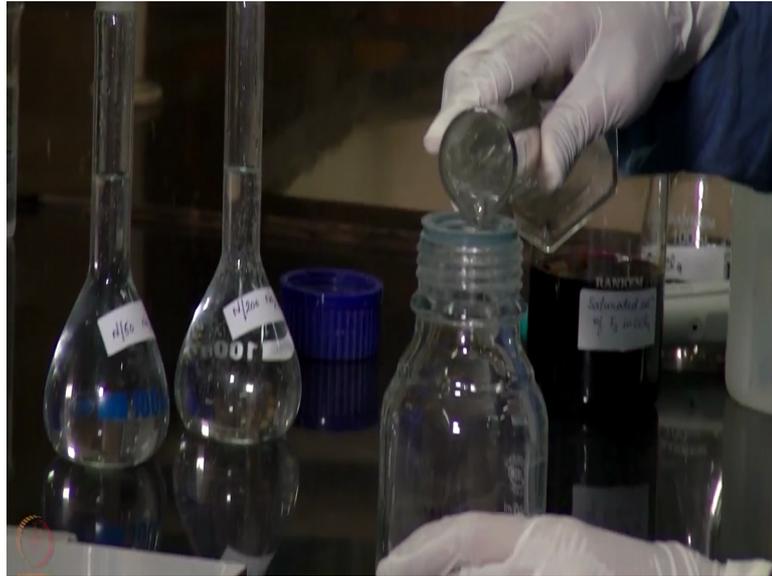
We will be adding 200 ml of saturated solution of iodine and CCL 4 to this stoppered bottle.

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Then will be adding 5 ml of CCL 4.

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Now, will be adding 200 ml of distilled water.

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Now, that we have prepared this solution, will add a magnetic bead to it.

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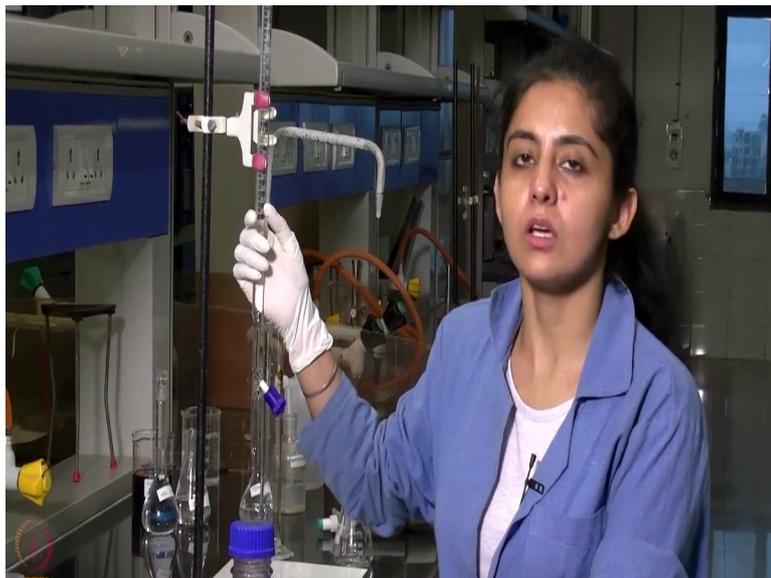


And we will be keeping it on a stirrer, for 1 hour.(Refer Slide Time: 06:46).



After the stirring for 1 hour is complete, this is how the solution has settled, now will allow it to settle for another half an hour.

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After the solution has settled for half an hour will be taking out the aqueous layer and then the organic layer and titrating them separately against the n by 200 sodium thiosulphate solution, which we have taken inside this burette.

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So, first we will be taking out 25 ml of the aqueous layer here and then titrating it.

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Experimental Procedure

1. Determination of partition coefficient

Following solution is prepared in stoppered bottles:

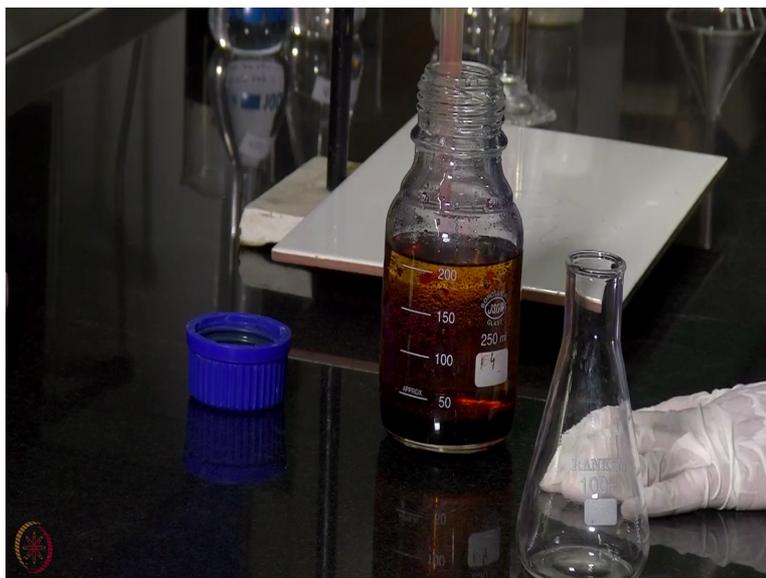
Volume of saturated solution of I ₂ in CCl ₄ (mL)	Volume of CCl ₄ (mL)	Volume of H ₂ O (mL)
20.0	5.0	200.0

- The solution is stirred vigorously for about an hour and then left undisturbed for half an hour.
- Two separate solutions of 250mL sodium thiosulphate with concentrations as N/50 & N/200 are prepared. Pipetted out 25mL of aqueous layer from Bottle in a conical flask and is titrated with N/200 Na₂S₂O₃ solution. 2mL of starch is added when the solution becomes pale yellow and the titration is continued until the blue colour (which appears after the addition of starch) disappears. Three values are recorded for this titration.
- Pipetted out 2mL of organic layer from bottle in a conical flask and is titrated with N/50 Na₂S₂O₃ solution. After the titration is started, a yellow layer above the organic layer is seen. 2mL of starch solution is added when this yellow colour becomes pale and the titration is continued until the colour disappears. Three values are obtained for this titration.



So, in the first part of the experiment, we prepared a stoppered bottle, which contained a fixed volume of saturated solution of I₂ in CCl₄ and 5 ml of CCl₄ and 200 ml of water. After the solution is settled for after stirring for 1 hour and then letting it settle for another half an hour, the aqueous layer and the organic layers are withdrawn and the titrations are carried out.

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Proper care must be taken, when we are withdrawing the solution from this bottle. So, that the contents, the aqueous layer and the organic layer do not mix up.

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This is the 25 ml of aqueous layer that we have taken out and now we will start titrating it, against the sodium thiosulphate solution.

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After adding some volume of sodium thiosulphate solution when the colour of the solution turns pale yellow we will be adding few drops of starch indicator.

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After the addition of starch indicator the colour of the solution turns blue, which is because of the formation of starch and iodide complex.

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Now, we will be again titrating it, against the sodium thiosulphate solution and after the colour of solution becomes colourless, that will be the end point of titration and we note down the titer value.

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Now that the solution has turned colourless, this indicates the end point of this titration and will be noting down the titer value from the burette reading. Now we will again withdraw aqueous layer from that stoppered bottle and we will repeat this titration 2 more times to get concordant values.

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Now, we will be withdrawing 2 ml of the organic layer from this stoppered bottle and adding it to this conical flask, the lower layer is the organic layer and the one above is the aqueous layer that, we had earlier withdrawn.

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After, we have withdrawn the organic layer, we will be titrating this 2 ml, against sodium thiosulphate solution, which is of normality n by 50 using similar procedure as we followed earlier for the aqueous layer will be adding starch as an indicator and then titrating it and noting down the titer value. The titer value is that we obtained after the

titration of organic layer and the aqueous layer against, sodium thiosulphate solutions will be used to determine, the concentration of iodine in both the layers and then these values will be used to determine the partition coefficient value, which is a ratio of the concentrations of iodine in both the layers.

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Observations

1. Titration of aqueous layer against N/200 $\text{Na}_2\text{S}_2\text{O}_3$

Volume of aqueous layer pipetted out (mL)	Volume of $\text{Na}_2\text{S}_2\text{O}_3$ used (mL)
25.0	4.0
25.0	3.9
25.0	3.9

Average volume of $\text{Na}_2\text{S}_2\text{O}_3$ used = 3.93 mL

2. Titration of organic layer against N/50 $\text{Na}_2\text{S}_2\text{O}_3$

Volume of organic layer pipetted out (mL)	Volume of $\text{Na}_2\text{S}_2\text{O}_3$ used (mL)
2.0	7.8
2.0	7.7
2.0	7.6

Average volume of $\text{Na}_2\text{S}_2\text{O}_3$ used = 7.7 mL

These are the results that were obtained after titrating the aqueous layer and the volume of sodium thiosulphate, which was consumed as mentioned here and concordant readings were obtained and the average volume of thiosulphate, which was consumed is 3.39 ml, when the aqueous layer was titrated against n by 200 sodium thiosulphate solution. Similarly, when the organic layer was titrated against n by 50 sodium thiosulphate solution, these are the values which were obtained as 7.8, 7.7 and 7.6 ml and the average volume of sodium thiosulphate corresponds to 7.7 ml.

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Calculations

Calculation of concentration of I_2
The reaction between I_2 and $Na_2S_2O_3$ is:
$$2 Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2 NaI$$

For Bottle :
Volume of aqueous layer (V_2) = 25ml; Normality of $Na_2S_2O_3$ (N_2) = 1/200; Volume of Normality of $Na_2S_2O_3$ (V_1) = 3.93ml
Using the relation, $N_1V_1 = N_2V_2$
Therefore, Normality of I_2 in aqueous layer = $7.8 \times 10^{-4} N$
So, Molarity of I_2 in aqueous layer = $2(7.8 \times 10^{-4}) = 0.0016 M$

Volume of organic layer (V_2) = 2ml; Normality of $Na_2S_2O_3$ (N_2) = 1/50; Volume of Normality of $Na_2S_2O_3$ (V_1) = 7.7ml
Using the relation, $N_1V_1 = N_2V_2$
Therefore, Normality of I_2 in organic layer = 0.0770N
Therefore, Molarity of I_2 in organic layer = $2 \times 0.0770 N = 0.1540 M$

Calculation of partition coefficient K_D
Partition coefficient $K_D = \frac{[I_2]_{org}}{[I_2]_{aq}}$
$$K_D = 0.1540 / 0.0016 = 96.25$$

$[I_2]_{org}$
 $[I_2]_{aq}$

After the readings were obtained, the calculations were done to obtain the partition coefficient. So, the reaction between for the calculation of concentration of iodine, the reaction between iodine and sodium thiosulphate is given as $2 Na_2S_2O_3$ combine with one mole of iodine to give $Na_2S_4O_6$ plus $2 NaI$. So, after the titration the calculations are done as follows, the volume of aqueous layer, which we took was 25 ml and the normality of sodium thiosulphate solution was n by 200 and the volume, which was consumed was 3.93 ml. So, using the normality equation, which is given by $N_1 V_1 = N_2 V_2$, the normality of iodine in aqueous layer is obtained as 7.8×10^{-4} normals and the molarity.

So, the molarity of iodine in aqueous layer is given by twice the normality, which turns out to be 0.0016 normal after this, the titration of organic layer was carried out, which was 2 ml and the normality of sodium thiosulphate that was used for titration at N by 50 and the titer value is given by 7.7 ml, which was obtained. So again, using the normality relation, we can calculate first the normality and then the molarity of iodine and organic layer.

So now, that we have the values of iodine, which is present inorganic layer and also iodine, which is present in aqueous layer, we can calculate the value of partition coefficient, which is I_2 in the organic layer divided by I_2 in the aqueous layer and the value of partition coefficient, which we obtain here is 96.25.

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In the next part of the experiment, we will be determining the equilibrium constant of the reaction. For this purpose, we have these 3 solutions, which is the saturated solution of iodine CCl_4 and n by 10 KI solution.

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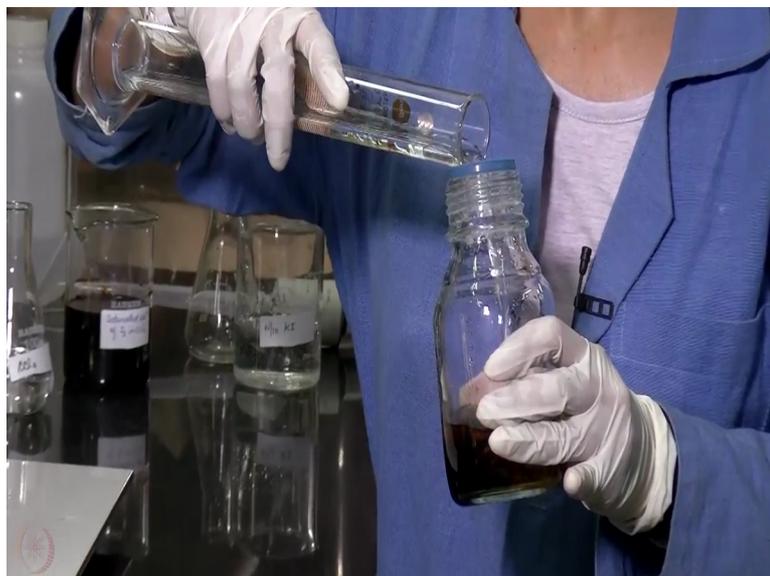
We will be taking out 20 ml of saturated solution of iodine in this stoppered bottle.

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Now, we will be adding 5 ml of CCL 4 to it.

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Then we will be adding 100 ml of KI solution to that stoppered bottle, just like we did earlier, we will be adding a magnetic bead to this stoppered bottle and stirring it for 1 hour and then let the contents settle down for another half an hour and then we will be titrating the organic as well as the aqueous layers against sodium thiosulphate solution.

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Experimental Procedure

1. Determination of equilibrium constant:

Following solution is prepared in stoppered bottles:

Volume of saturated solution of I ₂ in CCl ₄ (mL)	Volume of CCl ₄ (mL)	Volume of 0.1 N KI (mL)
20.0	5.0	100.0

- Pipetted out 10mL of aqueous layer from Bottle in a conical ask and is titrated with N/50 Na₂S₂O₃ solution. 2mL of starch is added when the solution becomes pale yellow and the titration is continued until the blue colour (which appears after the addition of starch) disappears. Three values are recorded for this titration.
- Pipetted out 2mL of organic layer from bottle in a conical ask and is titrated with N/200 Na₂S₂O₃ solution. After the titration is started, a yellow layer above the organic layer is seen. 2mL of starch solution is added when this yellow colour becomes pale and the titration is continued until the colour disappears. Three values are obtained for this titration.



The second experiment that, we carried out was preparing a stoppered bottle containing a 20 ml of saturated solution of iodine in CCL 4 and 5 ml of CCL 4 and 100 ml of K I, this was carried out to, this is carried out in order to determine the equilibrium constant of the reaction of KI with iodine in order to give KI 3.

So now, that we are done with our experiment. So, we can see that from the first part of the experiment, we can calculate the partition coefficient of the distribution of iodine between CCL 4 layer and aqueous layer and from the second experiment, we will we can find the equilibrium constant for the reaction. So, since from the second experiment, the titration of aqueous layer will give us the total value of I 2, which is present in the form of either I 3 minus or I 2 and from the titration of CCL 4 layer, we can found out the concentration of I 2 present in the CCL 4 layer. Now since, we already have our partition coefficient from first set of experiment, we can find the concentration of I 2 in aqueous layer using this partition coefficient and from these 2 values, we will get the value of I 3 minus present in the aqueous layer.

Now since, we have the value of I 2, I 3 minus in our aqueous layer, what we need to determine next, is the value of I minus present in the aqueous layer for determining the value of I minus in the aqueous layer. We subtract the concentration of I 3 minus present in the aqueous layer from total concentration of I minus, the total concentration of I minus will correspond to the concentration of initially taken K I, which was 0.1 molar.

So, from this we will have all the values of I minus I 3 minus and I 2 from which, we can easily determine our equilibrium constant.

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Observations

1. Titration of aqueous layer against N/50 $\text{Na}_2\text{S}_2\text{O}_3$

Volume of aqueous layer pipetted out (mL)	Volume of $\text{Na}_2\text{S}_2\text{O}_3$ used (mL)
10.0	7.0 ✓
10.0	6.9 ✓
10.0	6.9 ✓

Average volume of $\text{Na}_2\text{S}_2\text{O}_3$ used = 6.93 mL

2. Titration of organic layer against N/200 $\text{Na}_2\text{S}_2\text{O}_3$

Volume of organic layer pipetted out (mL)	Volume of $\text{Na}_2\text{S}_2\text{O}_3$ used (mL)
2.0	7.1 ✓
2.0	7.0 ✓
2.0	7.0 ✓

Average volume of $\text{Na}_2\text{S}_2\text{O}_3$ used = 7.03 mL

After the titration of aqueous and organic layers against, sodium thiosulphate solutions having molarity n by 50 and n by 200 respectively, these are the titer values, which were obtained. So, for the titration of aqueous layer, the titer values are obtained as 7, 6.9 and 6.9 ml and the average value is given by 6.93 ml. For the titration of organic layer against n by 200 sodium thiosulphate, the values which we are getting are 7.1, 7 and 7 ml, which gives an average value of 7.03 ml.

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Calculations

Calculation of equilibrium constant

Volume of aqueous layer (V_2) = 10ml; Normality of $\text{Na}_2\text{S}_2\text{O}_3$ (N_1) = 1/50; Volume of Normality of $\text{Na}_2\text{S}_2\text{O}_3$ (V_1) = 6.93ml
Using the relation, $N_1V_1 = N_2V_2$

Therefore, Normality of I_2 in KI layer = 0.0139N
So, Molarity of I_2 in KI layer = $2 \times 0.0139 = 0.0277\text{M}$

Volume of organic layer (V_2) = 2ml; Normality of $\text{Na}_2\text{S}_2\text{O}_3$ (N_1) = 1/200; Volume of Normality of $\text{Na}_2\text{S}_2\text{O}_3$ (V_1) = 7.03ml
Using the relation, $N_1V_1 = N_2V_2$

Therefore, Normality of I_2 in organic layer = 0.0176N
Therefore, Molarity of I_2 in organic layer = $2 \times 0.0176 = 0.0351\text{M}$



These are the calculations that will be doing, in order to calculate the equilibrium constant, the volume of aqueous layer is 10 ml, the normality of sodium thiosulphate is n by 50 and the and the volume of $\text{Na}_2\text{S}_2\text{O}_3$ that, we have used is 6.93 ml again using the normality equation, we will be calculating the value of normality of iodine in the KI layer, which turns out to be this and then the molarity is given by twice, this value which is point 0.0277 molars. Then, after the titration of organic layer, which was 2 ml and again using the normality equation, we can obtain the value of normality of iodine in the organic layer and then the molarity.

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Calculations

Initial concentration of I⁻ i.e. $[\text{I}^-]_{\text{initial}}$ = concentration of KI solution = 0.1N = 0.1M
Total concentration of I_2 in KI layer $[\text{I}_2]_{\text{total}} = 2 \times 0.0139 = 0.0277\text{M} \rightarrow [\text{I}_2] + [\text{I}_3^-]$
Concentration of I_2 in organic layer $[\text{I}_2]_{\text{organic}} = 0.0351\text{M}$
So, concentration of I_2 in aqueous layer $[\text{I}_2]_{\text{aqueous}} = 0.0351\text{M}/K_D = 0.0351/96.5 = 3.66 \times 10^{-4}\text{M}$
 $[\text{I}_2]$ combined in the form of $[\text{I}_3^-]_{\text{combined}} = [\text{I}_2]_{\text{total}} - [\text{I}_2]_{\text{aqueous}} = 0.0277 - 0.000366 = 0.0273\text{M}$
Free $[\text{I}^-]$ at equilibrium = $[\text{I}^-]_{\text{initial}} - [\text{I}_3^-]_{\text{combined}} = 0.1 - 0.0273 = 0.0727\text{M}$

For the reaction:

$$\text{KI} + \text{I}_2 \rightleftharpoons \text{KI}_3$$

Equilibrium constant is given as:

$$K_{eq} = \frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]} = \frac{0.0273}{(3.66 \times 10^{-4}) \times 0.0727} = 1.026 \times 10^3$$


So as we know, the initial concentration of I minus that we had, which was the concentration of KI solution that we had prepared and it is 0.1 normal. Now that, we know the total concentration of iodine in KI layer total concentration of iodine here, corresponds to the iodine, which is present in the form of I₂ and also the iodine, which is present in the form of I₃⁻ since, both of these will be reacting with sodium thiosulphate solution. After this, we also know the concentration of I₂ in the organic layer, which is this. The concentration of iodine in aqueous layer can be calculated, because we have the value of partition coefficient, which we earlier calculated. So, we will be dividing the value of I₂ organic with the partition coefficient. So, that we obtain the value of iodine in aqueous layer, which turns out to be this.

So, I₂ combined in the form of I₃⁻ is given by the total iodine concentration that we have minus the I₂ present in aqueous layer, which we just calculated. Now we can calculate, the free iodide at equilibrium, which is given by I minus which we initially had and then I₃⁻. So after, subtracting these we can calculate the free I minus at equilibrium. So, we are calculating the equilibrium constant for the reaction KI plus I₂ given KI₃. The equilibrium constant can be written as I₃⁻ divided by I₂ divided by I minus, now that we have the value of all these concentrations, which are 0.0273 and the value for I₂, which is this and the value for I minus we can easily obtain the value of equilibrium constant.

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Result

1. The partition coefficient for I₂ in CCl₄- water system = 96.25
2. The equilibrium constant for the reaction
$$\text{KI} + \text{I}_2 \rightleftharpoons \text{KI}_3$$
is obtained as $K_{\text{eq}} = 1.026 \times 10^3$



These are the results of our experiment. So, the partition coefficient for I₂ in CCl₄ water system is calculated as 96.25 and that and the value of equilibrium constant for this reaction is obtained as 1.026×10^3 .

So in this experiment, we see that we can use the concept of partition coefficient to determine, the equilibrium constant for a reaction in which, the determination of each of the ions or components involved in the reaction is not actually very precise. So, partition coefficients helps in determining the precise concentration of each of the components or each of the ion involved in the equilibrium reaction.