CHAPTER 6

Rate of dissolution of salt
OBJECT OF THE STUDY

Huge quantity of common salt is used for the manufacture of soda ash and caustic soda. Here salt is dissolved in water to prepare saturated or nearly saturated solution prior to its further processing to obtain the final product. Mostly soda ash manufacturers in India have their own salt works, which supply their salt demand but caustic soda manufacturers purchase salt from different salt works. Sometimes soda ash manufacturers also purchase salt from other sources. For both these industries good quality of salt is the first need, but when salts of similar quality are available selection can be made on the basis of their dissolution rates. The process of dissolution consumes some amount of energy, so by selecting a quick dissolving salt, good amount of energy is saved when large quantity of salt consumed by these industries is taken into account. Thus it affects the economics of the process to some extent.

The object of the present work is to obtain the comparative rates of dissolution of various common salt samples and to correlate them with their physical properties. This results may be useful for the above mentioned industries. Attempt is also made to calculate the diffusion coefficients of some salt samples from the equations given in the available literature.

RELEVANT LITERATURE ON RATE OF DISSOLUTION

Large number of publications have been devoted to the applied and theoretical studies of rate of dissolution of salt. The results of these investigations are
quite useful particularly in salt industry and chemical factories. Number of workers have also successfully utilised the results of dissolution rates of salt as one of the methods of physico-chemical analysis.

Ficks'\textsuperscript{71} was one of the first workers who explained the rate of solution on theoretical basis as early as in 1855, and enunciated the law which is well known as Fick's Law of diffusion. One of the ways of stating the law is to say that the quantity of solute $ds$, which diffuses through an area $A$, in time $dt$, when the concentration changes by an amount $dc$, through a distance $dx$ at right angles to the plane of $A$, is given by the expression $ds/dt = -DA_{0}dc/dx$, where $D$ is a constant. Further, Weber\textsuperscript{72} showed that diffusion constant decreases as the concentration rises. Noyes and Whitney\textsuperscript{73} proposed the following equation to evaluate the diffusion constant.

$$\frac{dc}{dt} = K (C_{s} - C)$$

where $C = \text{concentration of solid in solution in the beginning}$

$C_{s} = \text{concentration of solid in solution at saturation}$

$dc = \text{concentration of solid at time } t$

$K = \text{diffusion constant}$

They used two slightly soluble compounds for their work viz. benzoic acid and lead chloride. These salts were casted into small cylindrical sticks and dissolved in water in a wide mouth bottle kept with continuous rotating movement in a thermostat. The results obtained, supported the law derived by them. Number of other investigators \textsuperscript{74,75,76,78}
have reported evidence in favour of Noyes and Whitney's law in various kinds of reaction. Wood et al. carried out the first practical study on the effect of agitation on dissolution rates. They measured the rate at which the mixing of strong salt solution and a supernatant water layer took place under different stirrer speeds. The whole experiment was carried out in a wooden tank of 2700 litres capacity having a paddle agitator in centre. The distribution of salt was determined by means of electrical conductivity measurement at various fixed points.

Murphree studied the rate of dissolution of soluble crystals and worked out the mathematical formula based upon the change in the characteristic linear dimensions of the average crystals, during the progress of solution. His formula is based upon Noyes and Whitney's law, which he further elaborated by including the terms signifying weight, dimension and concentration before and after the experiment. He has dealt with four cases viz. (1) the weight of crystals going in solution is not sufficient enough to saturate the solution, (2) the weight of crystal is just sufficient to saturate the solution, (3) the weight of the crystal is slightly more than sufficient to make the saturated solution, (4) the weight of crystals is very large compared to the amount required to saturate the solution. Murphree supported his law by an experimental evidence of rate of dissolution of potassium dichromate in laboratory scale experiment.
The quantitative approach to the study of agitation in dissolution rate was advanced by Hixon and Crowell\textsuperscript{81}, who used a diffusion rate constant as an index of agitation in numerous experiments. These authors integrated Noyes and Whitney's equation after expressing surface area of the dissolving solid in terms of weight. The resulting function in which the cube root of the weight of solid appears as a term, was called "cube root law". This will be termed as equation 1 for future reference. The equation is as follows:

\[ K = W_0^{1/3} - W^{1/3} \]

where \( K \) = diffusion constant

\( W_0 \) = initial weight of the substance

\( W \) = weight of substance remained at time \( t \) after dissolution

Special cases were defined for initial weight of solid equal to that necessary for saturation and for systems with negligible change in concentration. Considerable study of the effect on diffusion rate constant by agitation variables, such as size of equipment, agitation speed, fluid viscosity and such other was made by Hixon and Wilkens\textsuperscript{82}.

Wilhelm et al\textsuperscript{83} advanced the study further and developed Noyes and Whitney's equation. This equation was integrated by them taking into consideration the volume of water used, amount of salt taken, size and shape of salt particles, concentration of solution and increase in volume of solution as dissolution of solid salt proceeds. They have assumed that salt particles are freely suspended in water or solution during dissolution process. The final form of the derived equation is given below. This equation will be
term as equation 2 for future reference.

\[ K = \frac{Z(P)}{P} \frac{V_1}{1/3} \frac{1}{2/3} \theta a(n) \frac{1}{W_s} \]

where \( K \) = diffusion rate constant i.e. weight of salt dissolved per unit time per unit area

\( P \) = density of solid, gms. per c.c.

\( V_1 \) = initial volume of water taken for dissolution in ml.

\( \theta \) = time in minutes

\( a \) = shape factor

\( n \) = number of particles

\( W_s \) = weight of salt in gms. required to saturate the volume of water taken for the experiment

\( Z \) = value given in the family curves in Fig.48 at known values of \( X \) and \( Y \).

\( X \) = weight of salt in gms. in solution at time \( \theta \) weight of salt in gms. required to saturate it

\( Y \) = weight of salt in gms. taken for dissolution experiment weight of salt in gms required for saturating the solution

Experimental evidence has been presented to show that their derivation is valid over entire concentration range of sodium chloride solution. They studied the rate of dissolution of rock salt samples of various particle size ranges and observed that the diffusion rate constant decreases with the decrease in particle size. Their experimental results are summarised in Table 80.
Fig. 48 Integral curves relating three variables $X, Y$ and $Z$ (After Wilhelm et al)
Table 80: Experimental results of rate of dissolution of rock salt of various particle sizes (after Wilhelm et al)

**Experimental conditions**

- **Vessel used**: Stoneware crock of 25 cms diameter and 30 cms height
- **Volume of water**: 10 Litres
- **Propeller rpm**: 1725
- **Temperature**: 15 - 16°C

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>gms. of salt</th>
<th>No. of particles</th>
<th>Average diameter in mm</th>
<th>Y</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>716</td>
<td>3060</td>
<td>5.9</td>
<td>0.2</td>
<td>0.61</td>
</tr>
<tr>
<td>2</td>
<td>1432</td>
<td>6100</td>
<td>5.9</td>
<td>0.4</td>
<td>0.60</td>
</tr>
<tr>
<td>3</td>
<td>2148</td>
<td>9190</td>
<td>5.9</td>
<td>0.6</td>
<td>0.58</td>
</tr>
<tr>
<td>4</td>
<td>2864</td>
<td>12230</td>
<td>5.9</td>
<td>0.8</td>
<td>0.59</td>
</tr>
<tr>
<td>5</td>
<td>3530</td>
<td>15300</td>
<td>5.9</td>
<td>1.0</td>
<td>0.57</td>
</tr>
<tr>
<td>6</td>
<td>4296</td>
<td>18380</td>
<td>5.9</td>
<td>1.2</td>
<td>0.56</td>
</tr>
<tr>
<td>7</td>
<td>1432</td>
<td>2820</td>
<td>7.7</td>
<td>0.4</td>
<td>0.68</td>
</tr>
<tr>
<td>8</td>
<td>1432</td>
<td>14320</td>
<td>4.4</td>
<td>0.4</td>
<td>0.57</td>
</tr>
<tr>
<td>9</td>
<td>1432</td>
<td>35800</td>
<td>3.3</td>
<td>0.4</td>
<td>0.52</td>
</tr>
<tr>
<td>10</td>
<td>1432</td>
<td>180600</td>
<td>1.9</td>
<td>0.4</td>
<td>0.50</td>
</tr>
</tbody>
</table>
FACTORS AFFECTING RATE OF DISSOLUTION

The factors affecting rate of dissolution can be grouped as follows:

Factors concerning solid.
Factors concerning solvent.
Factors concerning both solute and solvent.
Other factors.

Factors concerning solid: The rate at which a given mass of solid dissolves in liquid depends upon following, other variables being constant.

The rate of dissolution should be directly proportional to the specific surface of solute which is the average surface area per unit weight. The effective surface area in turn depends upon the particle size, shape and physical nature of the crystal. Thus, the uniform, spherical and compact solids should give less rate of dissolution than irregularly shaped, fractured and porous crystals. Different faces of many crystals show anisotropy i.e. their physical properties differ from one face to another. This may have certain definite effect on the rate of dissolution.

All the solids or soluble substances have a definite diffusion coefficient for a given solvent at particular temperature. So, if other conditions are identical, the rate of solution of two different solids should be proportional to their diffusion coefficient.

Factors concerning solvent: The movement of solvent in contact with the surface of solid i.e. layers immediately adjacent to solid surface is most important in deciding the
rate of solution. The presence of solute in solvent affects the rate of solution and usually as the concentration of solute in solvent increases, rate of solution decreases. Similarly increase in temperature increases the rate of dissolution of solute unless it has inverse solubility. Temperature also affects the viscosity and therefore the movement of solvent and so, with the increase in temperature of solvent the rate of dissolution normally increases.

Factors concerning both solute and solvent: If the solvent reacts chemically with solute, the products of reaction formed, can decrease or increase the rate of dissolution. Thus, when lime is added to sea water, magnesium hydroxide deposits around the calcium oxide particles and forms a protective layer which stops the further solution of lime in water. Similarly when zinc is dissolved in sulphuric acid, hydrogen gas liberated, agitates the solution and rate of dissolution increases.

The relative density of solute, solvent and solution have much to do on the rate of dissolution. The density difference can set up the currents and movement of solvent which may increase the rate of dissolution.

The proportion of solute and solvent governs the amount of total interfacial contact surface and therefore other factors being similar, the rate varies according to the contact surface between two phases.

Other factors: The average intensity of movement of the solvent may be higher or lower compared to the solvent film in immediate contact of the surface of solute. Fluctuation
in this causes variation in rate of dissolution. When the particles of solute are stirred in a beaker like cylindrical vessel, they get suspended at suitable speed of stirrer. Uniformity of agitation of solvent distributes the solute uniformly throughout the mass of solution but fluctuating stirring causes variation and influences the rate of dissolution.

DETERMINATION OF THE RATE OF DISSOLUTION OF VARIOUS SALT SAMPLES UNDER SIMILAR EXPERIMENTAL CONDITIONS

The salt samples used in this study were those used in washing experiments and their chemical composition and physical characteristics have been described earlier on page 95. The salt samples were either dissolved as such or fractionated to obtain required particle size range for dissolution experiments. The method of dissolution was batch as well as continuous.

**Batch method**

- **Beaker**: Stainless steel, capacity 4 litres 23 cms height and 15 cms diameter with a baffle arrangement
- **Stirrer**: Electric motor driven, with three propellers, covering area 7.5 cms and speed 1000 rpm
- **Quantity of water**: 3 litres
- **Quantity of Salt**: 1.125 Kg.

The water was taken in the beaker and stirrer was started. When the stirrer rpm became steady, the salt was added to the water in motion, quickly. The stopwatch was started simultaneously with the addition of salt to the water.
After this, to assess the rate of dissolution, samples of solution were collected while the process of dissolution was going on, at every one minute interval from a fixed depth by filter tipped pipette. The amount of solution sucked did not exceed 10 - 12 ml, from which 5 ml was diluted to 50 ml and 10 ml of the diluted solution was evaporated first on water bath and then at 110°C to determine the total dissolved solids. From these values the amount of salt dissolved at definite time interval was calculated.

For these experiments Kharaghoda, Bhavnagar, Porbandar and Tuticorin salt samples were used. For each salt samples two experiments were performed to obtain the amount of salt dissolved at various fixed time intervals in the experiments upto 10 to 16 minutes and average amounts were calculated from these results. These results are given in Table 81. These results are also plotted as concentration of salt in solution in grams per litre against time in minutes and are given in Fig.49.

Table 81: Dissolution of various salt as such by batch method

<table>
<thead>
<tr>
<th>Time interval in minutes</th>
<th>Kharaghoda (Grams salt per litre of solution)</th>
<th>Bhavnagar</th>
<th>Porbandar</th>
<th>Tuticorin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>162.4</td>
<td>189.3</td>
<td>199.3</td>
<td>199.6</td>
</tr>
<tr>
<td>2</td>
<td>208.3</td>
<td>232.0</td>
<td>241.2</td>
<td>235.9</td>
</tr>
<tr>
<td>3</td>
<td>231.2</td>
<td>259.1</td>
<td>264.7</td>
<td>256.0</td>
</tr>
<tr>
<td>4</td>
<td>242.3</td>
<td>284.5</td>
<td>278.1</td>
<td>273.2</td>
</tr>
<tr>
<td>5</td>
<td>252.1</td>
<td>288.2</td>
<td>288.1</td>
<td>278.0</td>
</tr>
<tr>
<td>6</td>
<td>257.6</td>
<td>295.6</td>
<td>295.7</td>
<td>283.6</td>
</tr>
<tr>
<td>7</td>
<td>252.9</td>
<td>300.4</td>
<td>301.5</td>
<td>287.0</td>
</tr>
<tr>
<td>8</td>
<td>269.4</td>
<td>306.9</td>
<td>304.1</td>
<td>291.8</td>
</tr>
<tr>
<td>9</td>
<td>273.0</td>
<td>308.2</td>
<td>307.2</td>
<td>292.6</td>
</tr>
<tr>
<td>10</td>
<td>278.8</td>
<td>312.5</td>
<td>311.0</td>
<td>296.1</td>
</tr>
<tr>
<td>11</td>
<td>281.6</td>
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<td>12</td>
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<td></td>
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<tr>
<td>15</td>
<td>282.6</td>
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<td></td>
</tr>
<tr>
<td>16</td>
<td>294.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 49. Rate of dissolution of salt samples as such by batch method.
Continuous method
Dissolution of salt samples as such: For comparison of dissolution rates of various salt samples by continuous method, a continuous dissolving column was prepared which is shown in Fig. 50. A is glass column of 1 meter length and 5 cms diameter. B is an inlet tube with a control valve C, by which a suitable rate of water flow can be adjusted. D is an exit tube from which the solution comes out. In the exit tube D, another small tube is inserted whose inside end is covered with a coarse mesh which allowed only solution to pass through it but not the salt crystals. The salt was fed to the column upto the height E and was fed continuously throughout the experiment to keep the bed of salt constant. F is a constant level reservoir which supplied the water to the column through the inlet tube. The water and salt travel in counter-current directions.

In the beginning of the experiment, the flow rate of water was adjusted. Then the glass column was filled with extra salt i.e. salt other than weighed and kept ready for the experiment. When the flowrate became practically constant at desired value, the salt weighed and kept separately for the experiment, was fed continuously and time required to dissolve the definite weight (3 or 5 Kg) of salt was noted with stopwatch. With each salt sample 3 to 5 experiments were carried out and average time for dissolution of 1.0 Kg of salt sample was calculated. The rate of dissolution of Kharaghoda, Bhavnagar, Porbandar, Tuticorin and Orissa were determined at six flow rates of
To compare the rates of dissolution of these salt samples in between them on the basis of their physical properties like bulk density, relative hardness and particle size distribution, these properties were also determined.

**Bulk density**: Bulk density was determined by taking 1.0 Kg of salt in 1.0 litre capacity measuring cylinder and tapping it gently upon the hard surface (wooden table with a cloth cushion). After 50 taps, the volume of salt in the measuring cylinder was noted and from the weight and volume, the bulk density was calculated. Average of 3 consistent readings was taken.

**Relative hardness**: Relative hardness was determined by ball mill test. 500 gms of +5 B.S. mesh salt was placed in ball mill with definite number of balls inside. The ball mill was run for 1 hour and the salt was removed. The salt was again sieved through 5 B.S. mesh and from the weight of salt passed through the mesh, the per cent salt disintegrated was calculated. This was taken as a measure of hardness of salt sample. Here also average of 3 readings was taken into consideration.

**Particle size distribution**: Particle size distribution was obtained from the sieve analysis of 1 Kg samples of various salts. Up to 5 mesh, British Standard sieves were used but for coarser sizes, sieves with 6.45, 4.84, 3.23 and 1.61 sq.cms. holes were prepared locally and used. Average of 3 - 5 analyses was taken for comparison.

Above mentioned properties are also given in Table 82 along with the dissolution rates.
Fig. 50. Sketch of continuous dissolving column.
### Dissolution Rates and Physical Properties of Various Salt Samples

<table>
<thead>
<tr>
<th>Flow rate L/min</th>
<th>Kharaghoda</th>
<th>Bhavnagar</th>
<th>Porbandar</th>
<th>Tuticorin</th>
<th>Orissa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>11 55</td>
<td>36 6</td>
<td>0</td>
<td>5 55</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>6 7 4</td>
<td>32 4</td>
<td>4 34 4</td>
<td>4 27 16</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>5 38 3</td>
<td>18 3</td>
<td>2 18</td>
<td>3 3 3</td>
<td></td>
</tr>
<tr>
<td>1.25</td>
<td>4 50 14 2</td>
<td>30 2</td>
<td>2 31 5</td>
<td>2 2 2</td>
<td></td>
</tr>
<tr>
<td>1.50</td>
<td>4 50 14 2</td>
<td>30 2</td>
<td>2 31 5</td>
<td>2 2 2</td>
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<tr>
<td>2.00</td>
<td>3 43 2</td>
<td>10 2</td>
<td>2 10 2</td>
<td>2 2 2</td>
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</table>
Table 82 continued

<table>
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<tr>
<th>Physical properties</th>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density lbs/cft</td>
<td>77.8</td>
<td>65.2</td>
<td>68.7</td>
<td>67.4</td>
<td>60.7</td>
</tr>
<tr>
<td>Relative hardness</td>
<td>3.6</td>
<td>20.6</td>
<td>46.5</td>
<td>16.5</td>
<td>68.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Particle size distribution</th>
<th>per cent present in composite sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average dia. mm.</td>
<td>0.44</td>
</tr>
<tr>
<td>1/4&quot; + 5 B.S.</td>
<td>23.70</td>
</tr>
<tr>
<td>5 + 6&quot;</td>
<td>4.60</td>
</tr>
<tr>
<td>6 + 8&quot;</td>
<td>8.02</td>
</tr>
<tr>
<td>8 + 10&quot;</td>
<td>6.93</td>
</tr>
<tr>
<td>10 + 12&quot;</td>
<td>0.32</td>
</tr>
<tr>
<td>12 + 14&quot;</td>
<td>4.08</td>
</tr>
<tr>
<td>&lt; 1.3</td>
<td>5.54</td>
</tr>
</tbody>
</table>
Dissolution of fixed particle size range of the salt samples

Similar experiments as mentioned above were done with fixed particle size range viz. \(-6.4 + 3.3\) mm (\(\frac{1}{4}\" + 5\) B.S. mesh) of the same salt samples at two flow rates and dissolution rates were compared with their bulk densities, relative hardness and approximate surface area. These results are given in Table 83.

Table 83: Dissolution rates of fixed particle size of various salt samples and their physical properties

<table>
<thead>
<tr>
<th>Name of salt</th>
<th>Time required for the dissolution of 1 Kg. salt (Min. Sec.)</th>
<th>Bulk density (lbs/ft(^3))</th>
<th>Relative hardness</th>
<th>Approximate surface area (sq.m./Kg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flow rate of water (L/min.)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5 L/min.</td>
<td>1.0 L/min.</td>
<td>0.5 L/min.</td>
<td>1.0 L/min.</td>
</tr>
<tr>
<td>Kharaghoda</td>
<td>7</td>
<td>42</td>
<td>4</td>
<td>47</td>
</tr>
<tr>
<td>Bhavnagar</td>
<td>6</td>
<td>53</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Porbandar</td>
<td>6</td>
<td>44</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>Tuticorin</td>
<td>6</td>
<td>55</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>Orissa</td>
<td>6</td>
<td>42</td>
<td>4</td>
<td>11</td>
</tr>
</tbody>
</table>

The results of Tables 82 and 83 are plotted graphically and are given in figures 51 and 52.
Fig. 51. Chart showing rate of dissolution of 1 kg. of salt sample as such, at different flow rates in continuous dissolving column.
Fig. 5.2. Chart showing rate of dissolution of 1 kg of fixed particle size range of salt at different flow rates in continuous dissolving column.
Evaluation of results:

When the rates of dissolution of Kharaghoda, Bhavnagar, Porbandar, Tuticorin and Orissa salt samples as composite salt samples are compared from the results given in the tables 81 and 82, it will be observed that Kharaghoda salt dissolves at slowest rate in water in batch as well as continuous method, than rest of the sea salt samples. On the otherhand, seasalt samples viz. Bhavnagar, Porbandar, Tuticorin and Orissa show practically similar rates of dissolution under identical experimental conditions. The similarity of rates of dissolution of sea salt samples can be explained on the basis of their bulk densities and particle size distribution. The bulk densities of composite salt samples of Bhavnagar, Porbandar, Tuticorin and Orissa are 65.2, 68.7, 67.4 and 60.7 lbs/cft. respectively (Table 82), which can be considered similar that except of Orissa salt which is lower. Secondly if now particle size distribution of these salt samples is compared from the same table, it will be observed that Porbandar, Tuticorin and Orissa salt samples show broadly similar salt distribution of various size crystals except Bhavnagar/Which is some what coarser. Relative hardness of these salt samples however showed irregular trend and could not be correlated with their dissolution rates. Similarly when bulk density, particle size distribution and relative hardness of Kharaghoda salt is compared with the rest of the samples one can easily explain the slowest rate of dissolution of it,compared to other salts, under same conditions. Thus the reasonable cause for the slow dissolution of Kharaghoda salt is its
maximum bulk density 77.8 lbs/cft, presence of coarsest size crystals and crystal aggregates and maximum relative hardness 3.2 in comparison to all sea salt samples.

These observations are also valid for the dissolution rates of fixed particle size range of these salt samples (Table 83). Here it will be seen that, Bhavnagar, Porbandar and Tuticorin salt samples have similar bulk densities which are 58, 60 and 56 lbs/cft, similar relative hardness 25, 29 and 27 and similar calculated surface areas 23, 24 and 29 sq.m. per Kg. and therefore have similar rates of dissolution. On the other hand Kharaghoda salt has higher bulk density 65.3 lbs/cft, higher relative hardness 16.2 and lower surface area 12.3 sqm/Kg show comparatively slower rate of dissolution. Orissa salt though showed similar rate of dissolution as former three samples, its physical properties could not be correlated.

The results of rate of dissolution of various salt samples from Tables 81, 82 and 83 have been graphically represented in figures 49, 51 and 52 for easy and ready comparison.

DETERMINATION OF DIFFUSION RATE CONSTANT OF SALT BY EQUATION 1 AND 2

As mentioned earlier equation 1 and 2 are modifications of Noyes and Whitney's law. The former has been derived by Hixon and Crowell and latter by Wilhelm et al. They are as follows:

\[
K = W_0^{1/3} - W_{1/3} \quad \text{Equation 1}
\]

\[
K = \frac{Z (p)^{2/3} V}{\theta_a (n)^{1/3} W_s^{2/3}} \quad \text{Equation 2}
\]
The meaning of various terms in these equations has been defined earlier. To calculate the diffusion rate constant in equation 1, it is necessary to know the values of $W_0^{1/3}$ and $W^{1/3}$. These values can be easily calculated from the amount of salt present in solution at zero time or beginning i.e. $W_0$ and that present at time $t$ i.e. $W_t$. Now suppose that the amount of salt present in solution at various time intervals are $W_0$, $W_{t_1}$, $W_{t_2}$, $W_{t_3}$ and so on, for finding out $K$ value for first time interval, values $W_0^{1/3}$ and $W_{t_1}^{1/3}$ are calculated and from their difference $K$ is obtained. Similarly for finding out $K$ for second time interval values $W_{t_1}^{1/3}$ and $W_{t_2}^{1/3}$ are calculated and their difference gives the required $K$ value. Thus for subsequent time intervals $K$ values can be calculated and average of these is diffusion rate constant $K$.

Dissolution experiments with fixed particle size range $-6$ to $8$ B.S. mesh of Bhavnagar, Porbandar and Tuticorin salt were carried out in duplicate by batch method and $K$ values were calculated for various time intervals by equation 1, as described above. These results are given in Table 84 along with the common conditions of experiment.
For calculating $K$ values by equation 2, it is necessary to know all the values of the terms given on right hand side of it. This is slightly complicated and is made clear by following sample calculation.

**Sample calculation:** 3 litres of water was agitated by power driven stirrer. To the water 1075 gms of -6 +8 B.S. mesh size salt was added. After an interval of 1 minute, the solution was analysed and found to contain 225.1 gms of salt per litre of water. The solubility of salt was taken as 358 gms per litre as that of pure sodium chloride at room temperature (20 - 25°C). The number of particles of salt in 1075 gms of salt were 70530 (calculated by weighing five sets of 100 particles and finding average value which was converted for total weight of salt). The density and shape factor of salt particles were taken as given by Wilhelm in his paper i.e. 2.16 gms/cc and 6.2 respectively. The value of $Z$ was obtained from $X$ and $Y$.

\[
X = \frac{\text{Weight of dissolved salt in initial volume of water at time } \theta}{\text{Weight of salt in gms required to saturate the initial volume of water}} = \frac{225.1 \times 3}{1074} = 0.62
\]

\[
Y = \frac{\text{Initial weight of salt taken for the experiment}}{\text{Weight of salt in gms required to saturate initial volume of water}} = \frac{1075}{1074} = 1.0
\]

Now from the family curves given in lower part of Fig. 48 at the above $X$ and $Y$ value, the value of $Z$ is 1.75. Placing all these values in equation 2, it becomes
Bhavnagar sea salt sample of different particle size range was dissolved in water under identical experimental conditions by batch method and samples of resulting solution were drawn at every one minute intervals. From these samples, the amount of salt dissolved at definite time interval was found out and corresponding K values were calculated as shown above. Z values were taken from the graphs given in Fig.48.

The results of these experiments are given in Table 85 along with the common conditions of experiment.

Table 85: Rate of dissolution of various particle size ranges of Bhavnagar salt in terms of diffusion constant K

Experimental conditions

<table>
<thead>
<tr>
<th>Beaker</th>
<th>4 L capacity, with baffle arrangement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of water</td>
<td>3 L</td>
</tr>
<tr>
<td>Wt. of salt taken</td>
<td>1.125 Kg</td>
</tr>
<tr>
<td>Stirrer r.p.m.</td>
<td>750 - 800</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time in B.S. mesh minutes</th>
<th>+5</th>
<th>-5 to 6</th>
<th>-6 to 8</th>
<th>-8 to 10</th>
<th>-10 to 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td></td>
<td>K</td>
<td>K</td>
<td>K</td>
<td>K</td>
</tr>
<tr>
<td>1</td>
<td>0.53</td>
<td>0.39</td>
<td>0.33</td>
<td>0.17</td>
<td>0.12</td>
</tr>
<tr>
<td>2</td>
<td>0.45</td>
<td>0.34</td>
<td>0.28</td>
<td>0.13</td>
<td>0.11</td>
</tr>
<tr>
<td>3</td>
<td>0.41</td>
<td>0.30</td>
<td>0.26</td>
<td>0.13</td>
<td>0.10</td>
</tr>
<tr>
<td>4</td>
<td>0.37</td>
<td>0.34</td>
<td>0.23</td>
<td>0.13</td>
<td>0.10</td>
</tr>
<tr>
<td>5</td>
<td>0.39</td>
<td>0.37</td>
<td>0.22</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td>6</td>
<td>0.38</td>
<td>0.32</td>
<td>0.22</td>
<td>0.11</td>
<td>0.099</td>
</tr>
<tr>
<td>7</td>
<td>0.34</td>
<td>0.27</td>
<td>0.22</td>
<td>0.11</td>
<td>0.098</td>
</tr>
<tr>
<td>8</td>
<td>0.33</td>
<td>0.24</td>
<td>0.20</td>
<td>0.11</td>
<td>0.099</td>
</tr>
<tr>
<td>9</td>
<td>0.30</td>
<td>0.21</td>
<td>0.18</td>
<td>0.11</td>
<td>0.099</td>
</tr>
<tr>
<td>10</td>
<td>0.28</td>
<td>0.20</td>
<td>0.17</td>
<td>0.12</td>
<td>0.099</td>
</tr>
</tbody>
</table>
Evaluation of results

From the results given in Table 84 it will be seen that the diffusion rate constant $K$ calculated by Hixon and Growell's equation does not show consistency. In duplicate experiments also fluctuations in $K$ values when compared at same time intervals are wide. In the individual experiments also, it first increases, reaches to a maximum and again decreases. In between 20 to 60 second time interval the deviation from one another is less. Hixon and Growell have carried out numerous dissolution experiments by subjecting solid and liquid to various types of agitational movement and claimed that the $K$ values calculated by equation 1 in each experiment showed only 3 to 5 per cent deviation from an average value. However, the present experiments with sea salt samples given in table 84 show that applicability of the said equation is not good.

From the results given in Table 85 it is seen that diffusion rate constant calculated by equation 2 shows better consistency. It shows good consistency for finer particle size ranges viz. -6 +8, -8 +10 and -10 +12 B.S. mesh than coarser particle size ranges viz. +5 and -5 +6 B.S. mesh. For finer sizes it is almost constant from 2 minutes onwards but for coarser sizes it decreases considerably after 7 minutes. For all particle sizes, the 1 minute values are higher than subsequent time interval values, which may be due to some time gap in the adjustment of steady state of experiment. From 2 to 8 minutes time interval the deviation
in K values is less. When mean K values are calculated by averaging 2 to 8 minutes values for each particle size the following values were obtained.

<table>
<thead>
<tr>
<th>Particle size B.S. mesh</th>
<th>Mean K value</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 6 + 8</td>
<td>0.23</td>
</tr>
<tr>
<td>- 8 + 10</td>
<td>0.12</td>
</tr>
<tr>
<td>- 10 + 12</td>
<td>0.10</td>
</tr>
<tr>
<td>- 5 + 6</td>
<td>0.31</td>
</tr>
<tr>
<td>- 5 + 5</td>
<td>0.38</td>
</tr>
</tbody>
</table>

The above K values show decrease with the decrease in particle size and confirm the observations made by Wilhelm et al.

The partial inconsistency of K values in the coarser size ranges in these experiments is supposed to be due to following reasons. Wilhelm et al have derived the equation by carrying out dissolution of rock salt in their experiments. Compared to sea salt crystals which are of highly irregular shapes, fractured and porous to some extent, rock salt crystals (obtained from crushing the rock salt) are spheroidal, compact and free from irregularities. Due to this difference in the physical characteristics one cannot get salt of definite surface area even after fractionating the former in narrow size range, but in the case of latter it is possible. Secondly, the experimental set up used in Wilhelm's experiment is larger than in present work. The dimension of vessel taken for dissolution and speed of stirring have definite effect on flow pattern i.e. relative solid liquid movement. Due to these reasons some deviation was observed in K values however, on the whole the applicability of Wilhelm's equation is good.