

1. Which species will experience greater ion-dipole forces in H_2O : Mg^{2+} or Na^+ ? Briefly explain your choice.

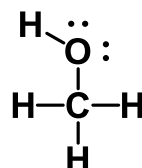
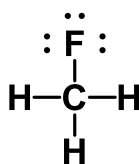
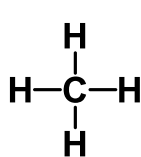
The ion-dipole energy is directly proportional to the charge of the ion and the dipole of the molecule, and inversely proportional to the distance between the ion and the molecule.

$$E \propto \frac{|z|\mu}{r^2}$$

The charge is higher for Mg^{2+} than Na^+ (2+ and 1+ respectively), and r is shorter for Mg^{2+} because it has a smaller ionic radius than Na^+ . Therefore, the greatest ion-dipole force is experienced between Mg^{2+} and H_2O .

2. Which type of intermolecular interactions need to be overcome to convert each of the following liquids to gases? Draw Lewis structures to support your answer.

a) CH_4 b) CH_3F c) CH_3OH



Methane (a) is non-polar therefore only London dispersion forces need to be overcome to boil methane. CH_3F (b) is polar, therefore London dispersion and dipole-dipole interactions need to be overcome when boiling fluoromethane. CH_3OH (c) is polar and has an H-O bond, therefore London dispersion and hydrogen bonding (a type of dipole-dipole interaction) needs to be overcome when boiling methanol.

3. The boiling points of the Group 14 and Group 15 hydrides (CH_4 , SiH_4 , GeH_4 , NH_3 , PH_3 , AsH_3) are given in the tables to the right. Provide a rationale for the observed trend of each group and explain why ammonia does not fit the trend.

Group 14 Hydride	Boiling Point ($^{\circ}\text{C}$)
Methane (CH_4)	-164
Silane (SiH_4)	-112
Germane (GeH_4)	-88

Group 15 Hydride	Boiling Point ($^{\circ}\text{C}$)
Ammonia (NH_3)	-33
Phosphine (PH_3)	-88
Arsine (AsH_3)	-63

Group 14 hydrides are non-polar and experience only London dispersion interactions, whose strength increases with increasing polarizability which in turn is proportional to the number of electrons (both core and valence). For this reason London dispersion interactions are strongest for germane and weakest for methane (silane's are in between). Stronger interactions produce higher boiling points which explains the observed trend of increasing values going down the group.

The Group 15 hydrides have the same number of electrons as their Group 14 counterparts, so one expects the dispersion interactions to be very similar. However, the Group 15 boiling points are all corresponding higher because the compounds are also polar and have attractive dipole-dipole interactions (in fact, the dipole moments for NH_3 , PH_3 , and AsH_3 are 1.48 D, 0.58 D, and 0.20 D, respectively following the trend in EN values). Thus, a dipole of 0.20 D raises the boiling point of AsH_3 by 25°C compared with GeH_4 , and a dipole of 0.58 D (~3 times stronger than AsH_3) raises the boiling point of PH_3 by 24°C compared with SiH_4 . Thus, one expects the boiling point of NH_3 , with a dipole of 1.48 D (~2.5 times stronger than PH_3), to be raised by a similar or slightly greater amount compared with CH_4 . However, the experimental data shows an increase of 131°C ! This is very high and far beyond the expected value based upon scaling the dipole moments. This anomalously high boiling point is the main experimental evidence for hydrogen bonding, which only ammonia can do, pointing to something "beyond just dipole-dipole interactions".

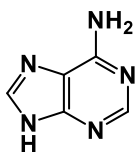
4. **Good Question.** Arrange the following species in order of increasing boiling point: Ar, H_2O , H_2Se , H_2S , NaCl.



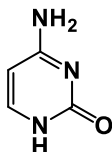
5. **Good Question.** Despite the fact XeO_4 has a greater number of electrons than XeO_3 , XeO_4 exists as a gas at room temperature whereas XeO_3 is a solid. Explain this experimental observation.

XeO_4 molecules are non-polar (tetrahedral molecular shape) and experience only London dispersion interactions. XeO_3 molecules are polar (trigonal pyramidal molecular shape) and experience stronger dipole-dipole interactions. These stronger interactions are enough to make the solid stable at room temperature.

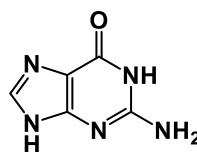
6. **Good Question.** DNA is a double helix made-up of a mixture of four bases (guanine, cytosine, thymine, and adenine) held together by intermolecular forces. Briefly explain why the G-C interaction is harder to break than the T-A one.



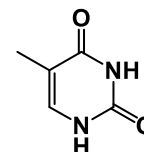
Adenine



Guanine

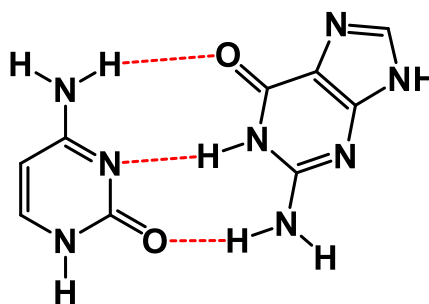
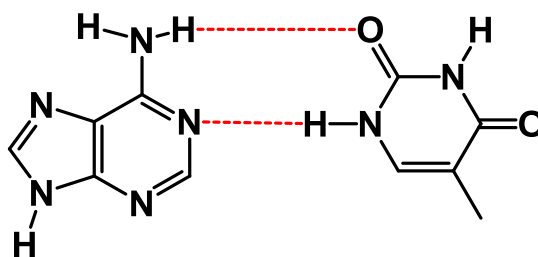


Cytosine

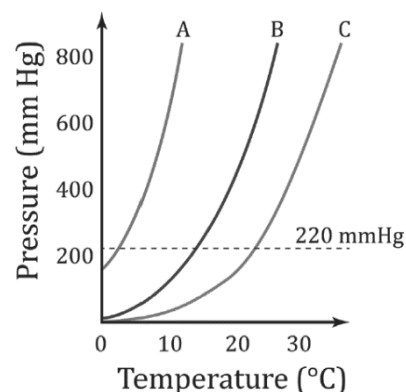


Thymine

H-bonding between adenine and thymine results in TWO hydrogen bonds (red dots shown below). Guanine and cytosine form THREE hydrogen bonds (see below). Hydrogen bonding between adenine and guanine or adenine and cytosine are not strong because the number of hydrogen bonds possible is not maximized.

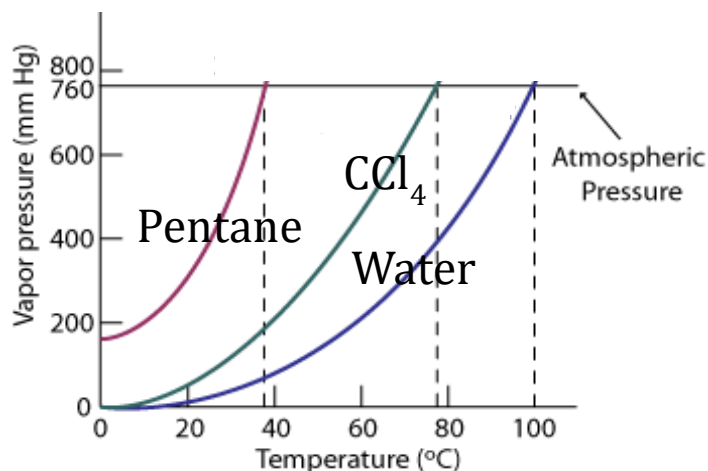


7. The vapour pressure of three substances as a function of temperature is shown to the right. Which substance(s) (A, B, or C) is/are most likely to boil at 20°C at the top of Mount Everest (atmospheric pressure at Mount Everest ~220 mmHg shown as a dashed line on the plot)? Briefly explain.



Liquids boil when their vapour pressure equals atmospheric pressure. At 20 °C, the vapour pressure of liquid C is less than 220 mmHg so it will not boil. It will vapourize in an open container but not boil. At 20 °C, the vapour pressures of liquids A and B are both greater than 220 mmHg which means if they are taken to Mount Everest in the liquid state (perhaps held at temperatures below their boiling points?) they will boil. However, they will not boil at 20 °C but rather at the temperatures where their vapour pressures are 220 mmHg (which estimating from the graph is approximately 2 °C and 15 °C, respectively).

8. On the diagram to the right, draw traces that represent the vapor pressure of carbon tetrachloride (CCl_4), water (H_2O), and pentane (C_5H_{12}). Clearly label the trace that corresponds to each substance and briefly explain their relative positions.



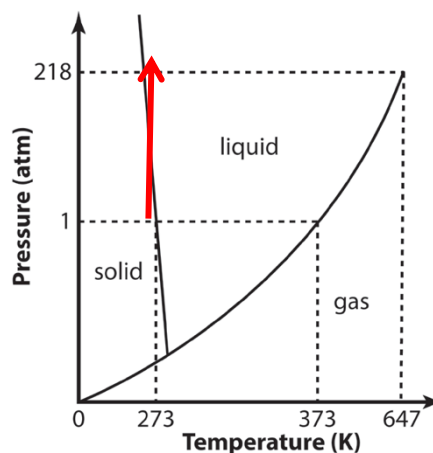
The blue trace corresponds to H_2O . Water is the only molecule of the three listed that has hydrogen bonds, and therefore has the greater intermolecular forces and the highest boiling point.

The green trace corresponds to CCl_4 . CCl_4 is more polarizable (has more electrons) than pentane and so has greater London dispersion forces, and therefore boils at a higher temperature than pentane.

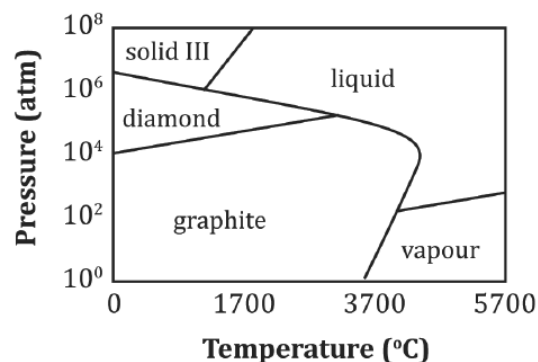
The red trace corresponds to pentane. Pentane has weaker London dispersion forces than CCl_4 and so boils at a lower temperature.

9. In the ice block experiment demonstrated in class, two metal weights are connected by a fine metal wire and hung over an anchored ice block. Use the phase diagram for water (right) to explain the results of the experiment.

Assuming the temperature of the ice block remains constant below the freezing point means the experiment occurs along a vertical line in the phase diagram close to the dashed line at 273 K. The weights cause the local pressure under the wire to increase dramatically, so much so the system moves vertically through the solid towards the liquid part of the phase diagram (as indicated by red arrow). The pressure induces a solid to liquid phase transition in the ice block just under the wire. This allows the weights/wire to melt its way through the block. As it moves through the block, the water above it will refreeze because the pressure there is now atmospheric, where the system is in the solid part of the phase diagram. At the end of the experiment the weights/wire have melted their way through the ice block, yet the ice block remains whole. Note that this behaviour is only possible because the slope of the solid/liquid coexistence curve is negative, which makes the liquid state more stable at higher pressures. This is also the phenomenon behind ice skating. The pressure on the blades of the skates locally melts the ice under them, creating a low friction surface one can skate on. This is only one of the many interesting and anomalous properties of water.



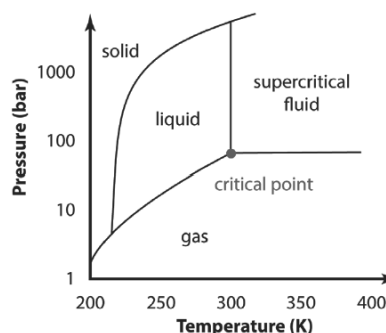
10. In order to pay their CHEM 154 tuition bill, one of your classmates started "Diamonds-R-Us". The company intends to create custom-order diamonds from recycled pencil 'lead' (graphite). Since you need a summer job, you apply for a position at Diamonds-R-Us. At the interview, you are given the phase diagram for carbon and asked to answer the following questions in order to be considered for the job.



- The phase transition from diamond to graphite can be best described as: **(A). Endothermic**
 - Based on the phase diagram, how many triple points exist for carbon? **(D). 3**
 - What phase change occurs by going from 4700 °C to 2700 °C at 10 atm pressure? **(C). Deposition**
11. **Good Question.** One of the engineers at *Diamonds-R-Us* proposes that the diamonds could be separated from graphite by placing them in a pool of liquid carbon at 1700 °C. They say the diamonds will float in the liquid carbon while the graphite will sink to the bottom. Is the engineer correct?

At 1700 °C the liquid state is the most dense state, followed by diamond, followed by graphite (least dense). Therefore, assuming they remain solid long enough (eventually they will also melt) both the diamonds and graphite will float on the liquid state, and cannot be separated. Thus the engineer is incorrect.

12. **Good Question.** The hanging ice-drop experiment is repeated, but the block of H₂O (ice) is replaced with a solid block of dry ice (CO₂). The phase diagram for CO₂ is shown to the right. Will the result of the experiment be the same? Explain.



According to the phase diagram shown, increasing pressure on solid CO₂ cannot induce a solid to liquid phase transition because moving vertically on the phase diagram in the solid phase keeps the state in the solid phase. Therefore, dry ice remains solid even under greater pressure so the mode of action in this experiment would not be the same. We would not expect the wire/weights combination to melt their way through the CO₂ block.

13. Use arguments based upon the phase diagram for water in Question 9 to answer the following:

a) What happens to a puddle of water on a sidewalk during a Vancouver summer day?

The temperature during a typical Vancouver summer day is about 300K, and the relative humidity is low, so according to the phase diagram in Question 9, the stable phase of water is vapour. However, the puddle is a liquid. This means the puddle is not in an equilibrium state and will spontaneously vapourize. Because the atmosphere is so large, the relative humidity is not changed even as the puddle evaporates, which means the puddle will completely evaporate. Note: a relative humidity of 100% means the partial pressure of water equals the vapour pressure. Under that condition (which occurs during foggy weather, for example) water liquid and vapour are in equilibrium, and puddles or drops of water are stable.

b) Some liquid water is sealed in an initially vacuated jar and submerged in English Bay. After some time, what phases are present in the jar?

The temperature near the bottom of English Bay is probably about 280K, and is constant as far as the jar is concerned. Because the initial pressure of water vapour in the jar is essentially zero, according to the phase diagram in Question 9, the stable phase of water is vapour and the liquid will vapourize. Unlike a), as the water vapourizes the partial pressure of water in the jar increases. If the amount of water is small, it will all vapourize and after some time, the jar will contain only water vapour. If the amount of water is large enough, the partial pressure will increase (moving vertically on the phase diagram) until it reaches the vapour pressure, at which point the system reaches equilibrium. In this case, after some time, the jar will contain liquid water and water vapour at the vapour pressure appropriate for the surrounding temperature.

c) Would your answer in b) be different if in addition to liquid water, nitrogen gas was pumped into the jar to make the total pressure 2 atm?

The arguments in b) apply just as well if there is nitrogen gas in the jar because the phase diagram involves the partial pressure of water, not the total pressure. As far as the water is concerned, it behaves the same way regardless of the presence of nitrogen gas (which is non-reactive and can be treated as an ideal gas – that is non-interacting).