

Repeat it twice. Similarly pipette out 10 ml of aqueous layer and titrate it against  $\frac{N}{10}$  thio solution. Repeat it twice or thrice.

Repeat the same titration for bottle 2.

- c. Calculate  $C_1$ ,  $C_2$  and  $C_3$  all in moles/lit and calculate  $K_c$  from equation (3). Take mean of the two sets. [Use  $K_D$  from the previous experiment].

### Results and Calculations

- a. Preparation of 250 ml 0.1 (M) KI solution:

Initial mass (g)	Final mass (g)	Mass of KI transferred (g)	Strength of KI solution
$w_1$	$w_2$	$(w_1 - w_2)$	$\frac{w_1 - w_2}{4.15} \left( \frac{M}{10} \right)$

- b. For standardisation of thio solution, follow the previous experiment.

- c. Titration results

Set No.	Volume of each layer taken (ml)		Volume of $\frac{N}{10}$ thio required for org. layer (ml)	Volume of $\frac{N}{10}$ thio * required for aq. layer (ml)	Strength of thio solution (Previously standardised)
	Organic	Aqueous			
1	5	10	...	...	... (N)
2	5	10	...	...	

\*If the titre value is low, dilute the solution five times.

- d. Determination of  $K_c$

Set Nos.	Mean $K_D$	$C_1$ moles/lit	$C_2$ moles/lit	$C_3$ moles/lit	$C_2 - \frac{C_1}{K_D}$ moles/L	$C_3 - \left( C_2 - \frac{C_1}{K_D} \right)$ moles/L	$K_c$ (mol <sup>-1</sup> lit)
1	...	...	...	...	...	...	...
2	...	...	...	...	...	...	...

Hence mean value of equilibrium constant ( $K_c$ ) = ... at  $t^\circ\text{C}$ .

[N.B.: Normal concentration of iodine must be converted to molar concentration and should be divided by 2].

Expected value of  $K_c = 7.14 \times 10^2$  at  $25^\circ\text{C}$  and  $6.2 \times 10^2$  at  $30^\circ\text{C}$ .

### Experiment 2

To show that benzoic acid dimerises in benzene.

**Theory:** The activities of a solute distributed between two phases at equilibrium at a constant temperature bear a fixed ratio. This is 'Nernst Distribution Law.'

This law is valid only when the molecular species is the same in the two phases. If the solute undergoes dissociation or association in any one of the phases, the distribution law as such will not hold.



According to Nernst Distribution Law when  $a_1$  and  $a_2$  are two activities of the solute in phases 1 and 2 respectively at equilibrium at a given temperature, then

$$a_1/a_2 = K_D \quad (K_D \text{ is unitless})$$

This  $K_D$  is called distribution coefficient or partition coefficient of the solute between phases 1 and 2 at experimental temperature.

For dilute solution,  $a \approx c$  (numerically,  $c$  = molar concentration).

$$\text{Then, } \frac{C_1}{C_2} = K_D.$$

When solid benzoic acid is shaken with two practically immiscible liquids, benzene and water, then benzoic acid remains as monomer and almost undissociated in aqueous phase (very small ionisation being neglected) but it dimerises in benzene phase.

If benzoic acid dimerises in benzene, then it can be shown that (derivation is given in general discussion of this chapter)

$\frac{C_w}{C_B}$  is not constant but  $\frac{C_w}{\sqrt{C_B}}$  remains constant at a given temperature. Here,  $C_w$  is the concentration (molar) of benzoic acid in aqueous layer and  $C_B$  is the molar concentration of benzoic acid in benzene.

Thus the aim of the present experiment is to show  $\frac{C_w}{C_B}$  for different sets of composition are not constant

but  $\frac{C_w}{\sqrt{C_B}}$  remains constant.

### Materials

- Nearly saturated solution of benzoic acid in benzene (200 ml).
- Pure benzene.
- Stoppered bottles (250 ml capacity, 4 nos.)
- Caustic soda solution  $\approx 0.1(N)$  500 ml.
- Standard oxalic acid solution 0.1 (N), 100 ml.
- Burettes, pipettes (25 ml, 10 ml, 5 ml), separating funnel.
- Phenolphthalein indicator solution..

### Procedure

- Dissolve  $\approx 10$ -12 gms of solid benzoic acid in pure benzene (200 ml) to prepare nearly saturated solution of benzoic acid in benzene.
- Make the following composition of sets taking the solution of benzoic acid in benzene:

#### Composition of Sets

Bottle nos. (stoppered 250 ml)	Volume of benzoic acid in benzene (ml)	Volume of pure benzene (ml)	Volume of distilled water (ml)	Total volume (ml)
1	50	0	100	150
2	40	10	100	150
3	30	20	100	150
4	20	30	100	150

[Measuring cylinder may be used to prepare the sets.]



- iii. Shake the bottles (sets) for an hour and then allow them to settle for at least 15 minutes.
- iv. Prepare 500 ml  $\approx \frac{N}{10}$  NaOH solution (dissolve  $\approx 2$  gm of NaOH pellets in 500 ml water) and standardise it against standard  $\frac{N}{10}$  oxalic solution which is prepared by accurate weighing. Dilute this standardised NaOH solution 10 times (25 ml is diluted to 250 ml) to prepare  $\frac{N}{100}$  NaOH solution.
- v. Take set no. 1. Separate the two layers using a separating funnel and collect the two liquids in two separate conical flasks and cover them with watch glass. Pipette out 25 ml of aqueous layer in a 125 ml conical flask and titrate it against  $\frac{N}{100}$  NaOH solution using phenolphthalein indicator. Repeat it for second and third times. Perform the same for bottles 2, 3 and 4. Pipette out 5 ml of benzene layer and pour into 25 ml distilled water in a 125 ml conical flask and titrate it against  $\frac{N}{10}$  NaOH solution using phenolphthalein indicator (shake well during titration). Repeat and perform the same for bottles 2, 3 and 4. Calculate  $C_W$  and  $C_B$  for each set.

## Results and Calculations

### i. Recording of laboratory temperature

	Before experiment	After experiment	Mean
Temperature →	°C	°C	°C

### ii. Preparation of 100 ml 0.1 (N) oxalic acid solution

Initial mass (gm)	Final mass (gm)	Mass of oxalic acid transferred (g)	Strength of oxalic acid solution
$w_1$	$w_2$	$(w_1 - w_2)$	$\frac{(w_1 - w_2)}{0.63} \left( \frac{N}{10} \right)$

### iii. Standardisation of NaOH solution against standard oxalic acid solution

Strength of oxalic acid	Volume of oxalic acid solution taken (ml)	Volume of NaOH solution required (ml)	Mean volume of NaOH solution (ml)	Strength of NaOH solution
...	a) 10	...	...	...
...	b) 10	...	...	...
...	c) 10	...	...	...

[25 ml of this NaOH solution is properly diluted to 250 ml to prepare  $\frac{1}{10}$ th strength of the NaOH solution, which is standardised.]



iv. Titration of aqueous layer

Set Nos.	Volume of aq. layer (ml)	Volume of NaOH solution (0.01N) required (ml)	Mean volume of NaOH solution (ml)	$C_w$ moles/lit
1	a) 25 b) 25 c) 25	a) b) c)	...	
2	a) 25 b) 25 c) 25	a) b) c)	...	
3	a) 25 b) 25 c) 25	a) b) c)	...	
4	a) 25 b) 25 c) 25	a) b) c)	...	

v. Titration of benzene layer

Set Nos.	Volume of benzene layer (ml)	Volume of NaOH solution (0.1N) (ml)	Mean volume of NaOH solution (ml)	$C_B$ moles/lit
1	a) 5 b) 5 c) 5	a) ... b) ... c) ...	...	...
2	a) 5 b) 5 c) 5	a) ... b) ... c) ...	...	...
3	a) 5 b) 5 c) 5	a) ... b) ... c) ...	...	...
4	a) 5 b) 5 c) 5	a) ... b) ... c) ...	...	...

vi. Table for calculated  $\frac{C_w}{C_B}$  and  $\frac{C_w}{\sqrt{C_B}}$

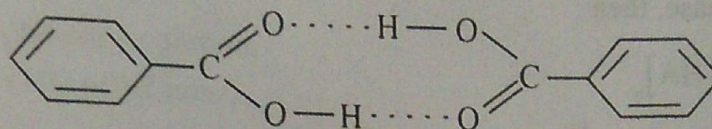
Set Nos.	$\frac{C_w}{C_B}$	$\frac{C_w}{\sqrt{C_B}}$ (moles lit <sup>-1</sup> ) <sup>1/2</sup>
1	...	...
2	...	...
3	...	...
4	...	...



vii. **Calculations:** Calculations of  $C_w$ ,  $C_B$ ,  $\frac{C_w}{C_B}$  and  $\frac{C_w}{\sqrt{C_B}}$

viii. **Interpretation of results:**

Since  $\frac{C_w}{C_B}$  are not constants but  $\frac{C_w}{\sqrt{C_B}}$  remain almost constant, so it may be concluded that benzoic acid dimerises in benzene, which may be represented as



The expected value of  $\frac{C_w}{\sqrt{C_B}} \approx 0.03$  at  $25^\circ\text{C}$ .

### Experiment 3

*Determination of dimerisation constant of benzoic acid in benzene medium.*

**Theory:** The activities of a solute distributed between two phases at equilibrium at a constant temperature bear a fixed ratio. This is 'Nernst Distribution Law'.

This law is valid only when the molecular species is same in the two phases. If the solute undergoes dissociation or association in any of the phases, the distribution law as such will not hold.

According to 'Nernst Distribution Law' when  $a_1$  and  $a_2$  are two activities of the solute in phases 1 and 2 respectively at equilibrium at a given temperature, then

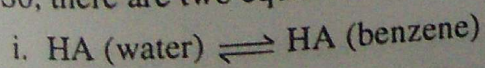
$$\frac{a_1}{a_2} = K_D$$

This  $K_D$  is called the distribution coefficient or partition coefficient of the solute between phases 1 and 2 at experimental temperature. For dilute solution when  $a \approx c$  (numerically,  $c$  = molar concentration), then

$$\frac{C_1}{C_2} = K_D$$

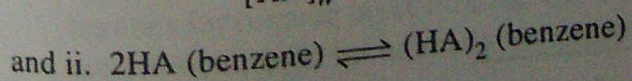
When solid benzoic acid (HA) is shaken with two practically immiscible solvents, benzene and water, then benzoic acid remains as monomer and almost undissociated in aqueous phase but it dimerises in benzene phase.

So, there are two equilibria,



$$K_D = \frac{[\text{HA}]_B}{[\text{HA}]_W}$$

(1)



(2)

$$K = \frac{[(\text{HA})_2]_B}{[\text{HA}]_B^2}$$