OFB Chapter 6
Condensed Phases and Phase Transitions

6-1 Intermolecular Forces: Why Condensed Phases Exist

6-2 The Kinetic Theory of Liquids and Solids

6-3 Phase Equilibrium

6-4 Phase Transitions

6-5 Phase Diagrams

6-6 Colligative Properties of Solutions

6-7 Mixtures and Distillation

6-8 Colloidal Dispersions
Intermolecular Forces: Why Condensed Phases Exist

- **Intermolecular Forces**
  - Chemical bonds
    - Strong
    - Directional
    - Short Range (relative)

- **Intermolecular Forces**
  - Weaker than chemical bonds, usually much weaker
  - Less directional than covalent bonds, more directional than ionic bonds
  - Longer range than covalent bonds but at shorter range than ionic bonds

- **Condensed Phases**
  - Solids and Liquids
  - Intermolecular forces: mutual attractions hold the molecules closer together than gases

- **Potential Energy Curves**
  - Distinction between *intra*molecular and *inter*molecular Forces
Potential Energy Curves

- **HCl + HCl**
- **Ar + Ar**
- **Cl + Cl**
- **K^+ + Cl^-**
Potential Energy Curves

- Atoms or molecules approach at large distance (zero PE (energy of position))
- PE goes negative as intermolecular forces come into play
- PE minimum energy well is a balance of Intermolecular forces and repulsive forces
- PE goes positive as repulsive forces dominate
Types of Non-Bonded (Intermolecular) Attractions

1. Dipole-Dipole Interactions
   – e.g., Hydrogen Bonding
2. Ion-Dipole Interactions
3. Induced Dipole Attractions
4. Dispersive Forces
   • temporary fluctuations in electron distribution
Types of Non-Bonded (Intermolecular) Attractions

1. Dipole-Dipole Interactions
   – e.g., Hydrogen Bonding
Types of Non-Bonded (Intermolecular) Attractions

1. Dipole-Dipole Interactions
   – e.g., Hydrogen Bonding

2. Ion-Dipole Interactions
Types of Non-Bonded (Intermolecular) Attractions

1. Dipole-Dipole Interactions
   – e.g., Hydrogen Bonding
2. Ion-Dipole Interactions
3. Induced Dipole Attractions
Types of Non-Bonded (Intermolecular) Attractions

1. Dipole-Dipole Interactions
   - e.g., Hydrogen Bonding

2. Ion-Dipole Interactions

3. Induced Dipole Attractions

4. Dispersive Forces
   - temporary fluctuations in electron distribution
Types of Non-Bonded (Intermolecular) Attractions

1. Dipole-Dipole Interactions
   - e.g., Hydrogen Bonding
2. Ion-Dipole Interactions
3. Induced Dipole Attractions
4. Dispersive Forces
   - temporary fluctuations in electron distribution
Types of Non-Bonded (Intermolecular) Attractions

1. Dipole-Dipole Interactions
   - e.g., Hydrogen Bonding
   - Between H₂O to H₂O or
   - R-OH to H₂O or
   - R-OH to R-OH
   - (R is an organic unit)
Kinetic Theory of Liquids and Solids

(a) 
(b) 
(c)
6-3 Phase Equilibrium

**Phase:** A sample of matter that is uniform throughout, both in its chemical constitution and in its physical state.

- Coexisting phase equilibrium
  - Vapor pressure
Correcting for the Vapor Pressure of Water in “Wet Gases”

• Many chemical reactions conducted in aqueous solution often generate gaseous products
• The gas collected will be “humid” or “wet” due to the coexistence of the gas and water vapor.
• A correction is made to account for the water vapor present

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Vapor Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.0</td>
<td>0.01683</td>
</tr>
<tr>
<td>17.0</td>
<td>0.01912</td>
</tr>
<tr>
<td>19.0</td>
<td>0.02168</td>
</tr>
<tr>
<td>21.0</td>
<td>0.02454</td>
</tr>
<tr>
<td>23.0</td>
<td>0.02772</td>
</tr>
<tr>
<td>25.0</td>
<td>0.03126</td>
</tr>
<tr>
<td>30.0</td>
<td>0.04187</td>
</tr>
<tr>
<td>50.0</td>
<td>0.1217</td>
</tr>
<tr>
<td>100.0</td>
<td>1.0000</td>
</tr>
</tbody>
</table>
Exercise page 6-2:

Passage of an electric current through a dilute aqueous solution of sodium sulfate produces a mixture of gaseous hydrogen and oxygen according to the following equation:

\[ 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{H}_2(g) + \text{O}_2(g) \]

One liter of the mixed gases is collected over water at 25\(^\circ\)C and under a total pressure of 755.3 torr. Calculate the mass of oxygen that is present. The vapor pressure of water is 23.8 torr at 25\(^\circ\)C.
Exercise page 6-2:

For ideal gas mixtures

P of a gas is proportional to the number of moles of gas

\[ 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{H}_2(g) + \text{O}_2(g) \]
Exercise page 6-2:

\[ P_{gases} = P_{total} - P_{H_2O} \]

\[ P_{O_2} = \frac{1 \text{mole } O_2}{1 \text{mole } O_2 + 2 \text{ moles } H_2} = \frac{1}{3} P_{gases} \]

\[ P_{O_2} V = n_{O_2} RT \]

\[ n_{O_2} = \frac{P_{O_2} V}{RT} \]

\[ n = \frac{m}{M} \]

\[ m_{O_2} = \]
6-4 Phase Transitions

Boiling
- liquid equilibrium gas

Boiling Point
- Vapor press = external pressure

Normal boiling point
- Vap press. = 1 atm

Melting
- solid equilibrium liquid

Melting Point
- Vapor press = external pressure

Normal melting point
- Vap press. = 1 atm
Intermolecular Forces and Phase Transitions

The stronger the intermolecular attractions in a liquid, the lower the vapor pressure at any temperature.
Special Case of Water

Due to Hydrogen Boiling

1. Water expands when it freezes

2. Water has a higher Boiling point and higher melting pint than expected for its Molar Mass, cf. other Group VI

3. The energy input to boil is exceptional high (45kJ) and the reverse (condensation of steam) release the same large amount.
Exercise 6-3:

Rank the following from lowest to highest in terms of expected normal boiling point: **NaBr**, **Ar**, **HCl**.
6-5 Phase Diagrams

Phase diagram:
A graph of pressure against temperature that shows the state of matter that is stable for every pressure-temperature combination.

Triple point:
A unique combination of pressure and temperature at which the gas, liquid, and solid phases coexist in equilibrium.
Phase diagram:
Critical point:

Critical pressure:

Critical temperature:
Exercise  page 6-4

Estimate the boiling temperature of diethyl ether \((\text{C}_2\text{H}_5\text{OC}_2\text{H}_5)\) atop a tall mountain (under a pressure of 0.50 atm), using the vapor pressure curve of diethyl ether in Figure 6-23
Exercise 6-5:

A sample of solid argon is heated at a constant pressure of 20 atm from 50 K to 150 K. Describe any phase transitions, and give the approximate temperatures at which they occur.
6-6 Colligative Properties of Solutions

- For some properties, the amount of difference between a pure solvent and dilute solution depend only on the number of solute particles present and not on their chemical identify.

- Called Colligative Properties

- Examples
  1. Vapor Pressure
  2. Melting Point
  3. Boiling Point
  4. Osmotic Pressure
Colligative Properties of Solutions

**Mass percentage (weight percentage):**

mass percentage of the component =

\[
\frac{\text{mass of component}}{\text{total mass of mixture}} \times 100\%
\]

**Mole fraction:** The chemical amount (in moles) divided by the total amount (in moles)

\[
X_1 = \frac{n_1}{n_1 + n_2}
\]

\[
X_2 = \frac{n_2}{n_1 + n_2} = 1 - X_1
\]
Molality

\[ m_{\text{solute}} = \ \text{moles solute per kilograms solvent} \]
\[ = \text{mol kg}^{-1} \]

Molarity

\[ c_{\text{solute}} = \ \text{moles solute per volume solution} \]
\[ = \text{mol L}^{-1} \]
Exercise 6-7:

Suppose that 32.6 g of acetic acid, CH₃COOH, is dissolved in 83.8 g of water, giving a total solution volume of 112.1 mL. Calculate the molality and molarity of acetic acid (molar mass 60.05 g mol⁻¹) in this solution.

\[
\text{Molality} = m_\text{solute} = \frac{\text{moles solute}}{\text{kg solvent}} = \text{mol kg}^{-1}
\]

\[
m_\text{solute} = \left( \frac{32.6 \text{ g}}{60.05 \text{ g mol}^{-1}} \right) \left( \frac{1 \text{ mol}}{1000 \text{ g}} \right) = \frac{0.543 \text{ mol}}{0.0838 \text{ kg}} = 6.48 \text{ mol kg}^{-1}
\]
Exercise 6-7:

Suppose that 32.6 g of acetic acid, CH₃COOH, is dissolved in 83.8 g of water, giving a total solution volume of 112.1 mL. Calculate the molality and molarity of acetic acid (molar mass 60.05 g mol⁻¹) in this solution.

Molarity = \( c_{\text{solute}} = \frac{\text{moles solute}}{\text{volume solvent}} = \text{mol L}^{-1} \)

\[
c_{\text{solute}} = \left( \frac{\frac{32.6 \text{ g}}{60.05 \text{ g mol}^{-1}}} {\frac{112.1 \text{ ml}}{1000 \text{ ml L}^{-1}}} \right) = \frac{0.543 \text{ mol}}{0.1121} = 4.84 \text{ mol L}^{-1}
\]
Converting among **Mass Fraction**, **Mole Fraction**, **Molality**, **Molarity**

- **Mass Fraction**:
  \[
  \text{Mass solute} / \text{Total mass}
  \]

- **Molality**:
  \[
  \frac{\text{Moles solute}}{\text{Mass of solvent}}
  \]

- **Molarity**:
  \[
  \frac{\text{Moles solute}}{\text{Volume of solution}}
  \]

- **Mole Fraction**:
  \[
  \frac{\text{Moles solute}}{\text{Total moles}}
  \]

- **Mass solvent**
  \[
  \text{Mass of solvent}
  \]

- **Mass solute**
  \[
  \text{Molar masses}
  \]

- **Total mass**
  \[
  \text{Density of solution}
  \]

- **Volume of solution**

- **Total moles**

© 2003 Thomson-Brooks/Cole
Ideal Solutions and Raoult’s Law

- Consider a non-volatile solute in a solvent
- \( X_1 = \text{mole fraction of solvent} \)

\[
P_1 = X_1 P^\circ_1
\]

Positive deviation

= solute-solvent attractions < solvent-solvent attractions

Negative deviation

= solute-solvent attractions > solvent-solvent attractions
Ideal Solutions and Raoult’s Law

• Lowering of Vapor Pressure
  – Vapor Pressure of a solvent above a dilute solution is always less than the vapor pressure above the pure solvent.

• Elevation of Boiling Point
  – The boiling point of a solution of a non-volatile solute in a volatile solvent always exceeds the boiling point of a pure solvent.
• Elevation of Boiling Point

$$\Delta T_b = mK_b$$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Chemical Formula</th>
<th>$T_b$ (°C)</th>
<th>$K_b$ (K kg mol$^{-1}$)</th>
<th>$T_f$ (°C)</th>
<th>$K_f$ (K kg mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>CH$_3$COOH</td>
<td>118.1</td>
<td>3.07</td>
<td>17</td>
<td>3.9</td>
</tr>
<tr>
<td>Benzene</td>
<td>C$_6$H$_5$</td>
<td>80.1</td>
<td>2.53</td>
<td>5.5</td>
<td>4.9</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>CCl$_4$</td>
<td>76.7</td>
<td>5.03</td>
<td>-22.9</td>
<td>32</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>C$<em>4$H$</em>{10}$O</td>
<td>34.7</td>
<td>2.02</td>
<td>-116.2</td>
<td>1.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C$_2$H$_5$OH</td>
<td>78.4</td>
<td>1.22</td>
<td>-114.7</td>
<td>—</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C$_{10}$H$_8$</td>
<td>—</td>
<td>—</td>
<td>80.5</td>
<td>6.8</td>
</tr>
<tr>
<td>Water</td>
<td>H$_2$O</td>
<td>100.0</td>
<td>0.512</td>
<td>0.0</td>
<td>1.86</td>
</tr>
</tbody>
</table>

<i>TABLE 6-2  Boiling-Point Elevation and Freezing-Point Depression Constants<sup>a</sup></i>

<sup>a</sup>At 1 atm pressure.

© 2003 Thomson - Brooks/Cole

• The Effect of Dissociation

$$i = \text{the number of particles released into the solution per formula unit of solute}$$

• Depression of Freezing Point

$$\Delta T_f = -mK_b$$
Osmotic Pressure

- Fourth Colligative Property
- Important for transport of molecules across cell membranes

\[ \text{Osmotic Pressure} = \Pi = g \cdot d \cdot h \]

\[ \Pi = c \cdot RT \]

\[ \Pi V = n \cdot RT \]

\[ \Pi V = i \cdot c \cdot RT \]
Exercise 6-17

A dilute aqueous solution of a non-dissociating compound contains 1.19 g of the compound per liter of solution and has an osmotic pressure of 0.0288 atm at a temperature of 37°C. Compute the molar mass of the compound.

Strategy

1.) use $\Pi = cRT$ to find the $c$ in mol/L

2.) Recall that mole = $\frac{g}{\text{Molar mass}}$

3.) Rearrange $M = \frac{g}{\text{mole}} = \frac{g/l}{\text{mole/l}} = \frac{\text{Given}}{c}$
Exercise 6-17

A dilute aqueous solution of a non-dissociating compound contains 1.19 g of the compound per liter of solution and has an osmotic pressure of 0.0288 atm at a temperature of 37°C. Compute the molar mass of the compound.

Solution

1.) use $\Pi = cRT$ or $c = \frac{\Pi}{RT}$

$$c = \frac{\Pi}{RT} = \frac{0.0288 \text{ atm}}{(0.0820 \text{ L atm mol}^{-1} \text{K}^{-1})(37 + 273.15\text{K})}$$

$$c = 1.132 \times 10^{-3} \text{ mol/l}$$

3.) Rearrange $M = \frac{g}{\text{mole}} = \frac{g}{l}$

$$M = \frac{1.19 g}{1.132 \times 10^{-3} \text{ mol/l}} = 1.05 \times 10^3 \text{ g/mol}$$
6-7 Mixtures and Distillations

• Raoult’s Law
  – Ideal Solutions
    • One volatile (the solvent)
    • One non-volatile (the solute)

\[ P_1 = X_1 P^\circ_1 \]

– Ideal Solutions
  • One volatile (the solvent)
  • One volatile (the solute)

\[ P_{\text{tot}} = P_1 + P_2 \]
– Ideal Solutions
  • One volatile (the solvent)
  • One volatile (the solute)

But…. For Real Solutions

• Henry’s Law (for dilute solutions)
  – The vapor pressure of a volatile in a sufficiently dilute solution is proportional to the mole fraction of the solute in the solution.

If component 2 is a sufficiently small value of the mole fraction, then

\[ k_H \] is Henry’s Law constant

\[ f (\text{Temp, and the solute-solvent interactions}) \]
Henry’s Law (for dilute solutions)

\[ P_2 = k_H X_2 \]

Dilute Solutions
- One volatile (the solvent)
- One dilute volatile (the solute)

According to Henry’s Law, as the pressure of a gas above a solution is increased, the mole fraction of the gas in solution increases in direct proportion.
Exercise 6-18

When the partial pressure of nitrogen over a sample of water at 19.4°C is 9.20 atm, then the concentration of nitrogen in the water is 5.76 x 10^{-3} mol L^{-1}. Compute Henry’s law constant for nitrogen in water at this temperature.

**Given**

\[ P_{N_2} = 9.20 \text{ atm} \]

\[ c_{N_2} = [N_2] = 5.76 \times 10^{-3} \text{ mol/l} \]

**Henry's Law**

\[ P_{N_2} = k_{N_2} X_{N_2} \]

\[ X_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{H_2}O} \approx \frac{n_{N_2}}{n_{H_2}O} \]
Exercise 6-18

When the partial pressure of nitrogen over a sample of water at 19.4°C is 9.20 atm, then the concentration of nitrogen in the water is $5.76 \times 10^{-3}$ mol L$^{-1}$. Compute Henry’s law constant for nitrogen in water at this temperature.

Given

$P_{N_2} = 9.20 \text{ atm}$

$c_{N_2} = [N_2] = 5.76 \times 10^{-3} \text{ mol/l}$

Henry's Law

$P_{N_2} = k_N X_{N_2}$

rarrange

$k_N = \frac{P_{N_2} X_{N_2}}{X_{N_2}}$ = \frac{\text{Given}}{\text{Find}}$

Next assume 1 Liter
Exercise 6-18

When the partial pressure of nitrogen over a sample of water at 19.4°C is 9.20 atm, then the concentration of nitrogen in the water is 5.76 x 10⁻³ mol L⁻¹. Compute Henry’s law constant for nitrogen in water at this temperature.

\[ k_N = \frac{P_N}{X_N} = \frac{\text{Given}}{\text{Find}} \]

\[ X_N \approx \frac{n_N}{n_{H_2O}} = \frac{5.76 \times 10^{-3} \text{ mol/l}}{\left( \frac{1000 \text{ g/l}}{18 \text{ g/mol}} \right)} = 1.0378 \times 10^{-4} \]

\[ k_N = \frac{P_N}{X_N} = \frac{\text{Given}}{\text{Find}} = \frac{9.20 \text{ atm}}{1.0378 \times 10^{-4}} = 8.86 \times 10^4 \text{ atm} \]
6-8 Colloidal Dispersions

• Colloids are large particles dispersed in solution
  – 1nm to 1000 nm in size
  – E.g., Globular proteins 500nm

• Examples
  – Opal (water in solid SiO₂)
  – Aerosols (liquids in Gas)
  – Smoke (solids in Air)
  – Milk (fat droplets & solids in water)
  – Mayonnaise (water droplets in oil)
  – Paint (solid pigments in liquid)
  – Biological fluids (proteins & fats in water)

• Characteristics
  – Large particle size colloids: translucent, cloudy, milky)
  – Small particle size colloids: can be clear
6-8 Colloidal Dispersions

– Tyndall Effect
  • Light Scattering
Chapter 6
Condensed Phases and Phase Transitions

Examples / Exercises
– All (6-1 thru 6-18)

Problems
– 4, 20, 26, 38, 44, 62