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Physical Pharmacy

Melting of solids

Freezing of Liquids

Contents

In this lecture you will learn:

- Melting/Freezing point
- Latent heat of Fusion
- Relationship between pressure and melting/freezing point
- Factors affecting melting point
- How to measure melting point (supplementary material)

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Melting point

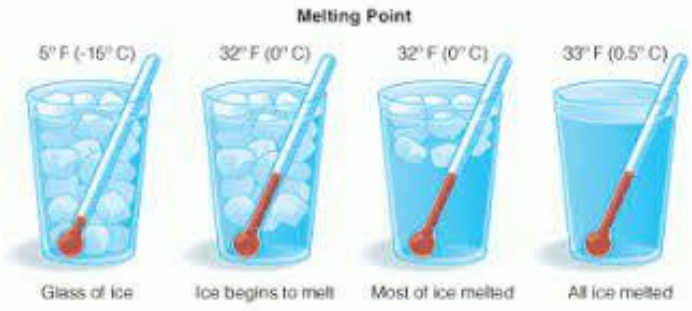
- **Melting point** is the temperature at which a solid turns into a liquid.

- In theory, the melting point of a solid is the same as the freezing point of the liquid – the temperature at which a liquid turns into a solid.

- **For example:**

a. Ice is a solid form of water that melts at **(0 °C)** and changes to its liquid form.

b. Water freezes at the same temperature **(0 °C)** and turns into ice.



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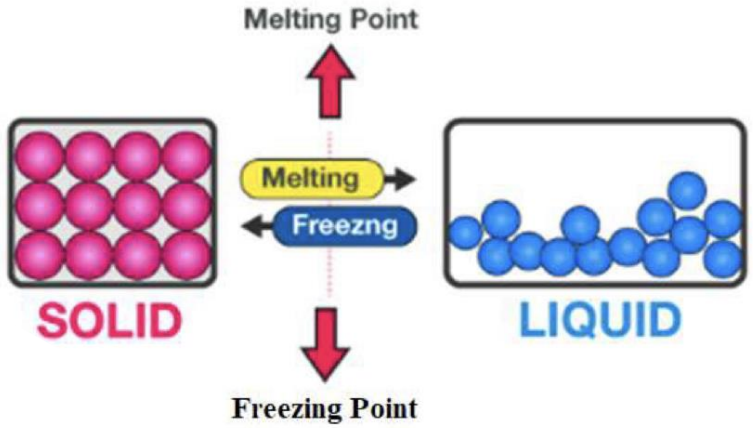
Melting point

- The normal freezing point or melting point of a pure crystalline solid is defined as “the temperature at which the pure liquid and solid exist in equilibrium”at specific external pressure of **1 atm**

- The melting point of a solid and the freezing point of a liquid are intrinsic properties of matter that can be used to identify it.



- **Determination of melting point is important in:**

a. Identification of solids and characterization of new compounds.
b. Indicator of compounds purity.

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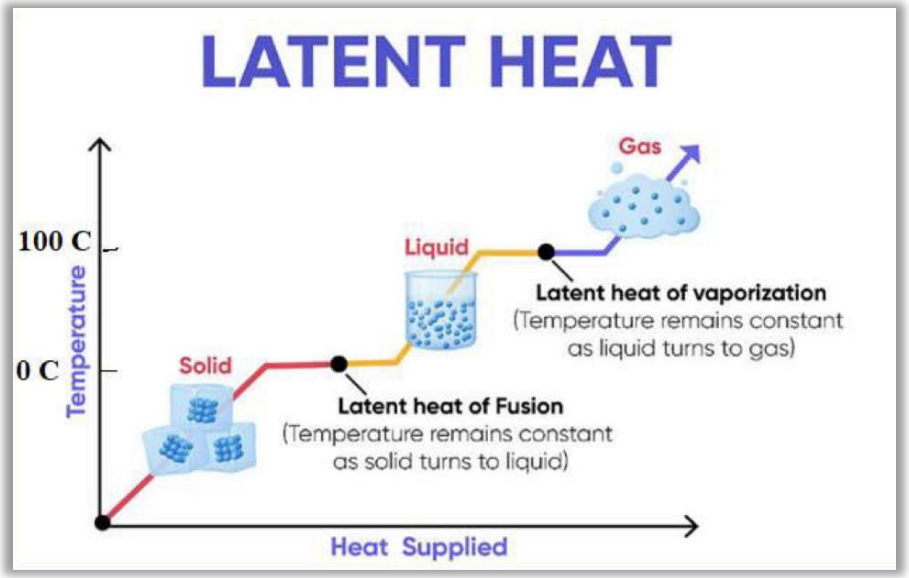
Melting of solids /Freezing of Liquids

Latent heat of fusion

- The process of melting requires absorption of specific amounts of heat known as latent heat of fusion.
- The heat of fusion may be considered as the heat required to increase the interatomic or intermolecular distances in crystals, thus allowing melting (increased molecular motion) to occur.



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Melting of solids /Freezing of Liquids

Latent heat of fusion

- It is defined as “the heat (energy) absorbed when 1 g of a solid melts”.
- **The value for water is 80 cal/g at 0°C**
- **The value for ethanol is 25 cal/g -120°C**
- When a solid such as ice is heated, the temperature changes as shown in the graph.
- During the conversion of solid to liquid, at the melting point, the temperature remains constant.
- This is because the heat is used by the molecules as energy in the conversion.

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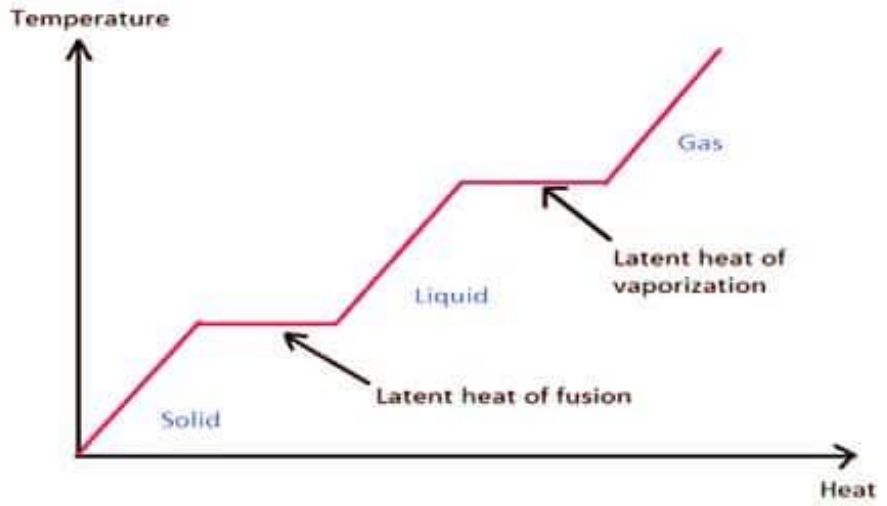
Melting of solids /Freezing of Liquids

Latent heat of fusion

- The temperature begins to rise only after all the ice (solid phase) has melted to water (changed to liquid phase).

- The same concept applies during the conversion of liquid to gas after reaching the boiling point



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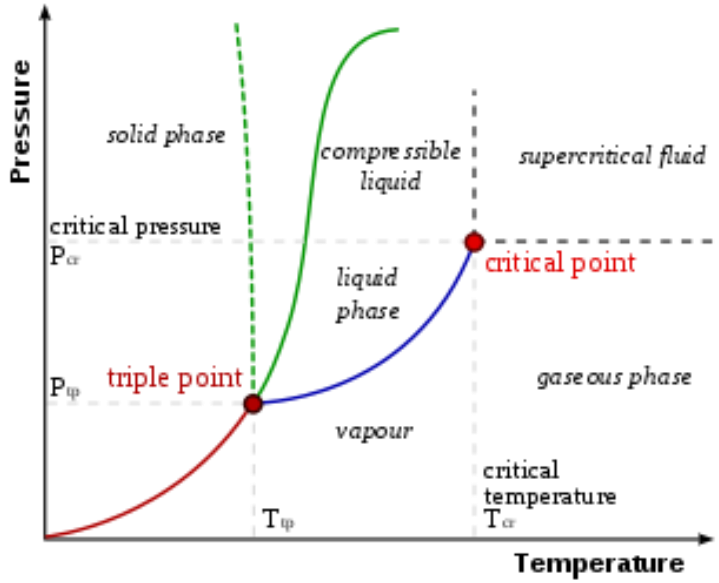
Melting of solids /Freezing of Liquids

Relationship between pressure and melting/freezing point

- For most substances, **melting/freezing point rises,** though only very slightly, with **increased pressure.**
- **This applies when the solid is more dense than the liquid.**
- Changes of the freezing or melting point with pressure can be obtained by using a form of the Clapeyron equation, written as:



$$\frac{\Delta T}{\Delta P} = T\frac{V1 - V_S}{\Delta Hf}$$

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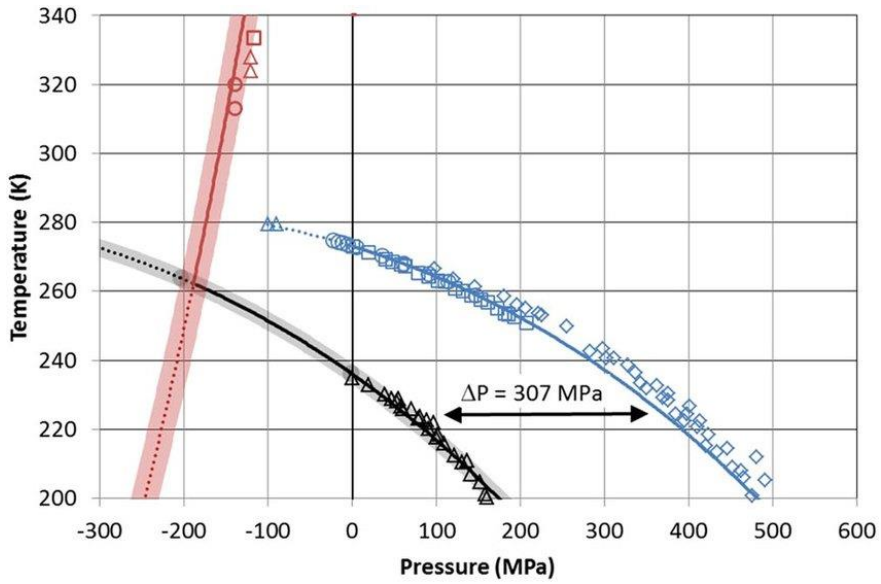
Melting of solids /Freezing of Liquids

Relationship between pressure and melting/freezing point

- where Vl and Vs are the molar volumes of the liquid and solid, respectively.
- Molar volume (volume in units of CM^3 /mole) is computed by dividing the gram molecular weight by the density of the compound.
- **ΔT** is the change of melting point brought about by a pressure change of **ΔP**.
- When ΔT/ΔP is positive, it means that the melting/freezing point increases with increasing pressure.



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Melting of solids /Freezing of Liquids

Relationship between pressure and melting/freezing point

- ΔHf is the Molar heat of fusion : it is the amount of heat absorbed when **1 mole** of the solid changes into **1 mole** of liquid.
- The heat of fusion may be considered as the heat required to increase the interatomic or intermolecular distances in crystals, thus allowing melting (increased molecular motion) to occur.
- When the solid is less dense than the liquid (liquid is more dense than the solid), the melting point/freezing point will decrease with increasing pressure.
- Such behavior is observed with water: it is one of the very rare substances that expands upon freezing (which is why ice floats)

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Melting of solids /Freezing of Liquids

Relationship between pressure and melting/freezing point

- **So:**Water has a larger molar volume in the solid state than in the liquid state (Vs > Vl) at the melting point.
- **(0.9168 g/CM^3 as compared with 0.9988 g/CM^3 for water at 0°C)**
- Therefore, **ΔT/ΔP** is negative, signifying that the melting/freezing point is lowered by an increase in pressure.

$$\frac{\Delta T}{\Delta P} = T\frac{V1 - V_S}{\Delta Hf}$$

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Melting of solids /Freezing of Liquids

Relationship between pressure and melting/freezing point

- By increasing the pressure, water molecules are prevented from proper arrangement and formation of a crystalline solid phase, so water cannot freeze at the **freezing point at 0° C**.

- **Practical application of the concept:**The lowering of the melting point with increasing pressure is taken advantage of in **ice-skating**:

- The pressure of the skate lowers the melting point and thus causes the ice to melt below the skate.

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Melting of solids /Freezing of Liquids

Relationship between pressure and melting/freezing point

- This thin layer of liquid provides lubricating action and allows the skate to glide over the hard surface.

- Of course, the friction of the skate also contributes greatly to the melting and lubricating action.

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Factors affecting on freezing/melting point

Critical Thinking Questions:

- Which freezes faster:
  a. Water or milk ?
  b. Water or salt water?
  c. Water or Soda ?
  d. Pure water or ocean water ?
- Why do we add salt during defrosting ?
- What happens when salt is added to ice cream?
- Does salt make ice last ?
- How does salt clear snowfall from roads ?

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Factors affecting on freezing/melting point

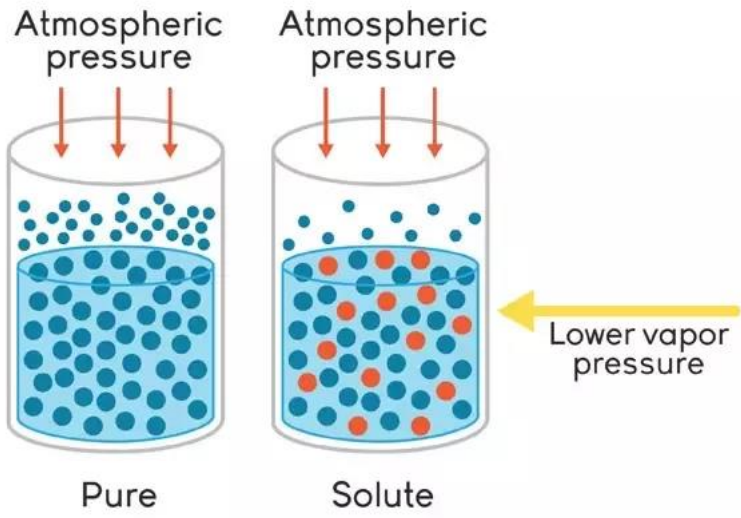
Factors that affect on melting point

1. Impurities:

- Pure solids have narrow range of melting point, usually only 1 to 2 °C, known as a **“sharp melting point”.**

- Thus: a sharp melting point is often evidence that a sample is fairly pure.

- Impure solids have a wide range of melting point (melting point range **(> 5 ° C**).



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Factors affecting on freezing/melting point

Factors that affect on melting point

- The presence of impurities cause structural defects that make the intermolecular interactions between the molecules easier to overcome, therefore they will lower the melting temperature **“melting point depression”** and make the solid melt over a wide range.

Type of matter	Freezing point
Pure water	0°C
Salt water	-21 °C
Sugar water	-39 °C

Which one of these freezes faster ?

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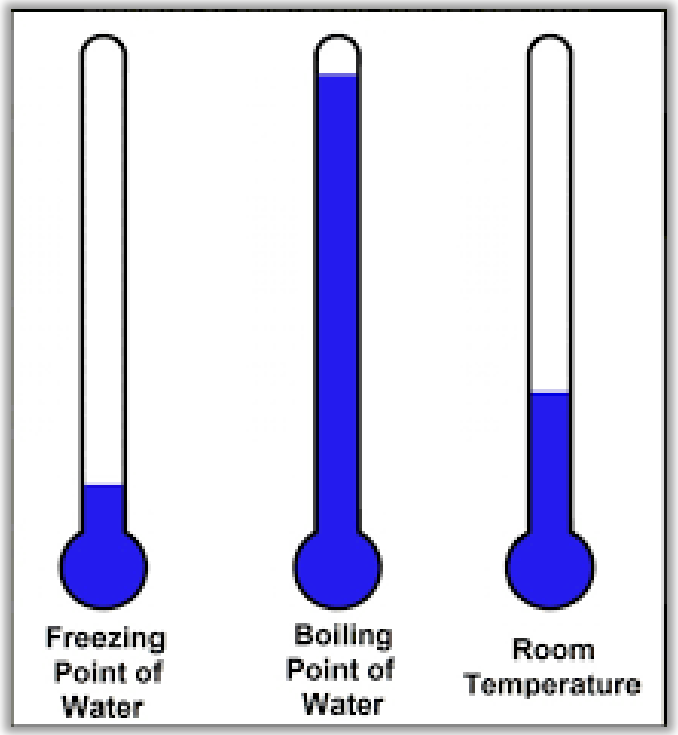
Factors affecting on freezing/melting point

Factors that affect on melting point

- The exact freezing point is determined by the quantity of solute particles dissolved in the solvent.
- The more solute particles there are in the water, the greater the freezing point depression of the solution.



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Factors affecting on freezing/melting point

Factors that affect on melting point

- Why is it that in hot countries we put salt on ice in the ice cream makers to keep the ice from melting, while in cold countries we put salt on ice to melt it? “

- In both cases, the answer is based on the fact that adding salt to an ice water mixture in equilibrium, lowers the freezing point (or melting point) of the equilibrium

- The depression in freezing point depends upon the concentration of salt added

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Factors affecting on freezing/melting point

Factors that affect on melting point

- When you add just ice to the ice cream maker, the ice absorbs heat from the surrounding and starts melting.
- At 0°C equilibrium is reached and the temperature cannot go any lower.
- This is not cold enough for making ice cream.
- When salt is added, there is lowering in freezing point and the equilibrium will be reached, and kept at the lower temperatures required so it’s easier to freeze the water (occurs at lower temperature) and make an ice cream.

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Factors affecting on freezing/melting point

Factors that affect on melting point

Factors affecting on freezing/melting point

Factors that affect on melting point

- If you sprinkle salt on ice, it will melt.
- The salt doesn’t actually “melt” the ice.
- Instead, it dissolves into thin layers of surface melt water on the sidewalks.
- Salt molecules prevents the melted water from packing and solidifying back into ice.
- It lowers freezing temperature of water so that the weather must get even colder before the sidewalks can freeze over again.
- However, there is a lower temperature limit for this process.

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Factors affecting on freezing/melting point

Factors that affect on melting point

- If the temperature is cold enough, the salt water can freeze. In practice, ordinary road salt isn't that effective below **-7 °C**.

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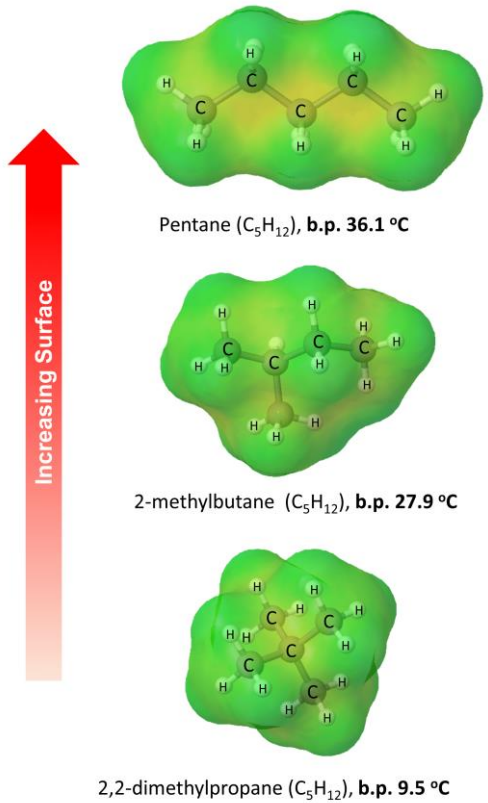
Factors affecting on freezing/melting point

Factors that affect on melting point

2. Intermolecular Forces:

- Melting requires the intermolecular forces that hold a solid together to be broken, thus the temperature a solid compound melts will depend on the structure and the nature of the intermolecular forces.

- A solid made up of particles having strong intermolecular bonds will have a high heat of fusion and a high melting point, whereas a solid that is bound together by weak forces generally has a low heat of fusion and a low melting point.



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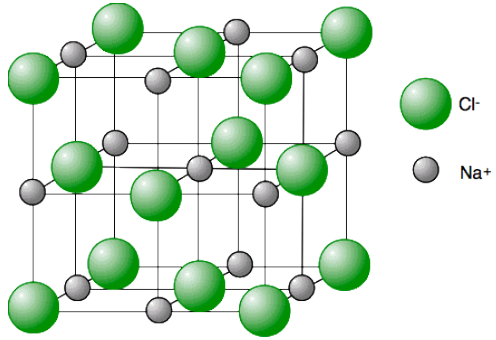
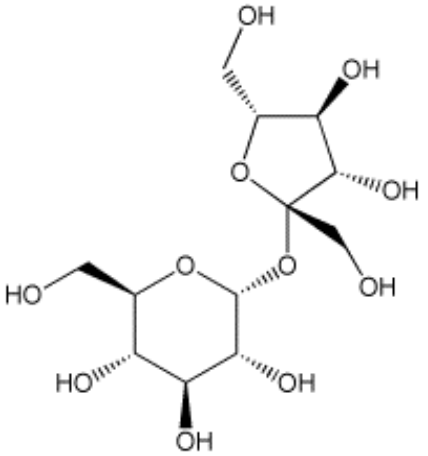
Factors affecting on freezing/melting point

Factors that affect on melting point

- **For example**: M.P of salt(**800.7 °C**)>M.P of sugar(**186°C**)



- **This is because:**Common salt (**NaCl**) is made up of strong ionic bonds and ion-ion interactions between the charged ions which are stronger than intermolecular **H** bonds of sugar (sucrose) molecules



- If there is compound of **2 polymorphic** forms, polymorph A which is held by higher attractive forces than is polymorph B: it is clear that more heat will be required to break down the attractive forces in polymorph A, and thus its melting temperature will be higher than that of polymorph B.

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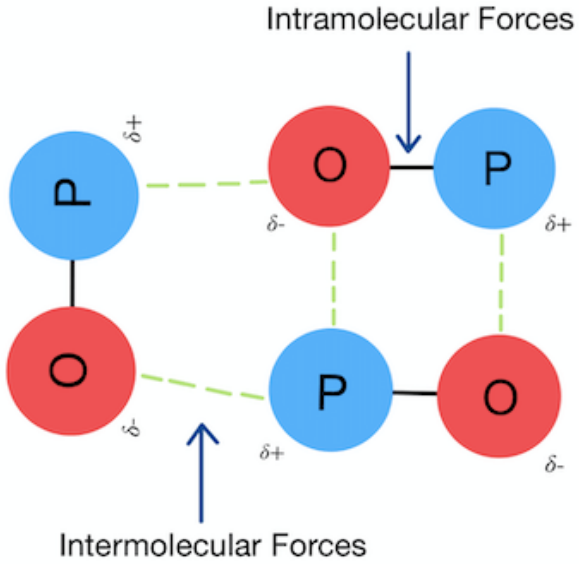
Factors affecting on freezing/melting point

Factors that affect on melting point

3. Molecular weight

- Increasing the number of carbons of normal saturated hydrocarbons (i.e., increasing the molecular weight) will increase the melting points (as well as the boiling).

- **This is due to greater van der Waals forces between molecules.**



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Factors affecting on freezing/melting point

Factors that affect on melting point

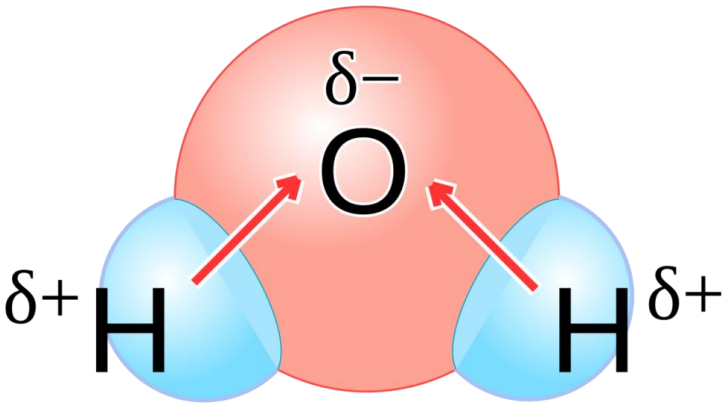
Name	Formula	Melting Point / °C	Boiling Point / °C
Methane	CH4	-182	-164
Ethane	CH3CH3	-183	-88
Propane	CH3 CH 2 CH3	-190	-42
Butane	CH3(CH2)2CH3	-138	0
Pentane	CH3(CH2)3CH3	-130	36
Hexane	CH3(CH2)4CH3	-95	69
Heptane	CH3(CH2)5CH3	-90	98
Octane	CH3(CH2)6CH3	-57	126
Nonane	CH3(CH2)7CH3	-51	151
Decane	CH3(CH2)8CH3	-30	174

Factors affecting on freezing/melting point

Factors that affect on melting point

4. Polarity:

- The melting points of polar substances are higher than the melting points of non polar substances with similar sizes.
- Thus: the presence of polarity, especially hydrogen bonding, usually leads to a higher melting point in organic compounds.
- Ionic crystals exhibit high melting (as well as boiling) points relative to those with weaker, **non- ionic bonds.**



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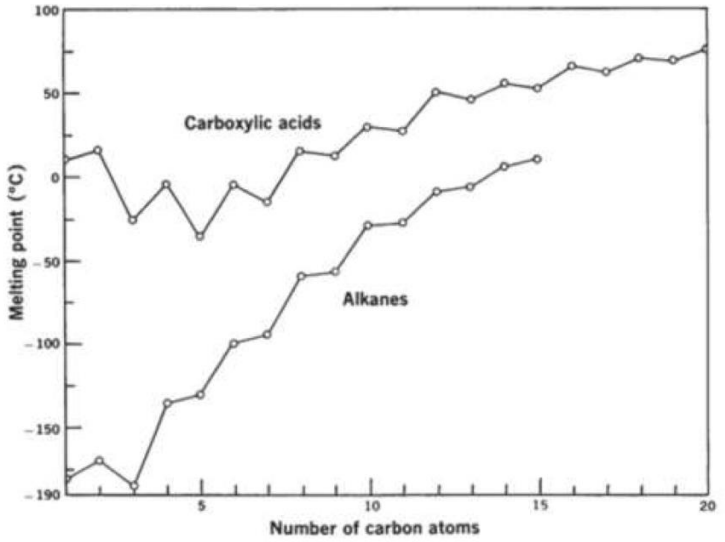
Factors affecting on freezing/melting point

Factors that affect on melting point

5. Molecular shape:

- The melting points of the alkanes or normal carboxylic acids with an even number of carbon atoms are higher than those with an odd number of carbon atoms.
- This is because alkanes with an odd number of carbon atoms are packed in the crystal less efficiently.



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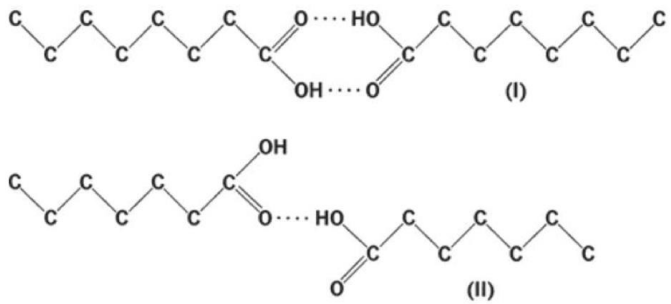
Factors affecting on freezing/melting point

Factors that affect on melting point

- Fatty acids crystallize in molecular chains as shown:



- The even-numbered carbon acids are arranged in the crystal as seen in the more symmetric structure I, whereas the odd- numbered acids are arranged according to **structure II.**

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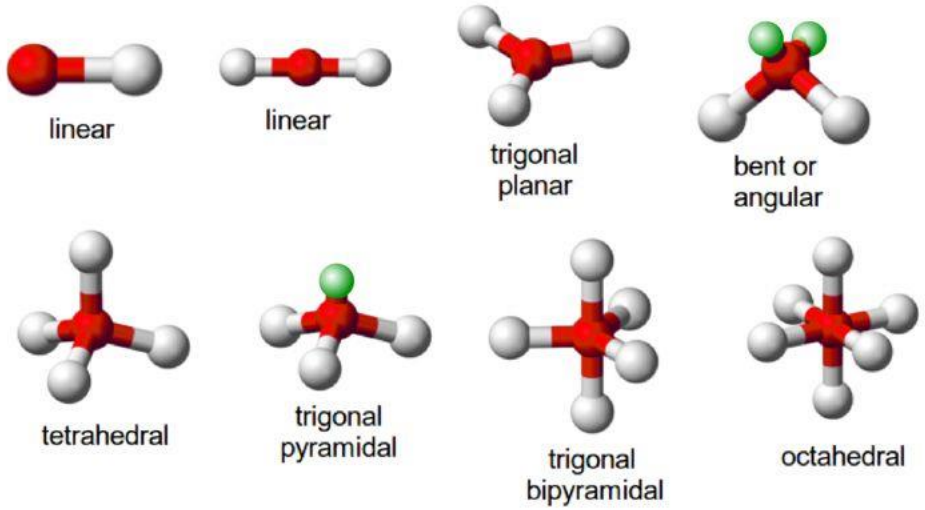
Factors affecting on freezing/melting point

Factors that affect on melting point

- The carboxyl groups are joined at two points in the even-carbon compound; hence, the crystal lattice is more stable and the melting point is higher.



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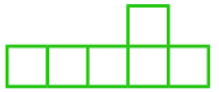
Factors affecting on freezing/melting point

Factors that affect on melting point

6. Molecular branching

- As we increase branching, we’re increasing melting point (but decrease the boiling point, **Why?**
- **Regarding the melting point: It's also about surface area.**
- Going from "branched" to "highly branched" makes a molecule more compact and sphere-like.

easy



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$CH_3CH_2CH_2CH_2CH_3$

melting point: –95°C

$CH_3CH(CH_3)CH_2CH_3$

melting point: –154°C

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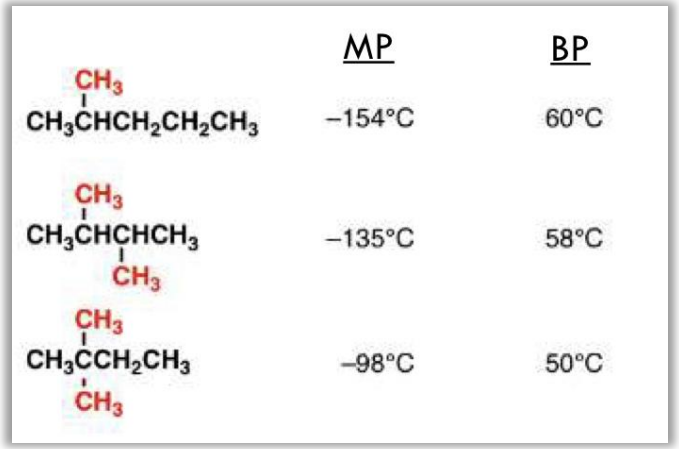
Factors affecting on freezing/melting point

Factors that affect on melting point

- As the surface area of the molecule decreases (remember that spheres have the lowest surface area/volume ratio of any shape) they will become more compact and thus easier to pack.

- **This explains the higher melting point phenomenon.**

Increasing branching



within the branched series, increased symmetry leads to higher melting point, lower boiling point

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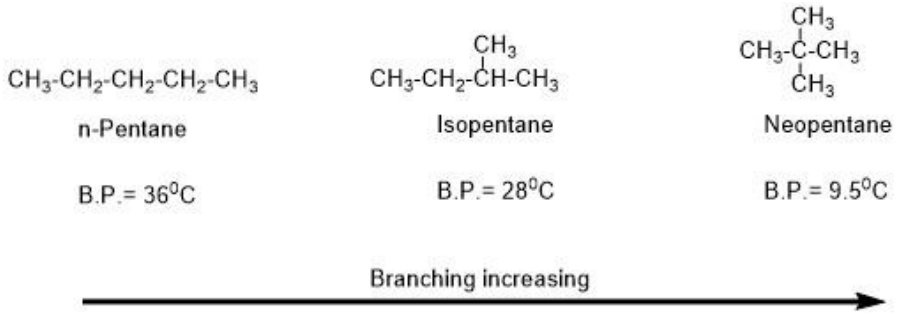
Factors affecting on freezing/melting point

Factors that affect on melting point

- What about boiling point?
- Boiling point is related to the forces between molecules, which in the case of hydrocarbons is Van Der Waals interactions
- As surface area of the molecule decreases, we are going to decrease intermolecular Van Der Waals interaction and therefore decrease boiling point.



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How to measure a melting point?

- A small amount of the finely powdered material is placed into a capillary tube that is sealed at one end.
- The capillary tube is inserted into a melting point apparatus in which the temperature can be measured when heated.
- To obtain an accurate melting point it is necessary to heat SLOWLY, proceeding through the melting point at no faster than 1°C per minute, The melting is visually observed through a lens in the apparatus.

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How to measure a melting point?

- Two temperatures are recorded: the temperature at which the substance begins to liquefy and the temperature at which it becomes completely liquefied, The observed melting-point range is the interval between these two temperatures.

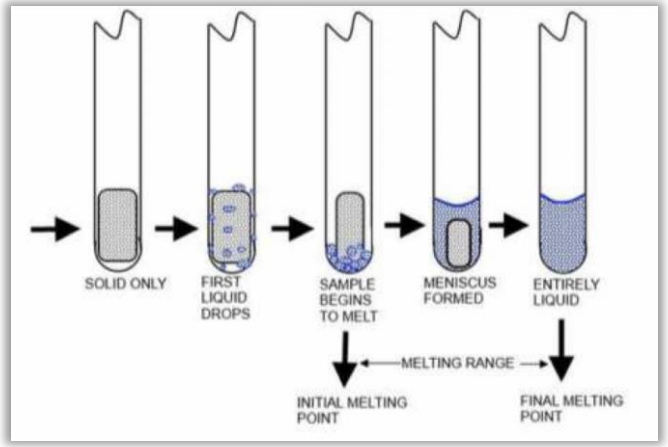
- **The observed melting-point range can be influenced by:**

a. The purity of the material but also by the size of the crystals.

b. The amount of material.

c. The density of its packing in the tube.

d. The rate of heating.



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How to measure a melting point?

Melting point apparatus

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Thank You !

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