

**Table 2: Standardisation of NaOH solution by standard oxalic acid solution**

No. of titrations	Vol. of oxalic acid solution	Burette reading		Vol. of NaOH required (ml)	Mean vol. of NaOH soln. (ml)	Strength of NaOH Soln. (N)
		Initial (ml)	Final (ml)			
1	10.0	0.0	...	...	...	...
2	10.0	...	...	...	...	...
3	10.0	...	...	...	...	...

**Table 3: Titration of saturated benzoic acid solutions at different temperatures against standard NaOH solution**

Temp. (°C)	Vol of Satd. benzoic acid solution	Burette reading		Vol. of NaOH soln. required (ml)	Strength of benzoic acid soln. S (mol/l)
		Initial (ml)	Final (ml)		
50	10.0	0.0	...	...	...
40	10.0	...	...	...	...
35	10.0	...	...	...	...
25	10.0	...	...	...	...

**Table 4: Results for solubility curve and  $\Delta H$  of the solution**

Temp. (°C)	Solubility S (mol/l)	$\log_{10} S$	T (K)	$\frac{1}{T}$
50	...	...	323	...
40	...	...	313	...
35	...	...	308	...
25	...	...	298	...

**Results:** From the graph of  $\log S$  vs.  $\frac{1}{T}$ ,

$$\Delta H = -\text{Slope} \times 2.303R$$

$$= \dots \text{ kJ/mol.}$$

### Conclusion

**Solubility curve:** From the nature of graph, it is seen that solubility of benzoic acid in water (increases/decreases) with temperature.

**$\Delta H$ :** Since the value of  $\Delta H$  is (+ve/-ve), hence the process of dissolution of benzoic acid in water is (endothermic/exothermic).

### Experiment 2

**Determination of the heat of solution of oxalic acid at its saturation from the solubility measurements at different temperatures.**

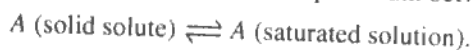
**Theory:** Solubility of a substance is defined as the number of grams of the substance required to saturate 100 grams of a solvent through dissolution at a particular temperature. This definition leaves solubility a unit less quantity.

However, solubility may also be expressed in molality unit, which comes from the above definition.

If  $x$  be solubility at a particular temperature, then the solubility will be  $\frac{10x}{M}$  molal,  $M$  being the molar mass.

Determination of solubility in molal unit is a little bit labourious work. For determination of heat of solution, it may be calculated in molar unit, i.e., number of moles of the solute present in 1000 ml of saturated solution of the substance. However, in contrast to solutions of low soluble compounds like benzoic acid, salicylic acid, etc, molality cannot be regarded as molarity for solution of oxalic acid, as it is sufficiently soluble in water.

For saturated solution of any compound with any degree of solubility, the existence of solid and solution together actually establishes an equilibrium between the two phases, i.e.,



$\therefore$  the equilibrium constant

$$K = \frac{a_{A(\text{soln.})}}{a_{A(\text{solid})}} = a_{A(\text{soln.})} \quad [\because a_{A(\text{solid})} = 1].$$

$$\therefore K = a_{A(\text{soln.})} \quad (1)$$

Using molar concentration,  $S$ , for activity,

$$K = S_{A(\text{soln.})} \quad (2)$$

Using equation (2), the heat of solution ( $\Delta H$ ) of a solute in its saturated solution can be computed. The temperature dependence of equilibrium constant has been mathematically expressed by van't Hoff isochore as

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad (3)$$

From (2) and (3), we have

$$\frac{d \ln S}{dT} = \frac{\Delta H}{RT^2} \quad (4)$$

On integration, (4) becomes

$$\ln S = -\frac{\Delta H}{RT}$$

$$\text{or, } \log_{10} S = -\frac{\Delta H}{2.303R} \cdot \frac{1}{T} \quad (5)$$

(assuming  $\Delta H$  be independent of  $T$ , at least for the present purpose, which is not a complicated dissolution process).

Now, plot of  $\log_{10} S$  vs.  $\frac{1}{T}$  will give a straight line, from the slope of which  $\Delta H$  can be calculated.

$$\Delta H = -2.303R \times \text{slope} \quad (6)$$

**Equipments:** Thermostat, 5 ml and 10 ml pipettes, burette, 250 ml reagent bottle, 100 ml conical flask, thermometer with  $\frac{1}{10}$ th graduation.

**Materials:** Oxalic acid, NaOH, phenolphthalein.

**Procedure**

1. Prepare 250 ml ~ 0.5 (N) NaOH solution. Required weight = 5 g (a small larger weight is preferred).
2. Prepare 50 ml standard oxalic acid solution of ~ 0.5 N strength. Weight required = 1.575 g.
3. Standardise NaOH solution with the standard oxalic acid solution.
4. Prepare about 100 ml saturated oxalic acid solution in the 250 ml reagent bottle and keep it in the temperature bath set at 35 °C.

[Because of high solubility of oxalic acid, it is advisable not to exceed the temperature beyond 40 °C].

5. Carefully pipette out 5 ml oxalic acid solution with the rubber-tubing-cum-withdrawal tube arrangement as in the previous experiment and keep in the 100 ml conical flask. Immediately add 25-30 ml water and titrate against standard NaOH solution from the burette.

[The addition of excess water is to avoid setting down any oxalic acid crystal due to temperature fall. **It is better to keep water first and then to add the solution.**]

6. Set the bath at 30 °C and allow the original solution to avail of this temperature. Check the temperature with thermometer. Pipette out 5 ml solution into conical flask with some water and titrate against standard NaOH solution.
7. Perform the procedure (6) at 25 °C and 20 °C temperatures.
8. Calculate the solubility ( $S$ ) of oxalic acid in water in **mol/l** unit, at the above-said temperatures, viz. 35 °C, 30 °C, 25 °C and 20 °C using  $v_1s_1 = v_2s_2$  equation. Divide the normalities so obtained by 2 to get the results in mol/l unit.

9. Plot  $\log_{10} S$  vs.  $\frac{1}{T}$  and calculate  $\Delta H$  from equation (6).

**Results and Calculations**

**Table 1: Preparation of 50 ml standard ~ 0.5 N oxalic acid solution**

Required weight = 1.575 g

Use Table 1 in experiment 1.

**Table 2: Standardisation of NaOH solution by standard oxalic acid solution (use 10 ml acid solution).**

Use Table 2 in experiment 1.

**Table 3: Titration of saturated oxalic acid solutions at different temperatures against standard NaOH solution.**

Temp. (°C)	Vol. of saturated Oxalic acid Soln. (ml)	Burette reading		Vol. of NaOH soln. required (ml)	Strength of oxalic acid soln. $S_1$ (N)	Solubility of oxalic acid (mol/l) $S = \frac{S_1}{2}$
		Initial (ml)	Final (ml)			
35	5.0	...	...	...	...	...
30	5.0	...	...	...	...	...
25	5.0	...	...	...	...	...
20	5.0	...	...	...	...	...

**Table 4: Results for calculation of  $\Delta H$** 

Temp. (°C)	$T$ (K)	$\frac{1}{T}$	Solubility, $S$ (mol/l)	$\log_{10} S$
35	308	...	...	...
30	...	...	...	...
25	...	...	...	...

**Results:** From the plot of  $\log_{10} S$  vs.  $\frac{1}{T}$ ,

$$\Delta H = -\text{slope} \times 2.303 R \text{ kJ/mol.}$$

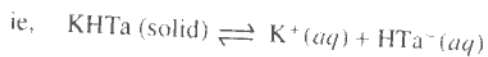
**Conclusion:** Since the value of  $\Delta H$  is (+ve/-ve), hence the process of dissolution of oxalic acid in water is (endothermic/exothermic) at its saturation point.

### Experiment 3

*Determination of solubility and solubility product of potassium hydrogen tartrate (KHTa) in water and in presence of different concentrations of a common ion (e.g., KCl) at room temperature.*

**Theory:** [Write definition of solubility, its units from theories of previous experiments or from introductory words].

Potassium hydrogen tartrate is a sparingly soluble salt in water. In its saturated solution an equilibrium is established between the solid phase and the ions.



(1)

Due to the low concentration, the activities may be regarded as molar concentrations and that of the undissolved solid is unity. Hence, the equilibrium constant of the solid-ion system [eqn. (1)].

$$K_a = \frac{a_{\text{K}^+} \cdot a_{\text{HTa}^-}}{a_{\text{KHTa}}}$$

$$\text{or, } K_{sp} = [\text{K}^+] [\text{HTa}^-]$$

(2)

where  $K_{sp}$  is the solubility product of KHTa and  $K_a$  is its activity solubility product.

In general, solubility product of a compound (generally a low soluble or sparingly soluble electrolyte) is defined as the product of the maximum concentrations of its constituent ions, raised to appropriate stoichiometric powers, at a particular temperature.

Presence of an ion, common to either of the ions produced from the electrolyte, lowers the solubility of the electrolyte. Thus, in presence of KCl, the solubility of KHTa decreases.

Let  $S$  be the solubility of KHTa in mol/l in presence of KCl and  $c$  be concentration of KCl in mol/l.

Then from eqn. (2),

$$K_{sp} = [\text{K}^+] [\text{HTa}^-]$$

$$\text{or } K_{sp} = (S + c)S$$

(3)