Name: Chow Ching Yue (7) Group: 4 Grade: _____

Date: 07/09/2010

Identifying an Unknown Carbonyl Compound

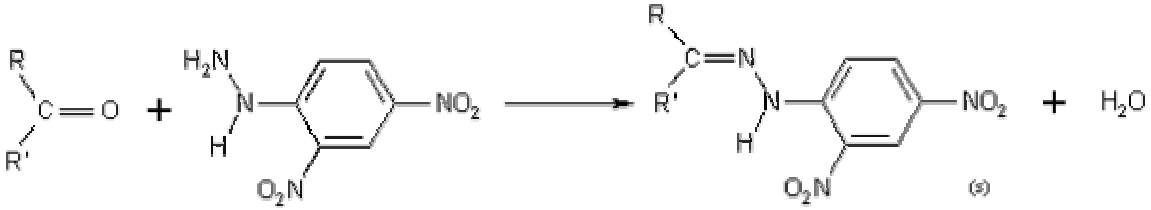
Aim

The purpose of this experiment is to classify a carbonyl compound by a simple test and to identity it by preparation of a derivative.

Introduction

In this experiment, we are provided with a sample of compound X, which is known to be a ketone from a given list. In the first part of the experiment, preparation of a derivative of the compound with 2,4-dinitrophenylhydrazine is required.

Owing to the high eleconegativity of oxygen, the carbonyl group in the compound is strongly polarized. The carbonyl carbon is electron deficient and is easily attacked by nucleophiles, forming precipitate with 2,4-dinitrophenylhydrazine by addition-elimination reaction. The precipitate formed, 2,4-dinitrophenylhydrazone, is a colored crystal which has sharp melting point:



where R' = H (aldehyde) or alkyl group (ketone)

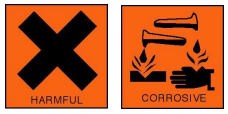
Before having the second part of experiment, the precipitate formed has undergone recrystalisation, which can increase the purity of the crystals. Thus, crystals with higher purity can give a more accurate result in the melting point determination.

In second part of experiment, by determinating the melting point and comparing with the data book, we can identify the particular ketone.

In this experiment, the variables are:

Controlled variables	Independent variable	Dependent variable
● Kind of derivative ● Data book source ● Amount of derivative used in melting	● Identity of carbonyl compound	● Melting point of the derivative

Hazard Warning

Methanol, CH_3OH 	2,4-dinitrophenylhydrazine 
Sulphric acid, dilute, 1M H2SO4 	Ethanol 
Petroleum 	

As all organic compounds have harmful vapors and con be toxic by absorption through the skin. Some are flammable. We must:

1. keep the stoppers in the bottles as much as possible
2. keep the bottles away from flames
3. wear safety spectacles and gloves
4. carry out experiment in good ventilation

Requirements – Part A

Apparatus				
Safety spectacles	× 1		Bunsen burner	× 1
Tripod	× 1		Gauze	× 1
Bench protection sheet	× 1		Beaker, 250cm^3	× 1
Boiling tube	× 2		Test-tube	× 2
Glass stirring rod	× 1		Protective plastic gloves	× 1
Measuring cylinder	× 2		Retort stand, boss and clamp	× 1
Apparatus for suction	× 1		Steam bath	× 1
Spatula	× 1		Small-sized dropper	× 2
Ice	Little			

Chemicals				
Unknown compound X	30 drops		2,4-dinitrophenylhydrazine solution	15 cm^3
Sulphuric acid, dilute H_2SO_4	2cm^3, 1M		Methanol, CH_3OH	3.0 cm^3
ethanol			NaCl	

Procedure – Part B

1. 30 drops of the unknown compound was put into boiling tube. 15cm^3 of the 2,4-dinitrophenylhydrazine solution was added and stirred.

2. 2cm^3 of dilute sulphuric acid was added to increase the amount of precipitation.

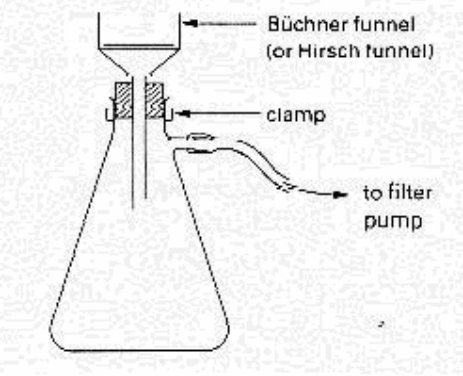


Fig. 8.4 Suction filtration

3. Suction filtration apparatus in Fig. 8.4 was used to filter the precipitate.

4. Suction was stopped by switching off the bump, and the precipitate was soaked in about 3.0 cm^3 of methanol.

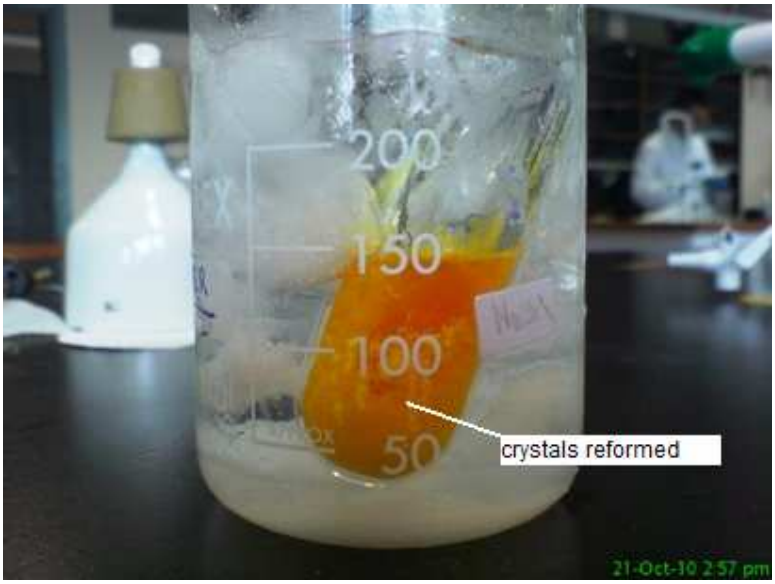
5. Suction was resumed and the crystals were dried by drawing air through them for a few minutes.

6. The solid was recrystallised by using the following procedures.

   a. The crystal was transferred to a boiling tube standing on a steam bath.

   b. The crystal was dissolve in the minimum amount of hot ethanol

   c. When the crystals had have dissolved, the solution was cooled in an icewater mixture until crystal reappear.



d. The crystals were filtered as before. Finally, the crystals were washed with a few drops of cold ethanol.

e. The crystal was pressed thoroughly between two wads of filter paper to remove excess solvent. Then the crystals was put on another piece of filter paper placed alongside a Bunsen burner and gauze, crystals was being turned over occasionally until they appear dry.

Requirements – Part B

Apparatus				
Safety spectacles	× 1		Bunsen burner	× 1
Tripod	× 1		Gauze	× 1
Bench protection sheet	× 1		Melting-point tube	× 2
Thermometer, 0-360℃, long stem	× 1		Boiling-tube, fitted with cork and stirrer	× 1
Rubber bang	× 1		Protective plastic gloves	× 1

Chemicals
Petroleum

Procedure – Part B

1. The ends of the thin capillary tubes were heat in Bunsen flame until the closure of the tube mouth to form melting-point tubes.

2. A pile of the derivative was pushed into the open end of the melting-point tube with the use of spatula until a few crystals have entered.

3. The closed end of the tube was tapped vertically against a hard surface, i.e. table

4. The filling and tapping procedures was repeated until a total length of about 0.5cm was compacted at the bottom of the tube. Another tube was prepared in this way.

5. One of the prepared melting-point tubes was attached to the thermometer, as shown in Fig. 8.5

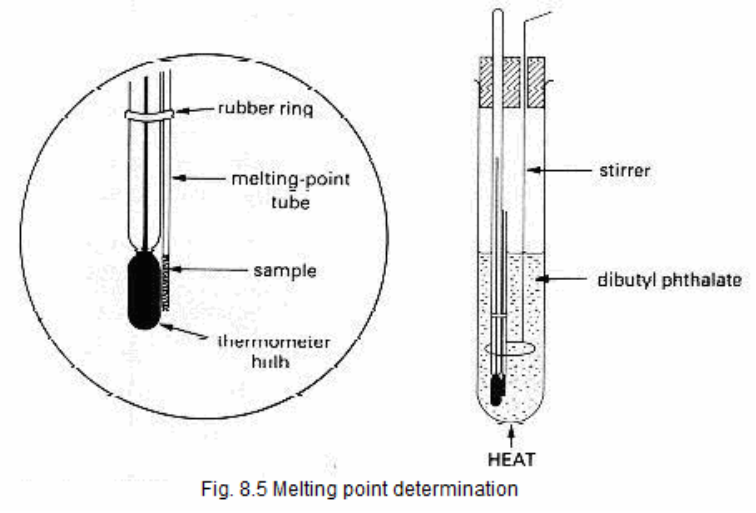
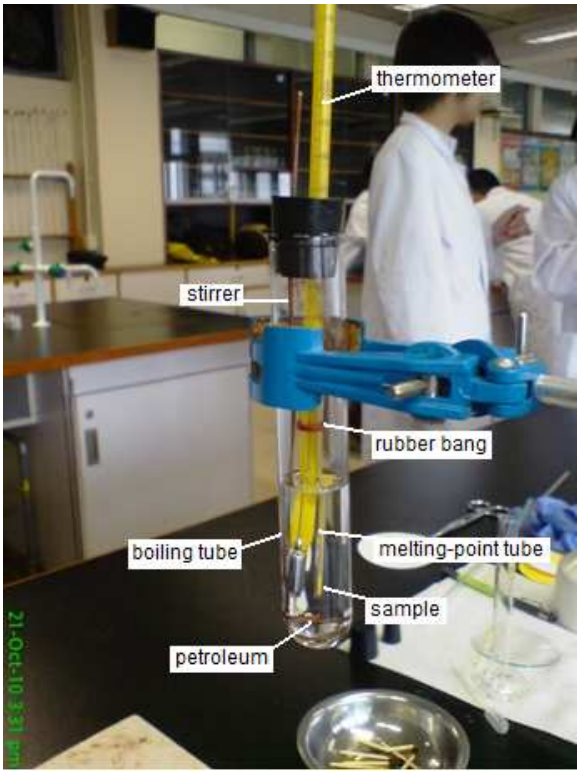


Fig. 8.5 Melting point determination



6. The boiling-tube was half-filled with petroleum and the thermometer was positioned with attached tube and the stirrer through the bung, as shown in Fig. 8.5

7. The apparatus was positioned over a low Bunsen flame and gauze and the apparatus was gently heated, the petroleum was being stirred all the time by moving the stirrer up and down.

8. The crystals was kept an eye and the temperature was noted as soon as signs of melting were seen (usually seen as a contraction of the solid followed by a damp appearance.) the range of temperature over the sample melt was recorded. The first reading gave a rough melting point but was a guide for the second determination.

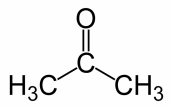
9. The burner and the old tube containing derivative was removed. The temperature was allowed to drop about 10 before positioning a fresh melting-point containing another portion of the derivative.

10. The above procedure was repeated in order to obtain a more accurate value of the melting point. The temperature was raised very slowly (about 2 rise per minute) until the crystals melt (take the formation of a visible meniscus as a sign of melting),

11. The melting point was compared with the value given the Table 8.1 and the unknown compound was identified.

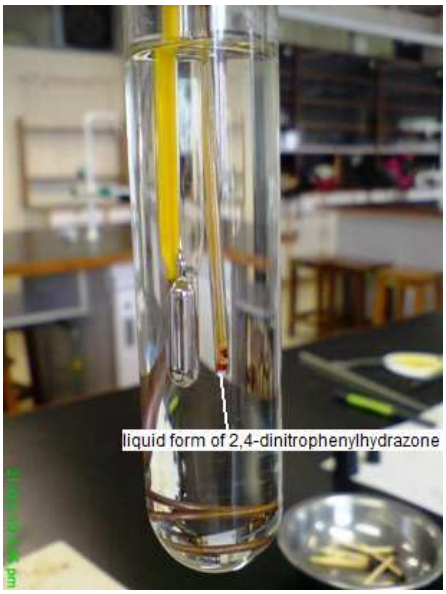
Result Table

	Trial	Test 1
Metlting Point of 2,4-dinitrophenylhydrazone/℃	123-128	127-128

Structural Formula of the Unknown Ketone	
Chemical Name of Unknown Carbonyl Compound	propanone

Result Inpertretation

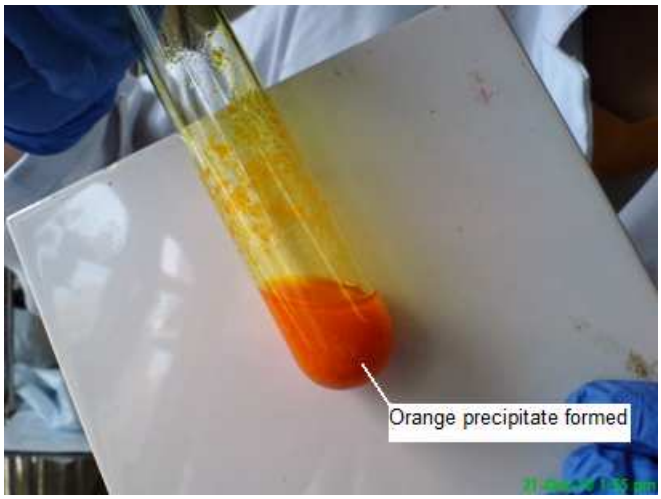
1. At 127□-128□, the orange crystals turns red and starts to melt, liquid separated into two layers was finally observed.



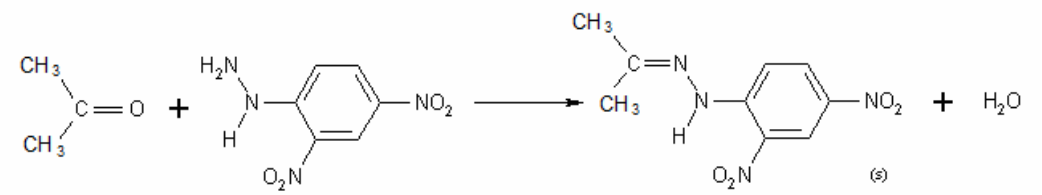
Name	Formula	Boiling point/°C	Melting point of 2,4-dinitrophenylhydrazone/°C
Aldehydes			
methanal	$HCHO$	−21	167
ethanal	CH_3CHO	21	146, 164 (2 forms)
propanal	CH_3CH_2CHO	48	156
butanal	$CH_3CH_2CH_2CHO$	75	123
2–methylpropanal	$(CH_3)_2CHCHO$	64	187
benzaldehyde	C_6H_5CHO	178	237
Ketones			
propanone	CH_3COCH_3	56	128
butanone	$CH_3CH_2COCH_3$	80	115
pentan-2-one	$CH_3CH_2CH_2COCH_3$	102	141
pentan-3-one	$CH_3CH_2COCH_2CH_3$	102	156
hexan-2-one	$CH_3CH_2CH_2CH_2CO_2CH_3$	128	107
4-methylpentan–2–one	$(CH_3)_2CHCH_2COCH_3$	117	95
cyclohexanone		156	162

When comparing the result table and the data table, we can match the melting point of 2,4-dinitrophenylhydrazone with the data table. At 127-128□, the unknown ketone is probably propanone.

2. When the unknown ketone X was added into 2,4-dinitrophenylhydrazine solution, orange precipitate formed, which is 2,4-dinitrophenylhydrazone.



Chemical Equation:



Conclusion

The unknown carbonyl compound X is propanone, with its 2.4-dinitrophenylhrazone melting point 128℃.

Questions and Answers

Q1. What factors decide the choice of solvent in the recrystallisation procedure?

[ANS] At first, the solvent used must not react with the solid formed in the experiment. The solid should be soluble in the solvent at high temperature, but insoluble at room temperature. If the solid is soluble in solvent at room temperature, no solid can be formed in the stage of recystallisation, which is not a appropriate solvent. Also, impurities should be insoluble to solvent thus theses can be removed before the recystallisation.

Q2. How were soluble impurities removed from the derivative?

[ANS] After the formation of the derivative, suction filtration was carried out. The derivative was soaked and washed by 3cm^3 of methanol when the bump was switched off. Soluble impurities dissolve in methanol, which was removed after resuming the suction to remove methanol.

Q3. In the recrystallisation procedure, why were the crystals dissolved on only minimum amount of ethanol?

[ANS] If excessive ethanol is used, the solution formed is not saturated. It make difficult for the recystallization as the crystals formed will be fine and the amount will be small, more time will be needed for recystallisation.

Q4. If your sample had contained insoluble impurities, such as pieces of filter paper, cork, etc., suggest how these might have been removed.

[ANS] After dissolving the crystals with minimum amount of ethanol, hot filtration can be used to remove the insoluble impurities before recrystallisation. In hot filtration, filtration apparatus is hot in order to stop the dissolved compounds crystallizing from solution during filtration, thus forming crystals on the filter paper or funnel.

Q5. Why is it not satisfactory to identify aldehydes and ketones by measuring their boiling points?

[ANS] For most of the aldehydes and ketones, there have close melting points. Take pentan-2-one and pentan-3-one as an example, both of their melting points are 102℃, it is impossible for us to distinguish between two of them by determining their melting points as their melting point are the same. However, by measuring the melting points of their derivatives, 2.4-dinitrophenyldrazone, they have two different melting points, which are 141 ℃and 156℃. Thus, the difference among two compounds is significant.

Discussion on Errors

1. In the trial, the result shows a large range of melting point (123℃-128℃). The large range of melting point is because of several reasons:

a. The crystals were not completely dried thus the range of melting point greatly increased.

[Improvement] More time should be provided for the drying of the crystals.

b. Crystals collected form different parts of the filter paper have different melting points. As the distance between the Bunsen burner and crystals varies, the dryness of crystals varies also.

[Improvement] We should only be collected crystals within a certain part of the filter paper. If impossible, try to collected crystals around a circular path.

c. The sample was being heated too fast that the thermometer is not sensitive enough to show the change of temperature of inside the boiling tube on time.

[Improvement] A heating rate of 1 to 2 degrees per minute is will give good results than five degrees per minute. If a compound has a high melting point, it can take a long time to reach it at 1 or 2 degrees per minute. It is advisable to have extra samples prepared ahead of time. Run the first sample at a high rate of heating to get an approximate mp range. Then repeat the procedure but slow down the rate of heating as you approach the expected melting point.

d. The sample was not firmly packed in the bottom of the tube that efficient heat transfer could not be insured.

[Improvement] Pack the sample in the bottom of the melting-point tube by tapping the closed end of the tube vertically against the table repeatedly.

2. Also, there are only one melting point determination test done that the data collected may be not precise enough, as there is no average result can be taken.

[Improvement] Increase the efficiency in carrying out the experiment in order to get more sets of data. This can be done by having division of labors and improving the technical skills in handling the experiments.

Discussion

1. Identification of the carbonyl compound as an aldehyde and ketone

In this experiment, we are given with the unknown compound, which is a ketone. But when we a given an unknown carbonyl compound, how can we identify whether the compound is an aldeyde or ketone? It can be done by following test:

Tollens test

The Tollens' reagent is mainly made up of diamminesilver(I) complex $[Ag(NH_3)_2]^+$, which is an oxidizing agent, reduced itself to silver metal, forming a "silver mirror" in a clean glass reaction vessel. This feature is used as a test for aldehydes, which are oxidized to carboxylic acids.

When adding the aldehyde or ketone to Tollens' reagent, put the test tube in a warm water bath. If the reactant under test is an aldehyde, Tollens' test results in a silver mirror. If the reactant is a ketone, it will not react because a ketone cannot be oxidized easily.

Simplified equation:

$$RCHO \text{ — } [Ag(NH_3)_2]^+, OH^-, H_2O, \text{warm} \rightarrow Ag(s) + RCOO\text{-}(aq)$$

a “silver mirror”

Fehling’s test

Fehling’s reagent is mainly made up of $Cu^{2+}(aq)$ complex. In the test, aldehyde is oxidized to acid and red precipitate (Cu_2O) formed. Ketones and aromatic aldehydes do not respond to the Fehling test.

When adding the aldehyde or ketone to Fehling' reagent, put the test tube in a warm water bath. If the reactant under test is an aldehyde, Fehling's test results in giving out red precipitate. If the reactant is a ketone, it will not react because a ketone cannot be oxidized easily.

Simplified equation:

$$RCHO \text{ — } CuSO_4, NaOH, \text{sodium potassium tartrate, warm} \rightarrow RCOO^- + Cu_2O(s)$$

Red precipitate formed

By using either Tollen test or Fehling’ test, we can distinguish whether the unknown

carbonyl is an aldehudye or ketone.

2. Mixed melting point determination.

Apart from the identification of combonyl compound by finding out the melting point of the purified sample of 2,4-dinitrophenylhydrazonde and comparing the melging point with the data book, but also using mixed melting point determination.

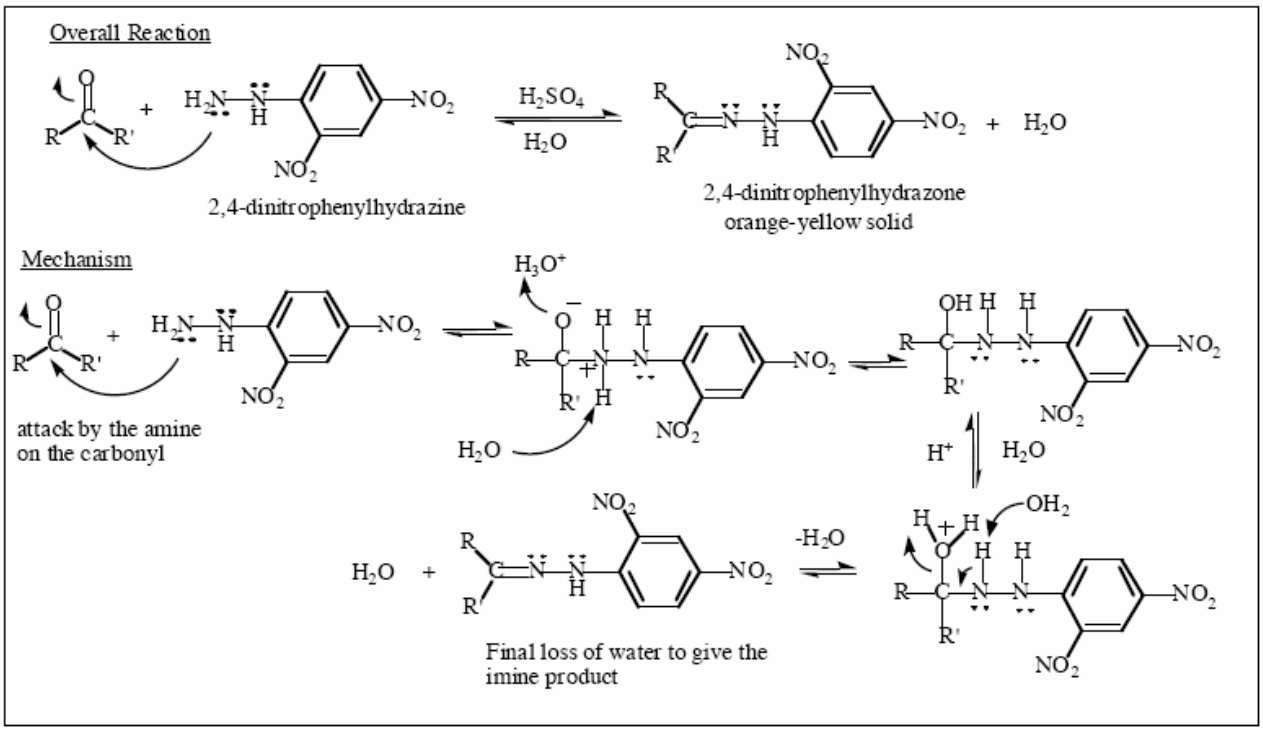
Such determination does not require the use of data book, but a various of knowm derivative of carbonyl compound.

Every pure substance has its fixed melting point. The presence of small amount of inmpuritiier lowers the melting group. Mixed melting point determination is used of identify a compound by adding small amount of a known compound with the sample for test. If the two substances are identical the melting point should be the same as that of either sample. If the two substances are not identical, then the melting point will be depressed.

3. Further about addition-elimination

In the experiment, the unknown ketone and 2,4 dinitrophenylhydrazine undergoes addition-elimination reactions. Addition-elimination reaction is reactions between aldehydes or ketones and derivatives of ammonia. The products of the reaction are alkanal or alkanone hydrazone. As water is give out in the reaction, this type of reaction can be regard as condensation also.

Take reaction between carbonyl compounds and 2,4 dinitrophenylhydrazine as an example:



Reference

1. AUS-e-TUTE
   http://www.ausetute.com.au/index.html
2. Melting Point Tips And Guidelines
   http://www.csi.edu/ip/physci/faculty/rex/mptips.htm
3. Wikipedia
   http://en.wikipedia.org/wiki/Main_Page