6. PHASE EQUILIBRIA

■ Number of Components and Degrees of Freedom

6.1. The region marked orthorhombic is a single-phase region. Since this is the phase diagram for pure sulfur, there is only one component. From the phase rule \( f = c - p + 2 \), with \( c = 1 \) and \( p = 1 \), the value of \( f \) is: \( f = 1 - 1 + 2 = 2 \). The two degrees of freedom are pressure and temperature. There is only one phase in the region marked monoclinic.

6.2. The compositions of the two phases at a particular temperature are: water saturated with nicotine, and nicotine saturated with water.

The number of degrees of freedom is
\[ f = c - p + 2 = 2 - 2 + 2 = 2 \]

This means that within the two-phase region, the temperature and weight percent may be varied without changing the two-phase character of the region.

6.3. a. For KCl and \( \text{H}_2\text{O} \) at the equilibrium pressure,
\[ f = c - p + 2 = 2 - 1 + 2 = 3 \]
Since the equilibrium pressure is specified, this reduces the number of degrees of freedom to 2.

b. Here, NaCl, KCl, and \( \text{H}_2\text{O} \) are present. This is actually a three-component system since the solution contains Na\(^+\), K\(^+\), Cl\(^-\), and \( \text{H}_2\text{O} \). The first three compositions are reduced to two independent ones by the electroneutrality condition. Therefore, \( f = c - p + 2 = 3 - 1 + 2 = 4 \), but with the restriction of constant pressure, the variance is reduced by 1, and is therefore 3.

c. Ice, water, and alcohol are only two components. Consequently, \( f = c - p + 2 = 2 - 2 + 2 = 2 \).

6.4. Aqueous sodium acetate is a two-component system even though the hydrolysis
\[
\text{Acetate}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HAc}
\]
takes place, since the equilibrium constant defines the concentration of OH\(^-\) and HAc if the concentration of sodium acetate is given.
6.5. Starting with pure CaCO$_3$, we have only one component present. When two of the three species are present, the third species is also present; but because of the equilibrium \( \text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2 \), there are only two components.

6.6. There are four individual gases, and the equilibrium equation reduces the number of independent components to three.

6.7. Use of the Lever Rule; Distillation

<table>
<thead>
<tr>
<th>( T/K )</th>
<th>( P/kPa )</th>
<th>Phases in Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>100</td>
<td>A, B, gas</td>
</tr>
<tr>
<td>300</td>
<td>300</td>
<td>A, B, liquid</td>
</tr>
<tr>
<td>400</td>
<td>400</td>
<td>B, liquid, gas</td>
</tr>
</tbody>
</table>

6.8. a. Wt % of B = \( \frac{99 \times 100}{33 + 99} = 75\% \)

From the graph at 75\% B, the first vapor appears at 60 °C.

b. The composition of the vapor is given by the intersection of the tie line at the vapor curve. In this case, the vapor has a composition of 88\% B.

c. The intersection of the liquid line at 65 °C corresponds to 53\% B in the liquid.

d. Using the average composition of the distillates as the value midway between initial and final composition of the distillates, we have

\[
\frac{1}{2}(88\% + 70\%) = 79\% \text{ B in distillate}
\]
Let \( W_R \) = mass of residue; \( W_D \) = mass of distillate

\[ W_R + W_D = 132 \]

Then, applying the condition that B is distributed through residue and distillate, we have

mass of B in residue + mass of B in distillate = 99 g.

\[ 0.53W_R + 0.79W_D = 99 \]

\[ 0.53(132 - W_D) + 0.79W_D = 99 \]

\[ 0.26W_D = 29 \]

\[ W_D = 111.5 \text{ g}; \quad W_R = 132 - 111.5 = 20.5 \text{ g} \]

In the distillate, therefore, 79% of 111.5 g or 88.1 g is component B, and 111.5 – 88.1 = 23.4 g is component A.

6.9. From Figure 6.14, the composition at 350 K at equilibrium between the single-phase water-rich region and the two-phase region is approximately 10% nicotine. For the equilibrium value on the nicotine-rich side, the value is approximately 75% nicotine. Using the lever rule, we have

\[ \frac{\text{Mass of water-rich layer}}{\text{Mass of nicotine-rich layer}} = \frac{75 - 40}{40 - 10} = \frac{35}{30} = 1.2 \]

6.10. From Eq. 6.21, since \( w = nM \), we write

\[ \frac{w_A}{w_B} = \frac{n_AM_A}{n_BM_B} = \frac{P_A^*M_A}{P_B^*M_B} \quad \text{or} \quad M_A = \frac{P_B^*w_AM_B}{P_A^*w_B} \]

The vapor pressure of pure chlorobenzene is 56.434 – 43.102 = 13.332 kPa. Substitution gives

\[ M_{\text{chlorobenzene}} = \frac{43.102}{13.334} (1.93) 18.02 = 112.4. \]

The value obtained by addition of relative atomic masses is 112.6.

6.11. a. The total pressure is: \( P = P_1 + P_2 \)

From Raoult’s law

\[ P_1 = x_1P_1^* \]

\[ P = x_1P_1^* + P_2 \quad \text{but} \quad P_2 = (1 - x_1)P_2^* \]

\[ = x_1P_1^* + (1 - x_1)P_2^* = x_1P_1^* + P_2^* - x_1P_2^* \]

\[ = P_2^* + (P_1^* - P_2^*)x_1 \]

This is Eq. 6.9.
b. From Eq. 6.8, \( y_1 = \frac{P_1}{P} = x_1 \frac{P^*_1}{P} \), upon solution of \( P \) just derived,

\[
y_1 = \frac{x_1 P^*_1}{P^*_2 + (P^*_1 - P^*_2)x_1}
\]

or solving for \( x_1 \) gives

\[
x_1 P^*_1 = y_1 P^*_2 + y_1(P^*_1 - P^*_2)x_1
\]

\[
y_1 P^*_2 = [P^*_1 - (P^*_1 - P^*_2)]x_1
\]

\[
x_1 = \frac{y_1 P^*_2}{P^*_1 + (P^*_2 - P^*_1)y_1}
\]

Then substitution of \( x_1 \) into Eq. 6.9 gives

\[
P = P^*_2 + (P^*_1 - P^*_2)
\]

\[
= \frac{P^*_2 [P^*_1 + y_1 P^*_2 - y_1 P^*_1 P^*_2]}{P^*_1 + (P^*_2 - P^*_1)y_1}
\]

Upon expanding and cancellation, we have Eq. 6.11.

6.12. To determine the masses of the material distilled, the numerator of Eq. 6.21 is multiplied by \( M_A \) and the denominator by \( M_B \). Since \( w = nM \),

\[
\frac{w_A}{w_B} = \frac{n_A M_A}{n_B M_B} = \frac{P^*_A M_A}{P^*_B M_B}
\]

6.13. The vapor pressure of water at 372.4 K is 98.805 kPa. The vapor pressure of naphthalene is therefore 101.325 kPa – 98.805 kPa = 2.52 kPa. The molar mass of naphthalene is 128.19 g mol\(^{-1}\). From the modified Eq. 6.21, we have

\[
w_{H_2O} = \frac{P^*_H2O M_{H2O}}{P_{naphth} M_{naphth}}
\]

\[
w_{H_2O} = \frac{98.805 \text{ kPa} (18.02 \text{ g})}{2.52 \text{ kPa} (128.19 \text{ g})} = 5.51 \text{ kg}
\]

6.14. The vapor pressure of chlorobenzene is 56.434 – 43.102 = 13.332 kPa. From Problem 6.12,

\[
\frac{\text{Mass of chlorobenzene}}{\text{Mass of water}} = \frac{13.332 \times 0.1125}{43.102 \times 0.01802} = 1.93
\]

The sample contains 1.93 g of chlorobenzene for each 1.00 g of water.

6.15. Using Eq. 6.18 and letting isobutyl alcohol be component 1, we have
6.16. Take the logarithms of both sides of \( \rho = \frac{m}{V} \): \( \ln \rho = \ln m - \ln V \). Partial differentiation with respect to \( T \) gives
\[
\left( \frac{\partial \ln \rho}{\partial T} \right)_p = -\left( \frac{\partial \ln V}{\partial T} \right)_p = -\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = -\alpha
\]

6.17. From the previous problem,
\[
\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \left( \frac{\Delta V}{\Delta T} \right)_p
\]
for small changes in \( V \) and \( T \). For an arbitrary quantity of water, say 1 gram exactly, the equation \( V = \frac{m}{\rho} \) gives \( V = 1.001\,769\,769 \) cm\(^3\) at 20 °C and \( V = 1.001\,982\,982 \) cm\(^3\) at 21 °C and 1 atm.

Using these values we have
\[
\alpha = \frac{1}{1.001\,769\,769} \left( \frac{1.001\,982\,982 - 1.001\,769\,769}{1\,K} \right) = \frac{0.000\,213}{1.001\,769\,769\,K} = 0.000213\,\text{K}^{-1}
\]

\[
\alpha \kappa = \frac{2.85 \times 10^{-4}\,\text{K}^{-1}}{4.49 \times 10^{-5}\,\text{atm}^{-1}} \times 6\,\text{K} = 38.1\,\text{atm}.
\]

6.20. Application of the lever rule gives
\[
\frac{\text{Mass of solid layer}}{\text{Mass of solid + liquid layer}} = \frac{\overline{se}}{be} = 0.18 = 0.58
\]
or 58% solid and 42% liquid in the two-phase region. The overall composition of the liquid above the liquidus line is \( x_{Si} = 0.31 \).
6.21. The temperature at which solid solvent is in equilibrium with liquid solvent of mole fraction $x_1$ is given by Eq. 5.115:

$$\ln x_1 = \frac{\Delta_{\text{fus}} H_m}{R} \left( \frac{1}{T_f^*} - \frac{1}{T} \right)$$

Values of $x_1$ and $T$ determined from this equation for each component give the desired liquidus lines in the regions near large values of $x_1$. Several values are:

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$T/K$</th>
<th>$x_1$</th>
<th>$T/K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.945</td>
<td>1650</td>
<td>0.969</td>
<td>1300</td>
</tr>
<tr>
<td>0.863</td>
<td>1600</td>
<td>0.924</td>
<td>1250</td>
</tr>
<tr>
<td>0.784</td>
<td>1550</td>
<td>0.879</td>
<td>1200</td>
</tr>
<tr>
<td>0.708</td>
<td>1500</td>
<td>0.783</td>
<td>1100</td>
</tr>
<tr>
<td>0.564</td>
<td>1400</td>
<td>0.681</td>
<td>1000</td>
</tr>
</tbody>
</table>

A plot is shown on which the points represent the data points and the solid curves are experimental curves of Figure 6.16. The dotted lines intersect at about $x_{\text{Si}} = 0.28$ compared to the actual $x_{\text{Si}} = 0.31$. However, the eutectic temperature is approximately 400 K too high.
6.22. We graph the data to generate a phase diagram of the phenol-water system:

![Phenol-Water Phase Diagram]

**a.** The tie lines drawn through the point (a) indicate that the two layers will have compositions 8.9% phenol and 70.0% phenol by mass, respectively (data at 30°C).

**b.** The point (b) lies in a region of the diagram where only one phase is present.

**c.** Two phases appear at 63.0°C. The composition of the layers will be 19.6% phenol and 52.5% phenol by mass, respectively.
6.23. Each halt corresponds to a line of three-phase equilibrium and each break to a boundary between a one- and a two-phase region. At 50% $Y_2O_3$, a compound is formed and may be written as $Fe_2O_3\cdot Y_2O_3$ or $YFeO_3$.

A compound unstable above 1575°C is indicated between 30 and 40% $Y_2O_3$. This might be taken to be $2Fe_2O_3\cdot Y_2O_3$ at 33% $Y_2O_3$, but actually the formula is $Y_3Fe_5O_{12}$, corresponding to $3Y_2O_3 + 5Fe_2O_3$ at 37% $Y_2O_3$. 
By extending the smooth curves drawn through the given data points to the eutectic temperature, the composition of the eutectic (marked with a symbol on the graph) is identified as 26 wt. % Au

6.25.  

b.  As liquid of 28 mass % MnO cools, $\beta$ first forms along with liquid. At 1430 °C, $\beta$ converts to $\alpha$ and $\alpha + L$ remain only briefly as the temperature is lowered about 50 °C, at which point all the liquid is reconverted to the $\alpha$ phase. The compositions are given by the lever rule. As 1200 °C is approached, some $\beta$ may again make an appearance.
6.26. From the graph, the first eutectic (680 °C) has a composition of 10.5 wt. % Mg, the second (560 °C), a composition of 35.0 wt. % Mg while the third (360 °C) has a composition of 65 wt. % Mg.

6.27 Assuming that there are 100 g of the first compound, we have 16.05 g Mg and 83.95 g Cu. The mole ratios of Mg : Cu are

\[
\frac{16.05}{24.305} : \frac{83.95}{63.546} = 0.660 : 1.321.
\]

Dividing both sides by the smallest number (i.e., 0.660), we get

\[
1 : \frac{1.321}{0.660} = 1 : 2.001.
\]

Therefore, the empirical formula of the first compound is MgCu₂. Proceeding in a similar manner, we find that the second compound has an empirical formula Mg₂Cu.
6.28. The diagrams are self-explanatory. The coexistence of the three phases is a clear indication of a peritectic-type diagram. A note of caution is in order here, however. In the range 0–10 mol % Au at 1430 °C to 1536 °C, still another phase, called δ, exists; and this would not be detected using only the compositions listed. One must be careful to use enough compositions to ensure that all the phases are identified. Also, the equilibrium between liquid and γ is not a simple curve and must be determined by careful experimentation.
6.29.

![Phase diagram for Al-Se system](image)

6.30. The diagram is self-explanatory. The lower phase field of the α-phase is less than 1%.

a.

![Phase diagram for Al-Ca system](image)
b.

![Graph showing the phase changes of a system with Ca and Al2Ca phases at different liquid compositions (15 mol% Ca and 80 mol% Ca).](image)

6.31.

![Graph showing the phase changes of a system involving CuSO4 and its hydrates at different temperatures.](image)
In the upper figure, the dilute CuSO₄ begins in a solution single-phase region. Pure CuSO₄·5H₂O precipitates out as the first phase boundary at a is crossed. Water continues to be removed as more CuSO₄·5H₂O precipitates until only pure CuSO₄·5H₂O is present at b. In the next two-phase region, CuSO₄·5H₂O dehydrates, forming progressively more CuSO₄·3H₂O until all of the pentahydrate is gone at c. The process repeats, the trihydrate forming the monohydrate until only monohydrate is present at d. The monohydrate dehydrates until at e only pure CuSO₄ is present.

In the lower figure, the vapor pressure of water drops as the amount of CuSO₄ increases (Raoult’s law) until the solution is saturated with respect to the pentahydrate. The system is invariant since three phases, vapor, saturated solution, and solid CuSO₄·5H₂O, are present at the constant temperature of 298.15 K. As the concentration of CuSO₄ increases (water is removed), the pressure remains constant until only CuSO₄·5H₂O is present. Removal of additional water causes some trihydrate to form, and the pressure drops. Again the system is invariant; three phases are present, vapor, CuSO₄·5H₂O, and CuSO₄·3H₂O. The process is continued as before at the other stages.

6.32. The system CaO–MgO–SnO₂:
6.33.

- Stable triple point R (red phosphorus, solid), liquid (L), vapor (V).
- Metastable triple point W (white phosphorus, solid), L, V. (The vapor pressure of the white form is greater than that of the red form.)
- Stable triple point W, R, L. If we assume that a solid cannot be superheated, the triple point W, R, L is totally unstable since it probably lies above the melting point of the liquid.

6.34.
6.35. The 500 K equilibrium line probably contains a eutectic since the temperature is below the melting points of both \( AB_2 \) and B. An unstable compound is ruled out because such a reaction would require cooling halts at both 900 K and 500 K. Instead, a peritectic reaction shown is the simplest explanation.

![Phase Diagram](image)

### Data Derived from Phase Diagrams of Condensed Systems

6.36. a. As water is added, the saturated liquid of composition \( b \) would be in equilibrium with two solids A and B. At approximately 20% C, when the composition crosses the line \( \delta B \), the solid A disappears and only solid B will be present in equilibrium with liquid of composition \( b \).

b. The two solid phases would not disappear until \( b \) is passed at approximately 50% liquid.

c. Added water will cause dilution and solid salt will cease to exist.

6.37. a. Peritectic point

b. Eutectic point

c. Melting point

d. Incongruent melting

e. Phase transition
6.38. As liquid is cooled, solid spinel first appears at about 1950 K in equilibrium with liquid. At approximately 1875 K, all of the liquid converts to solid spinel, the composition of which varies according to the lever rule. As the temperature falls to about 1400 K, a two-phase region appears that is Mn$_3$O$_4$ + spinel. Below about 1285 K, the spinel converts to corundum and Mn$_3$O$_4$ + corundum coexist.

6.39. The composition of the system is 30 mol % acetic acid, 50 mol % water, and 20 mol % toluene. The system point is practically on the $p'q''$ tie line, and there are therefore two liquids present. The ends of this line and thus the concentrations of the two liquids are approximately:

a. 95.5% toluene, 4% acetic acid, 0.5% H$_2$O and

b. 1% toluene, 37% acetic acid, and 62% H$_2$O.

The relative amounts of the two liquids are given by the lever rule:

$$\frac{15.4B}{3.8A} \text{ or } 4B \text{ to } 1A$$
It is clear from the phase diagram that A and C are only slightly soluble in each other in the absence of B. As B is added, two layers are formed, one rich in A and the other, rich in C. As B is added, the mutual solubility of A and C increases until at 30 mole % in B, the three liquids become miscible in all proportions.
a. Region System

<table>
<thead>
<tr>
<th>Region</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>$AEa$</td>
<td>$K_2CO_3$ in equilibrium with water-rich saturated solution</td>
</tr>
<tr>
<td>$Aac$</td>
<td>$K_2CO_3$ in equilibrium with conjugate liquids a and c</td>
</tr>
<tr>
<td>$abc$</td>
<td>Two conjugate liquids joined by tie lines</td>
</tr>
<tr>
<td>$AcB$</td>
<td>$K_2CO_3$ in equilibrium with alcohol-rich saturated solution</td>
</tr>
</tbody>
</table>

b. The state of the system will move along a line joining $x$ and $A$. Initially solution is formed; as more $K_2CO_3$ is added two layers $a$ and $c$ form, and once beyond point $z$, $K_2CO_3$ ceases to dissolve so that solid $K_2CO_3$ and the two liquids $a$ and $c$ coexist.

c. As long as two liquids exist, liquid with composition in the region $AcB$ is the alcohol-rich layer and may be separated from the water-rich layer by separatory funnel.

d. When water is added to an unsaturated solution of $K_2CO_3$ in alcohol, the state of the system moves along the line joining $y$ and $D$. Some $K_2CO_3$ will precipitate as the state moves into the $ABc$ region and then redissolves as it moves into the solution region again.

e. On evaporation of $F$, the system composition follows a line drawn from the water corner through $F$ to the $Ac$ line. At the first composition line, two liquids form and the compositions of the solutions move toward $a$ and $c$. When the system composition reaches the $ac$ line, $K_2CO_3$ begins to precipitate and is in equilibrium with the conjugate liquids $a$ and $c$. Further reduction of water moves the ratio of liquid $a$ to liquid $c$ in favor of $c$ until the line $Ac$ is crossed, at which time solid $K_2CO_3$ is in equilibrium with a single solution.