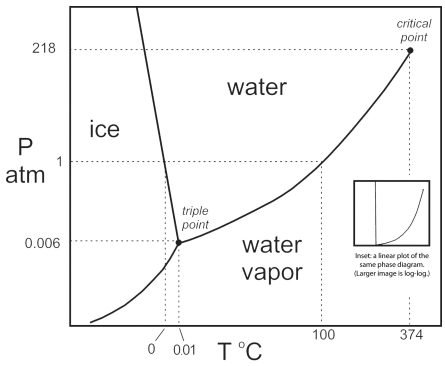
Phase transitions and phase diagrams

Phase transitions occur when a substance changes from one state of matter (solid, liquid, or gas) to another. The lines on a phase diagram indicate the combinations of temperatures and pressures at which phase transitions occur. Every molecule or solution (homogeneous mixture of different types of molecules) has a unique phase diagram. The phase diagram for water is shown at right.



Phase transition manipulation in cooking

Pressure cookers boil water in an enclosed container, so that the build-up of steam raises the pressure and increases the boiling point of the remaining water. The higher temperature reached by the boiling water allows the food inside to cook faster. A rotary evaporator applies a vacuum to vaporize volatile molecules, which are then collected when they revert to liquid state on a relatively-cold condenser coil. The pressure is naturally lower at high elevation, so water boils appreciably below 100°C. This causes water-containing foods cooked in the oven to dry out faster and foods cooked by boiling in water to take longer to reach their desired temperature/hydration.

Equation of the week

Molecules experience opposing pressures from the non-covalent bonds that tend to hold them together and the entropy they experience when they are unbound and free to move without constraint. The energy of interaction (U_{int}) is given by the strength of the non-covalent bonds between the molecules. The contribution of entropy is proportional to temperature. Phase transitions occur at a temperature T where these energies are equal:

$$U_{int} = ck_BT$$

where c is a constant that depends on the transition in question. Below this temperature, the energy of interaction is larger and so the molecules tend to remain in the more bound state (i.e., in solid or liquid phase), and vice versa. One corollary of this equation is that molecules with lower phase transition temperatures have lower interaction energies.

Melting points of fatty acids and triglycerides

In solid form, fat molecules bond through van der Waals (short-range, non-covalent) interactions between their hydrocarbon tails. More interactions are possible when the tails are longer, so U_{int} (and therefore, according to the equation of the week, the melting transition temperature) are higher for triglycerides and fatty acids with long tails. Unsaturated fats can be kinked, which makes it more difficult for each fat molecule to bond with many partners at once (the fat molecules do not pack as well), lowering U_{int} and thus the fat's melting temperature.

Solubility and boiling point elevation/freezing point depression

Solubility is the ability of one substance, called a solute, to dissolve homogeneously in another substance, called the solvent. Some substances do not dissolve appreciably in others, like water and oil; others, like water and ethanol, can be mixed in any ratio. In the majority of cases in cooking, though, there is a solubility limit: a maximum amount of solute that can be dissolved in a given amount of solvent. For example, 1 g salt (or 6 g table sugar) is the most that can be dissolved in 1 gof water at room temperature. The solubility limit increases with temperature.

Dissolving salt, sugar, or other non-volatile substances in water will increase the solution's boiling point and decrease its freezing point. The concentration of solute required to achieve an appreciable difference in boiling or freezing point is quite large.

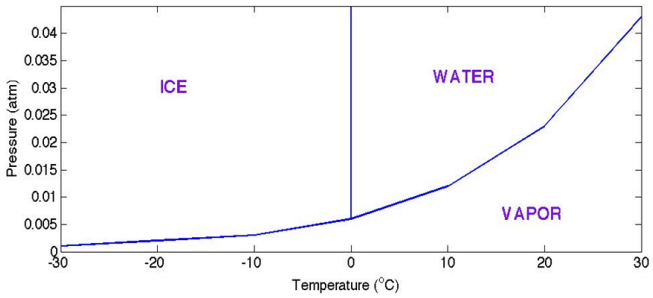
Advanced materials available online

- Derivation of $U_{int} = ck_BT$
- Gibbs free energy
- Enthalpy and entropy
- Protein denaturation
- Formula for b.p. elevation
- Solubility and temp.

Science Review Questions

1. Which of the fats depicted at right has the highest melting point?

2. Why does the fat you chose have a higher melting point?
   (a) it is shorter and thus has a higher interaction energy between molecules
   (b) it is shorter and thus has a lower interaction energy between molecules
   (c) it is longer and thus has a higher interaction energy between molecules
   (c) it is longer and thus has a lower interaction energy between molecules
   (d) it is bent and thus has a higher interaction energy between molecules
   (e) it is bent and thus has a lower interaction energy between molecules
3. Is molecule C a saturated or an unsaturated fat? Why?
4. Which of the following fats might molecule A correspond to: olive oil, butter fat, or coconut oil? Why?
6. One of today's videos shows Jordi Roca making a dessert using a distillate of eucalyptus leaves. He made the distillate by *boiling* the eucalyptus leaves at room temperature (23°C) using a rotovap. Using the phase diagram below, what should you adjust the pressure to, in order to bring the eucalyptus peel solution to a boil?



7. Considering the equation of the week, which of the compounds have the highest U_{int}, the eucalyptus compounds in the original flask, or the eucalyptus compounds in the collection flask?
8. When Jordi poured the liquid distillate of eucalyptus leaves onto his dessert, it grew into a tall ice structure. Would the same ice structure have been possible if Jordi had decided to make its flavor more interesting by adding 5 g cocoa powder to the distillate? Why?
9. You add 25 g salt and 25 g sugar to two separate beakers each containing 300 mL of ice water. Which solution will be colder?