Introduction
- In this chapter, we will develop a model to account for the differences in physical properties arising from differences in the attractions of individual molecules in the liquid phase.

Observation 1: Liquid-Vapor Phase Diagram
- There is a correlation between the volatility and boiling point of a liquid: substances with high boiling points have low vapor pressures.
- Consider water: at 1 atm, water boils at 100°C. The following graph also shows that the vapor pressure of water at 100°C is 1 atm, so the boiling point of water at 1 atm is the temperature at which the vapor pressure of water is equal to 1 atm.

Why is this true?
- Recall that observing the boiling point involves trapping liquid in a cylinder and raising the temperature until a phase transition occurs. The temperature at which the transition occurs is the boiling point. At that point, the vapor becomes stable – this is only possible if the vapor pressure is equal to the applied pressure from the piston.
- Since the vapor pressure equals the applied pressure at the boiling point, figure 1 gives both the vapor pressure of water as a function of temperature and the boiling point temperature of water as a function of applied pressure.
- Both phases are present at the boiling point; for every combination of temperature and pressure along the above curve, there is liquid-gas equilibrium.
- What if we stray from the line?
  - If we elevate the temperature while keeping the applied pressure constant, all of the liquid vaporizes and there is only gas left in the container. This is because the vapor pressure becomes greater than the applied pressure, which causes the liquid to evaporate.
  - If we lower the temperature while holding the pressure constant, all of the gas condenses into liquid. The applied pressure is greater than the vapor pressure.
  - Figure 1 can be referred to as a “phase diagram” since it shows the phase of water at given temperature and pressure combinations.

Observation 2: Solid-Liquid-Gas Phase Diagrams
- Continuing from the previous section, we want to “complete” the phase diagram with information about the solid phase.
Using the same cylinder-piston apparatus, we continue to lower the temperature. Recording the relationship between pressure and temperature reveals a (virtually unnoticeable) break around 0°C.

- At temperatures below 0°C, the water in the container becomes an equilibrium mixture of vapor and ice with no liquid present. This direct transition from solid to gas is called sublimation.
- The new solid-gas curve (shown below) can be interpreted as:

- The vapor pressure of the solid water as a function of temperature; or
- The sublimation temperature as a function of applied pressure.

This diagram is incomplete without the combinations of temperature and pressure at which solid and liquid are in equilibrium.

- Experimental data shows that the solid-gas and liquid-gas lines intersect at 0.01°C.
- At that point, all three phases are at equilibrium in the container. This is the triple point.
- Unfortunately, figure 3 doesn’t exist (tf hutch??) so I can’t put it here 😓

• Observation 3: Boiling Points and Intermolecular Forces
  - The normal boiling point is simply the boiling point at 1 atm applied pressure.
    - A liquid with a higher normal boiling point requires a higher temperature to reach a vapor pressure of 1 atm.
    - Remember: temperature is proportional to kinetic energy, which is used to overcome IMFs between the liquid molecules.
    - Therefore, when we compare two normal boiling points, we are also comparing the strengths of the IMFs in those liquids.
  - Comparing the boiling points in liquids across the periodic table reveals a trend based on periods:

- This reveals that heavier mass molecules have higher boiling points.
When all sixteen hydrides are placed on a graph of boiling point versus period, some interesting trends appear:

- Hydrides from group IV are the lowest boiling point compounds
- The boiling point increases as we move down the periodic table (for similar types of molecules, the molecules with larger atoms have stronger IMFs)
  - All of these hydrides are neutral. However, the large number of protons and electrons in the molecules create attractions when they are near each other. When the molecules are close enough to each other, charge rearranges so that attractions become more favorable.
  - The net attractive force created between two molecules as a result of the process above is known as the London dispersion force (LDF).
- The dispersion force is made larger with the addition of positive and negative charges. Molecules with more charges are more polarizable.
- Comparing molecules in the same period from groups IV and VII (SiH₄ vs HCl):
  - The boiling point of HCl is larger, even though the number of charges on both molecules is the same.
  - Refer to electronegativity, molecular geometry and molecular polarity:
    - HCl is a polar linear molecule because Cl is much more electronegative than H.
    - SiH₄ is not polar due to its symmetrical tetrahedral geometry.
    - The molecule with a dipole moment will have stronger IMFs.
    - This explains why Group IV hydrides have the lowest boiling points: they are all symmetrical and nonpolar.
- What about the high boiling points of NH₃, H₂O and HF?
  - High boiling points are not expected – these molecules are small and have seemingly normal dipoles
  - However, N, O and F are all strongly electronegative and small. They also all have lone pairs of electrons. These characteristics provide very strong IMFs.
  - This type of bonding is known as hydrogen bonding, a strong form of dipole-dipole attraction that only occurs when a hydrogen atom bonds with an N, O or F atom.
  - Size also matters (as always): when comparing HCl to HF, the HF molecule has a higher boiling point. This is because Cl is too large to support a hydrogen bond.
  - Hydrogen bonds are ten times stronger than dipole-dipole attractions.
- Another comparison: octane and water
• While octane is symmetric and lacks N, O or F atoms, it has a higher boiling point than water. The magnitude of its dispersion forces is dominant since octane and water are so different in size.

McMurry & Fay 10.5, 10.11

Phase diagram (10.11)

A phase diagram shows which phase is stable at different combinations of pressure and temperature. When a boundary line between phases is crossed by changing either the temperature or pressure, a phase change occurs.

Phase diagram for water:

Points on the solid/liquid, solid/gas and liquid/gas lines represent pressure/temperature combinations at which the two phases are in equilibrium. The triple point is a unique combination of pressure and temperature at which all three phases exist in equilibrium.

At a high temperature and pressure, the critical point is reached. Beyond the critical temperature ($T_c$) and pressure ($P_c$), a gas cannot be liquefied and a liquid cannot be vaporized. At the critical point, a gas is under such high pressure that its molecules are pushed together to the extent that it becomes indistinguishable from a liquid. Concurrently, a liquid at the critical point has such a high temperature that its molecules spread far apart and it becomes indistinguishable from a gas. The two phases become one and form a supercritical fluid that is neither a true liquid nor gas.

The effect of pressure on the slope of the solid/liquid boundary line – negative for water and positive for many other substances – depends on the relative densities of the solid and liquid phases. In CO$_2$ and other substances, the solid phase is denser due to more concise packing – this favors the solid phase, giving the solid/liquid line a positive slope. Conversely, water becomes less dense when frozen, giving the boundary a negative slope.
CDS Chapter 18: Phase Equilibrium in Solutions

• Introduction
  o What happens to phase equilibrium when more than one component is present?
  o How does mixing things together change equilibrium?

• Foundation
  o A solvent is the major component in a solution and is typically (but not always) a liquid
  o A solute is a minor component of a solution; there may be more than one solute. It can be of any phase. Once in solution, it takes on different properties and is generally unrecognizable from its pure form.

• Observation 1: Lowering of the Vapor Pressure in Solution
  o What impact does the presence of a solute have on the properties of a solvent?
    ▪ First, observe the different behaviors of different solutes, including whether the solute is a solid, liquid or gas in pure form
  o Begin by dissolving a solid solute into a liquid solvent (since the solid solute is nonvolatile, it creates zero vapor pressure, does not evaporate and is easy to analyze). We can assume that a volatile solvent and nonvolatile solute has the same vapor pressure as the solvent alone.
    ▪ Again, trap some liquid in a cylinder with a piston, and pull the piston back to create a volume above the liquid. Measure the pressure of the volume.
    ▪ This solution is water and 1 M glucose. The vapor pressure of this solution is lower than pure water’s normal vapor pressure of 23.756 torr at 25°C – it is only 23.33 torr.
    ▪ At 2 M glucose, it is only 22.93 torr.
    ▪ A graph reveals that the vapor pressure decreases linearly with increasing solute concentration.

• Unfortunately, this is not actually a straight line. A straighter line is formed by changing the way the concentration of glucose is measured – here, we use the mole fraction
  \[ X_{\text{glucose}} = \frac{n_{\text{glucose}}}{n_{\text{glucose}} + n_{\text{water}}} \], the fraction of the total number of moles of substance that is glucose.

• The vapor pressure of the glucose solution is a linear function of the mole fraction of the glucose in the solution, described by
  \[ P_{\text{vap}} = P_{\text{vap}}^* (1 - X_{\text{glucose}}) \].
  \[ P_{\text{vap}} = \text{vapor pressure of pure water.} \]
• The above equation shows that it is only the number of moles of glucose (solute) that affects the vapor pressure of the solution.
• Using the fact that \( X_{\text{glucose}} + X_{\text{water}} = 1 \), the equation can be rewritten as \( P_{\text{vap}} = P^*_{\text{vap}} X_{\text{water}} \).
  o Experimental data from analysis of other aqueous solutions of nonvolatile solutes shows that the vapor pressure of an aqueous solution does not depend on the identity of the nonvolatile solute. It only depends on the number of moles of the nonvolatile solute. These results and the above equation are known as Raoult’s Law.
  o A model for Raoult’s Law:
    ▪ Start with pure water at its boiling point: \( T = 100^\circ\text{C} \); applied pressure = vapor pressure = 1 atm.
    ▪ Add glucose: the vapor pressure of the solution is less than the vapor pressure of the pure water, according to Raoult’s Law.
    ▪ Since the applied pressure is greater after the addition of glucose, all of the vapor must now condense into liquid and liquid-vapor equilibrium is disestablished.
    ▪ There are two ways to restore equilibrium:
      ▪ Lower the applied pressure; or
      ▪ Increase the temperature and maintain the applied pressure.
        o Recall \( P_{\text{vap}} = P^*_{\text{vap}} X_{\text{water}} \): we need \( P_{\text{vap}} \) to be 1 atm even though \( X_{\text{water}} \) is less than 1. This is only possible by increasing \( P^*_{\text{vap}} \) by increasing the temperature.
        o This leads to the discovery of a normal boiling point for the solution, which will be at a higher temperature than the pure liquid at the same applied pressure.
• Dynamic Equilibrium and Vapor Pressure Lowering
  o At liquid-vapor equilibrium, \( \text{rate}_{\text{evap}} = \text{rate}_{\text{cond}} \).
  o As explained above, the solute disrupts this equilibrium – but did it disrupt condensation, evaporation or both?
  o Examining condensation:
    ▪ Since the solute is nonvolatile, there are no solute molecules in the vapor phase.
    ▪ Therefore, the rate of condensation depends only on the number of moles per volume of solvent molecules in the vapor phase. This number doesn’t change with the addition of solute.
    ▪ The rate of condensation does not change.
  o Examining evaporation:
    ▪ The rate of evaporation must be disrupted to explain the change in equilibrium.
    ▪ Since the solute is added to the liquid phase only, it makes sense that evaporation would be affected.
    ▪ Since a new equilibrium is established at a lower vapor pressure, the rate of condensation must be lower than it was before the solute was added. This is only possible if the rate of evaporation is lower as well.
  o Why is the rate of evaporation lowered by the solute?
    ▪ Evaporation requires that solvent molecules overcome IMFs and escape the liquid phase.
    ▪ In order to escape, solvent molecules must be positioned near the surface of the liquid to avoid running into other molecules that will slow it down.
    ▪ Since the rate of evaporation is lowered by the solute, the solute particles reduce the number of solvent molecules that are positioned to escape the liquid phase.
    ▪ While solute particles occupy some of the surface area of the solution, this is not the full reason why they impede the solvent molecules’ evaporation.
    ▪ Solute molecules are surrounded by solvent molecules in a process called solvation, which ties up the solvent molecules, impeding their ability to escape the solution.
• The solvation process occurs in proportion to the fraction of solute molecules in the solution.

• Observation 2: Vapor Pressures of Solutions with Two Volatile Components
  o There are other types of solutions: two volatile liquids, for example.
    ▪ Not all liquids are miscible – a solution can only be formed when the IMFs between the two types of molecules are similar.
  o A good example: benzene and toluene
    ▪ These two molecules have very similar structures, which allows them to be mixed in any proportion.
    ▪ The independent (pure) substances have very different vapor pressures: 95.1 torr for benzene and 28.7 torr for toluene.
    ▪ Vapor pressure graph of benzene-toluene solution: 

![Vapor Pressure Graph](image)

• There is a simple linear relationship increasing from the vapor pressure of pure toluene ($X_{\text{benzene}} = 0$) to the vapor pressure of pure benzene ($X_{\text{benzene}} = 1$).
  • Equation: $P_{\text{vap}} = P_{\text{toluene}}^* + (P_{\text{benzene}}^* - P_{\text{toluene}}^*)X_{\text{benzene}}$
    ▪ Using the fact that $X_{\text{benzene}} = 1 - X_{\text{toluene}}^*$, this can be rearranged to $P_{\text{vap}} = P_{\text{benzene}}^*X_{\text{benzene}} + P_{\text{toluene}}^*X_{\text{toluene}}$
    ▪ Each term looks like Raoult’s Law for each component – this means each component is contributing to the total vapor pressure.

  o When two liquids mix in solution to combine their vapor pressures in a very simple way, the solution is ideal.
  o In the context of dynamic equilibrium
    ▪ Each component lowers the rate of evaporation of the other component (like in the previous section with nonvolatile solutes)
    ▪ Each component has a lower number of vapor molecules to balance the dynamic equilibrium.
    ▪ The vapor pressures of each component add to the total vapor pressure by Dalton’s Law and IGL.

• Observation 3: Equilibrium between Solids and Liquid Solutions
  o A solute in a liquid solvent also disrupts the equilibrium between the liquid solvent and its solid phase.
  o Most obvious example: freezing salt water
    ▪ Salt disrupts the normal solid-liquid equilibrium, allowing ice to melt at subzero temperatures.
  o Experimental data shows that the lowering of the freezing point is proportional to the mole fraction of the solute in the liquid phase.
  o A model for freezing
    ▪ When frozen water is in equilibrium with a salt solution, the solid water is pure water (no salt).
    ▪ Questions:
      ▪ Why is the solid ice made of only pure water?
      ▪ How does this disrupt dynamic equilibrium between solid and liquid?
- For a pure liquid in equilibrium with a pure solid (like ice and water) at 0°C and 1 atm, the rate of freezing and the rate of melting are equal.
  - The rate of melting depends on the fraction of molecules in the solid that have sufficient energy to break free of the solid crystal – this depends on temperature.
  - The rate of freezing depends on how frequently liquid-phase molecules collide with and deposit themselves on the surface of the solid (which results in a loss of energy). This depends on both temperature and applied pressure.
  - Adding a solute: the solute does not enter the solid phase, so the rate of melting is unchanged by the solute’s presence.
  - Since the freezing point is lowered, the dynamic equilibrium must be disrupted by the solute – so the rate of melting must be greater than the rate of freezing at the freezing point after the solute is introduced.
  - Therefore, the rate of freezing is reduced by the solute.
  - This is similar to the reduction in the rate of evaporation by solutes
    - In the case of freezing, solute molecules reduce the number of solvent molecules that are available to deposit on the solid surface. This is similar to the solute molecules reducing the number of solvent molecules available to evaporate.
  - Lowering the rate of melting restores equilibrium; this is achieved by lowering the temperature.
- Observation 4: Equilibrium between a Solvent and a Solution
  - Something something biology: we’re gonna observe a solvent in equilibrium with a solution containing that solvent. How can the solvent be separated from the solution so they’re in equilibrium with each other?

- Two flasks are connected by a short glass tube, in the middle of which is a semi-permeable membrane that permits the passage of small molecules.
- In this case, the membrane permits the passage of the solvent (water), but not the solute (glucose).
- Both flasks are filled with water – since the water can flow through the membrane, the level of water in both flasks will rise to the same level. The two flasks are in equilibrium.
- Add glucose to the right flask: the water level begins to rise in the flask on the right and falls in the flask on the left. This continues until equilibrium is reestablished.
- **Osmosis** is the process by which a pure solvent passes through a semipermeable membrane into a solution of the same solvent.
  - A model for osmosis:
    - The flow of water from the left to the right equals the flow from the right to the left when the two flasks contain only pure water.
    - **Adding the solute disrupts this equilibrium.**
    - Since the solute is added to the flask on the right, the solvent on the left is unchanged and the flow of water from left to right does not change.
    - Therefore, the flow of water from right to left must decrease when the solute is added to account for the net flow of water from left to right.
    - Like with evaporation and freezing, **the presence of the solute disrupts the flow of water through the membrane.**
      - Solute particles block some of the membrane passages.
      - Some of the water molecules are bound up in solvating the solute particles and can’t pass through the membrane.
    - **The left flask always contains pure water** since the solute can’t pass through the membrane from right to left.
    - After a while, dynamic equilibrium is unexpectedly reestablished.
      - The water piling up in the right column **generates an extra pressure on the water near the membrane**, increasing the right-to-left flow.
      - When the pressure is high enough, the right-to-left flow matches the left-to-right flow and equilibrium is reestablished.
      - **Osmotic pressure** ($\Pi$) is the pressure required to achieve equilibrium to counter osmosis. It is proportional to the molarity of the solute in solution: $\Pi = \text{MRT}$.

| Types of interactions in solutions (11.2) | • **Solvent-solvent interactions**: Energy is absorbed to overcome IMFs between solvent molecules. The molecules must be separated to make room for solute particles.
| • **Solute-solute interactions**: Energy is absorbed to overcome IMFs holding solute particles together in a crystal (in ionic solids, this is the lattice energy). Substances with higher lattice energies are less soluble than substances with lower lattice energies. Compounds with singly charged ions are more soluble than compounds with doubly/triply charged ions.
| • **Solvent-solute interactions**: Energy is released when solvent molecules cluster around solute particles and solvate them. For ionic substances, the amount of hydration energy is greater for smaller cations because water molecules can approach the positive nuclei of smaller ions more closely and bind more tightly. Hydration energy increases with ion charge magnitude. |
| Molality (11.3) | The **molality** ($m$) of a solution is the number of moles of solute per kilogram of solvent:
<p>| $\text{Molality (m) = \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}}}$ |
| The main advantage of molality is that it is <strong>temperature-independent</strong> (mass doesn’t change with temperature). |
| Colligative properties (11.5) | <strong>Colligative properties</strong> are properties that depend only on the amount of dissolved solvent but not on the solute’s chemical identity. Examples: |</p>
<table>
<thead>
<tr>
<th>Topic</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Boiling point elevation (11.7)</td>
<td>The change in boiling point for a solution is ( \Delta T_b = K_b \cdot m ) where ( m ) is the molal concentration of solute particles and ( K_b ) is the molal boiling-point-elevation constant characteristic of a given liquid.</td>
</tr>
<tr>
<td>Freezing point depression (11.7)</td>
<td>The freezing-point depression for a solution relative to that of a pure solvent depends on the concentration of solute particles (like boiling-point elevation). The change in freezing point for a solution is ( \Delta T_f = K_f \cdot m ) where ( m ) is the molal concentration of solute particles and ( K_f ) is the molal freezing-point depression constant characteristic of a given solvent.</td>
</tr>
</tbody>
</table>
| Uses of colligative properties (11.9) | - Sprinkling salt on streets to prevent freezing in winter.  
- Antifreeze in automobile radiators.  
- **Reverse osmosis** for seawater desalination  
  - Pure water and seawater are separated by a semipermeable membrane; water molecules pass from the pure side to the solution side faster than in the reverse direction  
  - Eventually, dynamic equilibrium is reestablished at 30 atm (25°C)  
  - If pressure is made even greater than 30 atm is applied to the solution side, the reverse passage of water is favored and pure water can be obtained from seawater.  
- Colligative properties can be used to determine the molecular mass of an unknown substance. |
| Fractional Distillation (11.10) | The towers of petroleum refineries are used for the separation of crude petroleum into usable fractions for the production of gasoline. In **Fractional distillation**, the separation of different liquids into fractions with different boiling points occurs when the mixture is boiled and the vapors are condensed.  
- The vapor is enriched in the component with the higher vapor pressure (Raoult’s Law)  
- The condensed vapors are also enriched in that component  
- Partial purification can be effected |
• If this is repeated a large number of times, complete purification of the more volatile component is achieved.

Fractional distillation can be represented via a liquid/vapor phase diagram by plotting temperature versus composition:

Between the liquid and vapor phases is a thin equilibrium region where the liquid and vapor coexist.

**How does this work?**

• **Point A:** Start in the middle with the 50:50 benzene/toluene mixture heated to its boiling point (92.2°C).

• The lower curve represents the liquid composition (50:50), but the upper curve represents the vapor composition (**Point B;** 71:29 at 92.2°C).

• A tie line connects points A and B to indicate that the temperature remains constant.

• **Point C:** Condensing the 71:29 vapor mixture by lowering the temperature gives a 71:29 liquid mixture.

• **Point D:** when this liquid mixture is heated to its boiling point (86.6°C), it has an 86:14 vapor composition (represented by another tie line).

• **Fractional distillation is a “stairstep walk” across successive tie lines in whatever number of steps necessary to reach the desired purity.**

In this apparatus, the mixture is boiled and rises through the distillation column, which is filled with hundreds of tiny glass balls. The vapor condenses on these glass balls and re-evaporates with a higher concentration of the more volatile component of the mixture (recall that volatility describes the ease with which a liquid evaporates). By the time the vapors reach the top of the column, the mole fraction of the more volatile substance is 1 (the gas is pure), and it can be recondensed as a pure liquid.