

Chemical Engineering 10.420/ 10.520
Solutions to Problem Set #1

1. The free radical chlorination of methane produces a variety of products: carbon tetrachloride (CCl_4), chloroform (CHCl_3), dichloromethane (CH_2Cl_2), chloromethane (CH_3Cl), and unreacted methane (CH_4).

- (a) If the mixture were fractionally distilled, predict the order that the compounds would be collected as distillates. Explain your reasoning in one sentence.

The order of the distillates would be CH_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 , and CCl_4 . Cl is larger than H and allows greater van der Waals contact.

- (b) As solvents, which compounds are the most polar? The most nonpolar?

The most polar solvent is CH_2Cl_2 because it has the largest aggregate dipole. The most nonpolar solvent is CCl_4 , where all dipoles cancel.

2. Methanol exists in equilibrium with dimethyl ether and water.

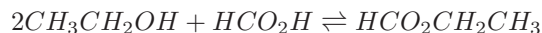


Using only your chemical intuition, explain which of the three compounds is likely to have the highest and lowest boiling points.

Water has the highest boiling point because it has the greatest degree of hydrogen bonding and is the most polar, allowing for high intermolecular force levels.

CH_3OCH_3 has the lowest boiling point because the intermolecular forces are primarily due to weak van der Waals bonds with no hydrogen bonding component as in the other molecules.

3. Ethanol and formic acid exist in equilibrium with ethyl formate.



Using only your chemical intuition, explain which of the three compounds is likely to have the highest and lowest boiling points.

Formic acid has the highest boiling point because its strong hydrogen bonding potential enables the formation of carboxylic acid dimers in both the liquid and gas phase, which stabilizes the molecule.

Ethyl formate has the lowest boiling point because it has no hydrogen bonding component and only has weaker van der Waals force interactions.

4. (a) Hydrogen sulfide is a gas at room temperature, while water is a liquid. Provide a one sentence explanation.

The smaller size of the oxygen atom allows for better orbital overlap between the hydrogen and oxygen, than with the sulfur and hydrogen.

- (b) Ammonia is a gas at room temperature, while water is a liquid. Provide a one sentence explanation.

The O-H bonds are more acidic than the N-H bonds, resulting in stronger hydrogen bonds for water and therefore a higher boiling point.

5. Acetone, butane, and nitromethane have similar molecular weights (MW = 58–61) but boiling points that differ by $> 100^\circ\text{C}$. Using your chemical intuition, assign the highest and lowest boiling compounds and provide a brief explanation.

Nitromethane has the highest boiling point because the NO_2 group has a very strong dipole that increases dipole-dipole interactions and raises the boiling point.

Butane has the lowest boiling point because it only forms van der Waals interactions, while acetone can also form dipole-dipole interactions.

6. Succinonitrile and malononitrile have boiling points that are ~ 200 °C higher than hexane and pentane, respectively.

- (a) Explain why these substitutions are responsible for the dramatic increases in boiling point.

The CN group has one of the highest dipole moments of any organic group, and the dipole-dipole interactions result in a dramatic stabilizing factor on the condensed phase.

In contrast with the above comparison, cyanogen has a boiling point that is > 20 °C lower than butane.

- (a) Provide an explanation for this difference that is compatible with your answer to part (a).

In cyanogen the dual CN group dipoles are oriented directly opposite one another in a linear molecule and thus provide no intermolecular dipole-dipole stabilization. The lower boiling point is due to reduced van der Waals contact as triple bonds are shorter than single bonds.