Ch 11   Liquid Phase

Volume and Density
-   Liquid and solid are condensed phases and their volumes are not simple to calculate.
-   That is different from gases, which have volumes that are easily calculated
    using the ideal gas and Van der Waal equations.
-   The molecules in the condensed phases are in close contact with each other.
    So, their volumes and densities are determined by their intermolecular
    attractions, as well as their molecular shapes and sizes.

Changes of State (Phase Transitions)
-   Generally, a phase transition is physically and thermodynamically reversible.
-   Melting (Fusion) is solid → liquid, and Freezing is liquid → solid.
-   Vaporization (Boiling) is liquid → gas, and Condensation is gas → liquid.
-   Sublimation is solid → gas, and Deposition is gas → solid.

Vapor Pressure of a Liquid
-   Vapor pressure is the partial pressure of a substance's vapor
    that exists in equilibrium above its liquid.
-   Vapor pressure increases nonlinearly as a function of temperature.
-   Here is a table of vapor pressure versus temperature for water.
    The same data is presented both graphically and with a table in Appendix E.
-   The rate of vaporization at constant T is a function of
    the liquid's surface area, which is nearly constant.
-   The condensation rate at constant T is a function of partial pressure.
    Partial pressure increases during vaporization as vapor concentration increases.
-   So, the condensation rate increases until it is the same as the vaporization rate.
-   When the rates become equal, the vapor pressure is no longer changing,
    and the liquid is in equilibrium with its vapor.
-   Normal Boiling Point (BP) is the T where the liquid's equilibrium partial pressure
    is exactly 1 atm (760 mmHg). These boiling points can be seen here, where the
    vapor pressure curves cross the line for pressure equal to 760 mmHg.
-   A solid or liquid can be completely converted into a gas by heating it at constant
    temperature if its vapor pressure equals the pressure of the gas above it.
-   As can be seen in the heating curve for water, the temperature does not change
    during the vaporization process.
-   Freezing Point is not significantly affected by pressure, however, because
    the change in volume between a substance's liquid and solid phases is small.

Enthalpy (Heat) of Phase Transition
- Heat input is needed to convert solid to liquid, or liquid to gas.
- These heats are called the enthalpies of fusion (ΔH_{fus}) and vaporization (ΔH_{vap}), respectively.
- For water, $\Delta H_{fus} = 6.009$ kJ/mol at 0 ^{o}C and $\Delta H_{vap} = 40.66$ kJ/mol at 100 ^{o}C.

Ex 11.01   Heat and Mass involved with Phase Changes
- 1,1,1,2-tetrafluoroethane, CF_3CH_2F, has $\Delta H_{vap} = 22.2$ kJ/mol and Mm = 102 g/mol.
- H_2O has $\Delta H_{fus} = 6.009$ kJ/mol and Mm = 18.02 g/mol.
- To find the mass of CF_3CH_2F which must vaporize (absorb heat) in order for 500.0 g of water to freeze (release heat), first calculate the heat that must be removed from the water.

$$q_{H2O} = (\text{moles } H_2O)(\Delta H_{fus}) = (500.0 \text{ g}) \left(\frac{1 \text{ mol}}{18.02 \text{ g}}\right) \left(\frac{-6.009 \text{ kJ}}{1 \text{ mol}}\right) = -166.7 \text{ kJ}$$

- This same amount of heat that is removed from the water must be absorbed by CF_3CH_2F. Note that the sign on q changes as a result .

$$- q_{H2O} = q_{CF3CH2F} = (\text{moles } CF_3CH_2F)(\Delta H_{vap})$$

- The amount of heat can then be used to find the moles and mass of CF_3CH_2F needed.

$$\text{moles } CF_3CH_2F = \frac{- q_{H2O}}{\Delta H_{vap}} = \frac{+166.7 \text{ kJ}}{22.2 \text{ kJ/mol}} = 7.51 \text{ mol}$$

$$\text{mass } CF_3CH_2F = (7.51 \text{ mol})(102 \text{ g/mol}) = 7.66 \times 10^2 \text{ g}$$

Molar Enthalpies of Vaporization (at Boiling Point)

Substance Name and Formula	Molar Enthalpy of Vaporization (kJ/mol)	Boiling Point (^{o}C)
Water, H_2O	40.7	100.0
Ammonia, NH_3	23.4	−33.3
Carbon Disulfide, CS_2	26.8	46.3
Dichlorodifluoromethane, CCl_2F_2	17.4	−29.8
1,1,1,2-tetrafluoroethane, CF_3CH_2F	22.2	−26.3
Methanol, CH_3OH	34.5	65
Ethanol, CH_3CH_2OH	38.7	78
Propanol, $CH_3CH_2CH_2OH$	41.8	97
Methane, CH_4	9.20	−161
Ethane, C_2H_6	14.7	−89
Propane, C_3H_8	18.1	−30

Clausius-Clapeyron Equation
-   This equation relates vapor pressure (P) to the temperature in Kelvins (K).
-   A function for the logarithm of pressure can create a straight line with a negative slope (−A).
-   $\ln(P) = -(A)\left(\frac{1}{T}\right) + B$
-   $\ln(P)$ is the y variable and $(1/T)$ is the x variable.
-   $A = \frac{\Delta H_{vap}}{R}$ where $R = 8.314$ J/K·mol (universal gas constant).
-   The function is linear, as in Figure 8.5.1.
-   Substituting for A, we get these results at temperatures T_1 and T_2:

$$\ln(P_1) = \left[-\left(\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{T_1}\right) + B\right]$$

$$\ln(P_2) = \left[-\left(\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{T_2}\right) + B\right]$$

-   Subtracting the first equation from the second, we get:

$$\ln(P_2) - \ln(P_1) = \left[-\left(\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{T_2}\right) + B\right] - \left[-\left(\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{T_1}\right) + B\right]$$

-   When the B's are cancelled, this reduces to:

$$\ln(P_2) - \ln(P_1) = \left(\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

-   The logarithms can be simplified as well:

$$\ln(P_2) - \ln(P_1) = \ln(P_2) + \ln\left(P_1^{-1}\right) = \ln(P_2) + \ln\left(\frac{1}{P_1}\right) = \ln\left(\frac{P_2}{P_1}\right)$$

-   The final result is:

$$\mathbf{\ln\left(\frac{P_2}{P_1}\right) = \left(\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$
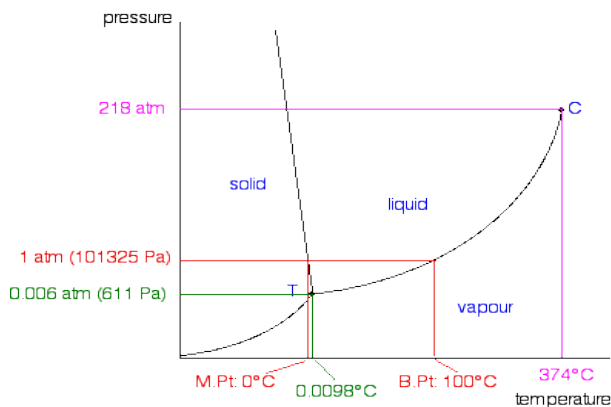
Ex 11.02   Find vapor pressure (P_2) of water at $T_2 = 70.00\ ^{\circ}C = 343.15$ K.
-   $\Delta H_{vap} = (40.66$ kJ/mol$)(1000$ J/kJ$) = 40660$ J/mole
-   $P_1 = 1.000$ atm at the normal boiling point ($T_1 = 100.00\ ^{\circ}C = 373.15$ K)

-   $\ln\left(\frac{P_2}{1.000\ \text{atm}}\right) = \left[\frac{40660\ \frac{J}{mol}}{8.314\ \frac{J}{K \cdot mol}}\right]\left[\frac{1}{373.15\ K} - \frac{1}{343.15\ K}\right]$

-   $\ln\left(\frac{P_2}{1.000\ \text{atm}}\right) = (4891\ K)(-2.343 \times 10^{-4}\ K^{-1}) = -1.146$

-   $\frac{P_2}{1.000\ \text{atm}} = \ln^{-1}(-1.146) = e^{-1.146} = +0.3179$

- $P_2 = (+0.3179)(1.000\ \text{atm}) = 0.3179$ atm $\times (760.0$ mmHg/atm$) = 241.6$ mmHg

Phase Diagrams
- Phase diagrams show graphically (P vs. T) where solid, liquid, and gas phases are stable, and where there are transitions from one phase to another.
  See the phase diagram for water (below left and in Figure 10.31).
- Where P = 1 atm (101 kPa), ice melts (s → L) at 0 °C and liquid boils (L → g) at 100 °C.
- Solids are generally stable at low T as long as pressure is not too low (left side of diagram).
- Liquids are generally stable at medium T and moderately-high P (top middle-right).
- Gases are generally stable at high T and low P (bottom right).
- The line (BD in Figure 10.31) in the middle-left of the diagram is the melting/freezing curve, where solid and liquid are in equilibrium with each other.
- The line (BC) on the right side of the diagram is the vaporization/condensation curve, where liquid and gas in equilibrium.
- The line (AB) in the lower-left of the diagram is the sublimation/deposition curve, where solid and gas in equilibrium.
- The three lines meet in the diagram at the triple point (point B in Figure 10.31).
- A triple point is a P and T where three different phases can exist together in equilibrium.
  For water, the triple point is at 0.006 atm (0.6 kPa) and 0.01 °C.
- A critical point is the P and T where liquid and gas have the same density.
  Liquid and gas become indistinguishable at T_{Crit}, and P_{Crit} is the vapor pressure at T_{Crit}.
  Above T_{Crit}, the substance is called a supercritical fluid.
  For water, this occurs at 374 °C and 218 atm (point C, below left).
- For CO_2, the phase diagram (below right and in Figure 10.34) appears similar.
  But, 1 atm (101 kPa) intersects the sublimation curve (not melting curve) at −78 °C.
  Dry ice at 1 atm converts directly to gas above this T, with no liquid phase involved.
  Liquid CO_2 cannot exist if P or T is below that of the triple point (5.11 atm and −56 °C)
- For sulfur, there are two distinct solid phases: orthorhombic and monoclinic crystals.
  As a result, there are three triple points in the phase diagram for sulfur.

Phase Diagram for H_2O Phase Diagram for CO_2
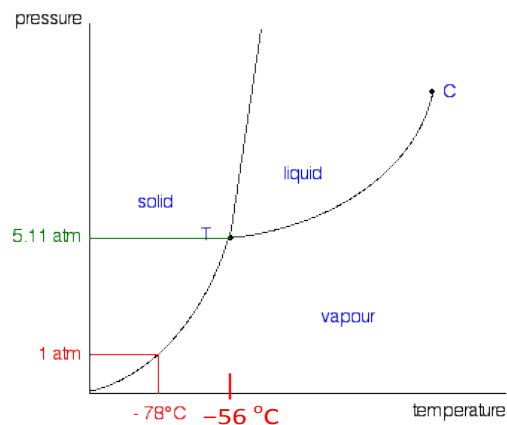
Surface Tension
- Surface tension is the energy needed to increase a liquid's surface area.
- It is generally expressed in units of N/m or J/m^2, where both units are equivalent to kg/s^2.
- A surface molecule feels a net force that is downward and towards the bulk liquid.
  This net force is due to intermolecular attractions, as in Figure 10.16.
- The result of these intermolecular forces is that they act to minimize the total
  amount of surface area for liquids, as in Figure 10.17.

Viscosity
- Viscosity is a fluid's resistance to flow and is caused by intermolecular interactions.
- Attractions between molecules and tendencies of long molecules
  to get tangled together both cause viscosity to increase.
- A liquid with a low viscosity, like water (small molecules), flows easily.
- A fluid with a high viscosity, like motor oil (long molecules), resists flowing.
  That is, not all of the fluid flows together. So, it shears instead of flowing.
  The result is that high viscosity fluids tend to be slippery.
- Gases typically have viscosities that are much lower than those of liquids.
  This occurs because gas molecules are much farther apart from each other.
  They have far fewer intermolecular interactions (only during molecular collisions).

Intermolecular Dipole-Dipole Forces
- Molecules with permanent dipoles (δ^+ and δ^-) are held together by their attractive forces.
- Polar molecules align together, δ^+ of one molecule near δ^- of neighboring molecule.
- For HBr, the electronegativity (e/n) difference is $2.8 - 2.1 = 0.7$.
  The e/n difference is slightly larger than the minimum of 0.5 for polar molecules.
  So, the molecule is moderately polar, with δ^+ H, and δ^- Br.
- A δ^+ H on one molecule will be attracted to the δ^- Br on a neighboring molecule.
- A similar situation exists with HCl molecules.

Intermolecular Hydrogen Bonding Forces
- H-bonding is an especially strong polar attraction that occurs
  where an H atom is attached to an N, O, or F atom.
- These H atoms are δ^+ and they bond with the nearby N, O, and F atoms, which are δ^-.
- Refer to Figure 10.10 for H-bonding in water.
- CH_3OH (methanol) can H-bond because it has a δ^- O attached to a δ^+ H.
  However, the three H's attached to the C are not δ^+ and cannot H-bond.

Intermolecular London (Dispersion) Forces
- London forces are attractions between molecules due to <u>instantaneous dipoles</u>.
- All atoms and molecules are instantaneously polar due to the random motion of e^{-1}'s.
- The e^{-1} density will instantaneously (not permanently) be greater
  on one side of an atom or molecule than on the other side.
- This results in a weak attractive force between **all** molecules, whether polar or not.
- Long-chain hydrocarbon molecules can twist around each other.
  This creates numerous contact points between the atoms for their London forces.
  As a result, longer hydrocarbon chains have greater London forces and higher boiling points.

Relative Strengths of Intermolecular Forces
- The strength order for intermolecular forces is H-Bonding > Dipole-Dipole > London.
- As intermolecular forces increase, the vapor pressure will decrease,
  and the boiling point will increase.

Ex 11.05 Relative Strengths of Intermolecular Forces
- C_4H_{10} (butane) has only C-C bonds (completely nonpolar) and C-H bonds (with e/n
  difference equal to 0.4). So, butane is nonpolar and has London forces only.
- CH_2Cl_2 (dichloromethane) is polar as a result of the C-Cl bonds. So, it has Dipole-Dipole
  forces. But, dichloromethane cannot H-Bond because the H's are both connected to C,
  rather than to O, N, or F. Dichloromethane also has London forces, as all molecules do.
- CH_3CH_2OH (ethyl alcohol) has a δ^+ H and a δ^- O as a result of its O-H bond.
  The molecule also has a dipole between the δ^+ C and the δ^- O of the C-O bond as well.
  So, ethyl alcohol possesses H-Bonding, Dipole-Dipole, and London forces.
- The overall trend result for both Intermolecular Forces and Boiling Points is the same:
$$CH_3CH_2OH > CH_2Cl_2 > C_4H_8$$

Ex 11.06 Relation between Intermolecular Forces and Vapor Pressure
- Vapor Pressures decrease as intermolecular forces increase, because those forces
  hold the molecules together more tightly in the liquid phase.
- The C=O bond polarities of carbon dioxide (O=C=O) oppose each other by 180° as a
  result of the molecule's linear geometry. Therefore, they cancel each other completely.
  So, CO_2 is completely nonpolar, has London forces only, and has a high vapor pressure.
- Diethyl ether ($CH_3CH_2OCH_2CH_3$) has two polar C-O bonds,
  but it has no δ^+ H because all of the H's are bonded to the C's.
  Diethyl ether has both Dipole-Dipole and London forces, but no H-Bonding.
- Methanol (CH_3OH) has polar C-O bonds and it has a δ^+ H with a δ^- O as a result of its
  O-H bond. Methanol has H-Bonding, Dipole-Dipole, and London forces.
- The molecule with the lowest amount of intermolecular forces has the highest vapor pressure.
  Vapor Pressure Trend: $CO_2 > CH_3CH_2OCH_2CH_3 > CH_3OH$