

Melting point and recrystallization



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Recrystallization was done to remove impurities from the sample. The percent recovery of benzoic acid during recrystallization is 23.02%. The difference between the pure and impure samples was observed by comparison of melting points. It was found that impure sample had a lower and wider melting point range of 120.1-122.2 (C). The pure sample melting point range was 121.3-122.5 (C). These ranges helped determine purity by comparing the known melting point of pure benzoic acid.

Introduction Most of the organic substances recovered from organic reactions are impure and require purification to obtain the desired pure product. The extracted benzoic acid still had impurities which can be removed through the process of recrystallization. Recrystallization is a purification technique that relies on the differing solubility of compounds within a mixture separating to form a pure crystalline solid of the desired product. Often the desired compound is present in a larger quantity within the solution.

Therefore, a pure sample of this compound can be crystallized from the solution while leaving the impurities dissolved within the solvent. Recrystallization is highly dependent upon the solubility of the two mixed compounds. Solubility is the property of how well a solute dissolves in a solvent. Solubility increases with an increase in energy within the system. This is due to the increased kinetic energy of the molecules leading to more collisions of the solvent with the solute. This process is called dissociation since the molecules of the solute become separated and surrounded by molecules of solvent.

Solvation occurs once the lattice has completely dissociated within the solution and no traces of solid compound remain. These steps can be explained by Gibb's Free Energy (ΔG) equation where a negative ΔG indicates a spontaneous reaction. The solvation of the lattice structure is a spontaneous reaction since the entropy and temperature increase within the system as the enthalpy becomes more negative (more exothermic). Hot water was used to dissolve the crude benzoic acid in these stages of solubility. For the recrystallization to occur properly a good solvent must be chosen.

The solute must be relatively insoluble in the solvent at room temperature but much more soluble in the solvent at higher temperature. At the same time, impurities that are present must either be soluble in the solvent at room temperature or insoluble in the solvent at a high temperature. For example, if you wanted to purify a sample of Compound X which is contaminated by a small amount of Compound Y, an appropriate solvent would be one in which all of Compound Y dissolved at room temperature because the impurities will stay in solution and pass through filter paper, leaving only pure crystals behind.

Also appropriate would be a solvent in which the impurities are insoluble at a high temperature because they will remain solid in the boiling solvent and can then be filtered out. When purifying a substance with this method, the solubility of the solvent must be taken into careful consideration. It is necessary that a solvent is a poor solvent at room temperature and a very good solvent at high temperatures. As a result, polarity, the uneven distribution of electron density, must be taken into consideration. The

polarity of the solvent should relatively be the opposite of the compound being dissolved.

This creates a high temperature coefficient with the compound only being slightly soluble at room temperature and highly soluble at high temperatures. This allows the substance to later crystallize from the solution as it cools. The solvent also cannot be highly reactive with the solute. This will entirely defeat the purpose of dissolution since products will be created that are not the intended crystals. Additionally, the solvent should be able to dissolve either the impurity or the product so the compounds can be separated through other methods.

The solvent also cannot have a boiling point higher than the melting point of the solute. If the solute melts prior to the boiling of the solvent, recrystallization will not be able to occur. For example, if you wanted to purify a sample of Compound X which is contaminated by a small amount of Compound Y, an appropriate solvent would be one in which all of Compound Y dissolved at room temperature because the impurities will stay in solution and pass through filter paper, leaving only pure crystals behind. Also appropriate would be a solvent in which the impurities are insoluble at a high temperature because they will remain solid in the boiling solvent and can then be filtered out. Finally, the solvent should be volatile enough as to evaporate from the surface of the compound and be of low financial cost. Impurities can be removed by adding charcoal to the solution and hot gravity filtration. Adding charcoal provides a charged surface that is able to absorb impurities. The impurities that were absorbed by the charcoal were trapped in the filter paper during hot gravity filtration.

Hot gravity filtration is the process by which the solution is filtered while on top of a heat source, such as a steam bath. This will remove any insoluble impurities (like charcoal used to remove the methyl orange) from the solution while maintaining the high temperature and high solubility coefficient of the solution. This prevents the solid from crystallizing from the solution while within the filtering apparatus. Fluted filter paper is also utilized to minimize the surface contact with the cooler funnel and to maximize the surface area over which the solution is filtered.

The recrystallization process is entropically disfavored because the overall order of the system increases with the formation of a solid product. This process involves an increase in temperature within the system, which thereby causes (ΔG) to become negative. The increase in temperature allows the process to occur spontaneously. Nucleation is the start of the crystallization process where one crystal precipitates out of the solution first and thereby provides a lattice structure upon which molecules of the same compound can connect.

This is all encompassed by the crystal lattice theory. The crystal lattice theory states that a growing solid will select similar molecules into its growing lattice. Sometimes, this does not happen spontaneously due to the solution not being sufficiently supersaturated. This is treated by "seeding" the solution with a small crystal of pure compound. This acts as a starting point for nucleation to occur. Additionally, the glass of the flask can be scratched with a glass rod. This provides a sharp edge upon which developing crystals can adhere and begin the nucleation process.

Once nucleation occurs, the solution must be cooled slowly. This allows the development of crystals to exclude any impurities from the lattice and create a pure compound. The melting point of a substance is an intensive property of a compound. This kind of property does not depend upon the amount of substance present (i. e. molecular weight, density), unlike an extensive property (i. e. mass, volume dependent upon amount present). Melting is defined as a phase change in which a solid substance becomes a liquid substance without changing its identity or chemical formula.

The melting point of a substance is defined as a range between the lower and upper melting points. The lower melting point is the temperature at which the substance's structure becomes obviously distorted. The upper melting point is the point at which the substance has become a liquid. This phase change can be observed and measured in a Melt Temp device. The melting point range therefore is the range between the lower and upper melting points observed. Pure substances tend to have a smaller melting point range at a higher temperature than impure substances. Table 1: Reagent Table (2)

Chemical Name	Chemical Formula	Molar Mass (g/mol)	Density (g/ml)	BP/MP (C)	Amount Used (mL)	Concentration (mol/L)
Benzoic Acid	C ₆ H ₅ COOH	122. 12	1. 27	249. 2/122. 41	- -	Methyl Orange
	C ₁₄ H ₁₄ N ₃ NaO ₃ S	327. 33	1. 28	-/> 300	- -	Charcoal
	H ₂ O	18. 0153	1	100/0	- -	Water

Experimental Prior to beginning the recrystallization experiment, the dry benzoic acid and watch glass were weighed and small portion of the crude benzoic acid was set aside for analysis in the melting point experiment. The remaining benzoic acid was

placed in a 250mL Erlenmeyer flask. 00mL of water in a 250mL boiling flask containing a few boiling stones was brought to a boil using a heating mantle. The heating mantle was situated on top of a raised lab jack and the boiling flask was clamped to monkey bars. Gloves were used whenever handling the heating mantle or boiling flask. Minimum amount of boiling water was slowly added to the crude crystals. The solution was kept at or near boiling point. A very small amount activated carbon (charcoal) was added to the solution. After this, hot gravity filtration was performed over a steam bath. The fluted filter paper was wet with some boiling water prior to filtration.

The solution was then carefully poured into the funnel. The filtrate was then removed from the steam bath and allowed to cool slowly at room temperature. These crystals were then collected by vacuum filtration, placed on a watch glass, and allowed to dry over a one week period. Prior to conducting the melting point experiment, the purified crystals were massed. The melting point experiment was performed by loading two capillary tubes: one with the impure benzoic acid set aside prior to the recrystallization experiment and the other with the pure benzoic acid obtained by recrystallization.

The samples were obtained by tapping the open end of the capillary tube on top of the desired compound. The tube was then repeatedly bounced (open end up) inside of an inverted funnel. The two tubes containing crude and pure crystals were then placed inside of the Melt Temp device. The heat was increased and the tubes were observed through a viewing port outside of the apparatus. The melting point range was recorded. Results Table 2: Data and Calculations Data| Mass (g)| Crude Benzoic Acid| 4. 04| Watch glass| 40. 23|

Watch glass with pure benzoic acid crystals| 41. 6| Pure benzoic acid crystals| . 93| Percent recovery of benzoic acid | 23. 02% | gBenzoic AcidgCrude Mix ? 100 =% Recovery of Benzoic Acid Figure 1: % Recovery

Sample Type	Lower Melting Point (°C)	Upper Melting Point (°C)	Melting Point Range (°C)
Crude Sample	120. 1	122. 2	120. 1-122. 2
Pure Sample	121. 3	122. 5	121. 3-122. 5

Observations * Benzoic Acid dissolved in hot water * Solution was a pink color * Addition of charcoal caused solution to turn a cloudy grayish color * Crystals formed early in filter paper Solution would no longer filter through paper properly * New filter paper resumed proper filtering * Filtrate was clear * Web-like white crystals began to form immediately after removed from the heat * Crude crystals started melting * Crude crystals appeared creamy white and distorted * Pure crystals lost their defined shape at lower melting point * Both crystals were liquefied Discussion As a slightly polar compound, benzoic acid was able to dissolve in water at a high temperature since the overall kinetic energy of the system increased to allow more collisions to occur within the solution.

Since it is only slightly soluble in water due to water's high temperature coefficient, the benzoic acid solution was consistently kept over a steam bath to prevent it from crystallizing out of the solution early. The pink color of the solution indicated that methyl orange was still present within the dried crude benzoic acid. Methyl orange is an acid indicator that turns pink in a solution of specific pH. The pink color of the solution was indicative of the fact that the benzoic acid solution was slightly acidic.

Charcoal (activated carbon) was added to this solution to remove this coloration. This was made possible by the process of adsorption in which the large nonpolar portions of the methyl orange molecule adhered to the large surface area of the nonpolar carbon molecules. Only a small amount of charcoal was needed to be used in order to remove the coloring of the solution. In this experiment, however, too much charcoal was added and therefore caused the solution to turn a cloudy gray color. This charcoal overload therefore created other problems later in the experiment.

Hot gravity filtration was carried out to remove any insoluble impurities still remaining in the solution. The temperature was kept high to keep the solubility coefficient increased so as to prevent premature crystallization from the solution. Fluted filter paper maximized the surface area over which the solution could be filtered and also minimized the contact the solution would have with the cooler funnel. This temperature difference could have also caused premature crystallization within the filter paper. The percent recovery for the benzoic acid was 23.02%.

This low recovery rate was primarily due to the fact of premature crystallization occurring within the filter paper during the hot filtration portion of the experiment. This was caused by the over-abundance of charcoal present within the solution. The charcoal provided a surface upon which the crystals could form as the solution became briefly highly concentrated within the filter paper. As a result, a significant amount of product was lost. The filter paper also had to be changed because the formation of crystals prevented the rest of the solution from being properly filtered into the flask.

This caused a significant loss in solution also containing the benzoic acid that could have crystallized within the flask. The exact amount of product lost was unable to be determined due to the presence of charcoal within the crystals, saturation of the filter paper, and the crystal's adherence to the filter paper. However, the weight of the filter paper, crystals, and other impurities was 7.63g, of which a substantial amount of the weight could be contributed to the saturated filter paper. Another source of error could have been that not all benzoic acid within the filtrate crystallized from the solution.

Even though the solution was cooled slowly and benzoic acid is only slightly soluble in water, the solubility of the benzoic acid still was enough to allow it to stay within the solution. Another source of error could be from a Eutectic reaction. This reaction forms a eutectic mixture, which is a mixture that behaves like a compound. The behavior of this mixture could skew conclusions by providing a sharp melting range, similar to pure compounds. Additionally, not enough boiling water could have been added which would prevent some benzoic acid from completely dissolving within the solution.

This remaining crystalline benzoic acid would then be lost during the filtration process. The filtrate that made it into the flask was clear and began forming crystals almost immediately after being removed from the heat. This was due to the fact that as temperature decreased, the solubility of the solvent decreased, creating a supersaturated solution. This therefore forced the less soluble component of the mixture (benzoic acid) to crystallize from the solution. The solution was cooled slowly to prevent any impurities from

adhering to the benzoic acid crystal lattice and thereby affecting the purity of the compound.

Once a few crystals formed, others began to form the crystal lattice with them in a process called nucleation. Melting points are a range between the lower melting point (where the crystals first become distorted) and the higher melting point (where the crystals are completely liquefied) of a substance. This range was identified using the Melt Temp apparatus which magnified the view of the sample capillary tubes to allow easy observation of the state of the crystals in relation to the temperature of the device, which was measured using a thermometer.

The melting point range for the crude benzoic acid was $120.1^{\circ}\text{C} - 122.2^{\circ}\text{C}$, and the range for the pure crystals was $121.3^{\circ}\text{C} - 122.5^{\circ}\text{C}$. The range for the crude benzoic acid was slightly larger at a 2.1°C difference because of the presence of impurities can decrease the lower range of the melting point and increase the upper range of the melting point. Both values for the crude and pure benzoic acid fell very close to the literature value of 122.38°C which therefore indicates that they were relatively pure.

However, the crude benzoic acid's range of 2.1°C was larger than the pure benzoic acid's range of 1.2°C . The fact that the crude benzoic acid range is wider than the pure range indicates that there are impurities within the crystals. A possible source of error for this portion of the experiment could have been human error in the interpretation of the thermometer or the delayed reaction between witnessing the lower and upper melting points and looking at the thermometer to record the temperature.

References

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