The melting point of a binary system

Related concepts
Melt, melting point, melting point diagram, binary system, miscibility gap, mixed crystal, eutectic mixture, Gibbs’ phase law.

Principle
In plotting the cooling curves of binary mixtures one determines the temperatures of melting and solidification of specimens with differing fractions (molar fractions) of the two components. These results are entered in a temperature versus concentration diagram.

Tasks
Record the melting point diagram of a mixture of biphenyl and naphthalene. Determine the composition of the eutectic mixture and its melting point from the melting point diagram.

Equipment
Cobra3 Chem-Unit 12153.00* 1
Power supply 12 V/2 A 12151.99 1
Data cable, RS232 14602.00 1
Software Cobra3 Chem-Unit 14520.61* 1
Thermocouple NiCr-Ni, sheathed 13615.01 1
Retort stand, h = 750 mm 37694.00 1
Right angle clamp 37697.00 1
Universal clamp 37715.00 1
Test tube, 18 x 188 mm 37658.03 2
Test tube rack, 12 holes, d = 22 mm, wood 37686.00 1
Powder funnel, \( d_o = 65 \text{ mm} \) 34472.00 1
Mircospoon 33393.00 1
Mortar with pestle, 70 ml 32603.00 2
Precision balance, 620 g 48852.93 1
Weighing dishes, 80 x 50 x 14 mm 45019.05 1
Teclu burner, natural gas 32171.05 1
Safety gas tubing 39281.10 1
Hose clips, \( d = 12...20 \text{ mm} \) 40995.00 2
Lighter for natural / liquified gases 38874.00 1
Napththalene, white, 250 g 48299.25 1
Biphenyl, 100 g 31113.10 1
Standard petrol, b.p. 65-95°C, 1000 ml 31311.70 1
PC, Windows® 95 or higher

Changes in the equipment required for use of the Basic-Unit:
(instead of * above mentioned)
Cobra3 Basic-Unit 12150.00 1
Measuring module, Temperature 12104.00 1
Software Cobra3 Temperature 14503.61 1

Set-up and Procedure
Grind sufficient quantities of biphenyl and naphthalene for the 11 different test mixtures listed in Table 1 separately to powder using a mortar and pestle. Make up the test mixtures, weighing the substances to an accuracy of 1 mg, and pour them into separate, appropriately marked test tubes.

Fig. 1. Experimental set-up.
Table 1: Molar fractions and weights of binary mixtures

<table>
<thead>
<tr>
<th>Molar fraction of naphthalene</th>
<th>Mass of naphthalene in g</th>
<th>Molar fraction of biphenyl</th>
<th>Mass of biphenyl in g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>0.1</td>
<td>0.338</td>
<td>0.9</td>
<td>3.662</td>
</tr>
<tr>
<td>0.2</td>
<td>0.688</td>
<td>0.8</td>
<td>3.312</td>
</tr>
<tr>
<td>0.3</td>
<td>1.051</td>
<td>0.7</td>
<td>2.949</td>
</tr>
<tr>
<td>0.4</td>
<td>1.426</td>
<td>0.6</td>
<td>2.574</td>
</tr>
<tr>
<td>0.5</td>
<td>1.816</td>
<td>0.5</td>
<td>2.184</td>
</tr>
<tr>
<td>0.6</td>
<td>2.220</td>
<td>0.4</td>
<td>1.780</td>
</tr>
<tr>
<td>0.7</td>
<td>2.639</td>
<td>0.3</td>
<td>1.361</td>
</tr>
<tr>
<td>0.8</td>
<td>3.075</td>
<td>0.2</td>
<td>0.925</td>
</tr>
<tr>
<td>0.9</td>
<td>3.528</td>
<td>0.1</td>
<td>0.472</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Clamp a test tube containing one of the test mixtures at an angle above the burner and carefully heat it until the solid substance melts and the resulting liquid is clear. Do not heat the liquid up to the boiling point! Insert the NiCr-Ni thermocouple in the melt and start measurement by pressing <Start measurement>. You can follow the course of the cooling curve by observing the monitor display. When the mixture has nearly reached room temperature, stop the measurement with <Stop measurement>. Save the data with <File><Save measurement as...>. Following this, briefly reheat the mixture to remove the thermocouple. Clean the thermocouple thoroughly with petrol. Use the same procedure to record the cooling curves for each of the other 10 mixtures.

Fig. 3 shows the graph as it is presented by the programme when the measurement is stopped.

**Theory and Evaluation**

Mixtures of two substances have lower melting points than those of the individual substances. This effect is greater, the more of the one substance that is mixed in the other substance. When graphs are plotted of the melting points of various mixtures against the content of the one substance in the other, descending curves are obtained. The two curves intersect at a lowest point, the eutectic point. The quantitative proportions of the two substances at this point is the eutectic mixture. The melting point diagram shows the dependence of the melting point on the composition of the system at constant pressure.

Biphenyl and naphthalene can be mixed in any ratio in their liquid phases. Since these substances do not form liquid crystals, a separation into two phases occurs when the melt cools down. Pure naphthalene crystallizes out first because it has the higher melting point. As this occurs, the relative concentration of biphenyl in the remaining melt increases and the melting point of the melt also decreases. Finally, the residual melt reaches the composition of the eutectic mixture and freezes as a fine mix of both types of crystals.
To plot the melting point diagram, the cooling curves of melts of several different compositions are measured. Each of these curves (Fig. 3) has a first critical point. This is the point at which the component with the highest melting point starts to crystallize out. The curve remains horizontal here for some time, as melting enthalpy is released. You can exactly determine this temperature using the <survey> function in the upper menu bar.

Subsequently, a second critical point indicates that the eutectic temperature has been reached. The cooling curve of the two pure components and the eutectic mixture only has a single critical point. This is indicated by a drop and then a rise in temperature. Only the first critical points of the cooling curves are of importance. The corresponding temperatures are plotted against the molar fraction of one of the components of the mixtures (Fig. 4). The molar fraction is the ratio of the quantity of one component to the total amount in the system (see also Table 1).

On extrapolating the two parts of the curve in the melting point diagram downwards, the composition and the melting point of the eutectic mixture can be read off at the point of intersection E. The melting point curves divide the diagram into four areas:

Area I: Unsaturated solution of the two substances B and N
Area II: Supersaturated solution of N in B
Area III: Supersaturated solution of B in N
Area IV: Heterogeneous mixture of N, B and the eutectic.

When only the melt and the gas phase are present, then the number of degrees of freedom is 2. The temperature and concentration can be varied within wide limits (area I in Fig. 4). On starting at a point in area I and lowering the temperature, deposition begins on reaching the melting point curve. Three phases are now present and the number of degrees of freedom is only 1; the melting point of the system is dependent on the concentration of the melt.

Point E in the melting point diagram is a quadruple point, because it marks the intersection of four phases (two solid, the liquid melt and the gas phase). The system is non-variant because, having two components and four phases, there are no degrees of freedom remaining. The eutectic mixture therefore behaves as though it were a single component system.

Data and Results
Naphthalene and biphenyl form a eutectic mixture which has the following composition:

\[ X_{\text{naphthalene}} = 0.44; \ X_{\text{biphenyl}} = 0.56. \]

The eutectic temperature is \[ T_E = 300.8 \text{ K}. \]
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