only the pure substance. As the temperature increases progressively from the temperature of the eutectic mixture to the melting point of the pure substance, the mole fraction of impurity in the liquid decreases constantly, since the quantity of liquified pure substance increases constantly. For all temperatures above the eutectic point:

\[ F = \frac{1}{F} \times x^*_2 \]  
(2)

\[ F = \text{molten fraction of the analysed sample}, \]
\[ x^*_2 = \text{mole fraction of the impurity in the analysed sample}. \]

When the entire sample has melted, \( F = 1 \) and \( x^*_2 = x^*_2 \). If equation (2) is combined with equation (1), the following equation is obtained:

\[ T = T_0 - \frac{x^*_2 RT^2}{\Delta H_f} \times \frac{1}{F} \]

The value of the heat of fusion is obtained by integrating the melting peak.

The melting point \( T_0 \) of the pure substance is extrapolated from the plot of \( 1/F \) versus the temperature expressed in kelvins. The slope \( \alpha \) of the curve, obtained after linearisation, if necessary, corresponding to \( \frac{RT^2}{\Delta H_f} \) allows \( x^*_2 \) to be evaluated.

The fraction \( x^*_2 \), multiplied by 100 gives the mole fraction in per cent for the total eutectic impurities.

THERMOMICROSCOPY

Phase changes may be visualised by thermomicroscopy, a method which enables a sample subjected to a programmed temperature change to be examined, in polarised light, under a microscope.

The observations made in thermomicroscopy allow the nature of the phenomena detected using thermogravimetry and differential thermal analysis to be clearly identified.

Apparatus. The apparatus consists of a microscope fitted with a light polariser, a hot plate, a temperature and heating rate and/or cooling rate programmer and a recording system for the transition temperatures. A video camera and video recorder may be added.

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2.2.35. OSMOLALITY

Osmolality is a practical means of giving an overall measure of the contribution of the various solutes present in a solution to the osmotic pressure of the solution.

An acceptable approximation for the osmolality \( \xi_m \) of a given aqueous solution is given by:

\[ \xi_m = \nu m \Phi \]

If the solute is not ionised, \( \nu = 1 \); otherwise \( \nu \) is the total number of ions already present or formed by solvolysis from one molecule of solute.

\( m \) = molality of the solution, that is the number of moles of solute per kilogram of solvent,
\( \Phi \) = molal osmotic coefficient which takes account of the interactions between ions of opposite charge in the solution. It is dependent on the value of \( m \). As the complexity of solutions increases, \( \Phi \) becomes difficult to measure.

The unit of osmolality is osmole per kilogram (osmol/kg), but the submultiple milliosmole per kilogram (mosmol/kg) is usually used.

Unless otherwise prescribed, osmolality is determined by measurement of the depression of freezing point. The following relationship exists between the osmolality and the depression of freezing point \( \Delta T \):

\[ \xi_m = \frac{\Delta T}{1.86} \times 1000 \text{ mosmol/kg} \]

Apparatus. The apparatus (osmometer) consists of:

- a means of cooling the container used for the measurement,
- a system for measuring temperature consisting of a resistor sensitive to temperature (thermistor), with an appropriate current or potential-difference measurement device that may be graduated in temperature depression or directly in osmolality,
- a means of mixing the sample is usually included.

Method. Prepare reference solutions as described in Table 2.2.35.-1, as required. Determine the zero of the apparatus using water R. Calibrate the apparatus using the reference solutions: introduce 50 µl to 250 µl of sample into the measurement cell and start the cooling system. Usually, the mixing device is programmed to operate at a temperature below that expected through cryoscopic depression to prevent supercooling. A suitable device indicates attainment of equilibrium. Before each measurement, rinse the measurement cell with the solution to be examined.

Table 2.2.35.-1. – Reference solutions for osmometer calibration

<table>
<thead>
<tr>
<th>Mass in grams of sodium chloride R per kilogram of water R</th>
<th>Real osmolality (mosmol/kg)</th>
<th>Ideal osmolality (mosmol/kg)</th>
<th>Molal osmotic coefficient</th>
<th>Cryoscopic depression (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.087</td>
<td>100</td>
<td>105.67</td>
<td>0.9463</td>
<td>0.186</td>
</tr>
<tr>
<td>6.260</td>
<td>200</td>
<td>214.20</td>
<td>0.9337</td>
<td>0.372</td>
</tr>
<tr>
<td>9.463</td>
<td>300</td>
<td>323.83</td>
<td>0.9264</td>
<td>0.558</td>
</tr>
<tr>
<td>12.684</td>
<td>400</td>
<td>434.07</td>
<td>0.9215</td>
<td>0.744</td>
</tr>
<tr>
<td>15.916</td>
<td>500</td>
<td>544.66</td>
<td>0.9180</td>
<td>0.930</td>
</tr>
<tr>
<td>19.147</td>
<td>600</td>
<td>655.24</td>
<td>0.9157</td>
<td>1.116</td>
</tr>
<tr>
<td>22.380</td>
<td>700</td>
<td>765.86</td>
<td>0.9140</td>
<td>1.302</td>
</tr>
</tbody>
</table>

Carry out the same operations with the test sample. Read directly the osmolality or calculate it from the measured depression of freezing point. The test is not valid unless the value found is within two values of the calibration scale.