314: Thermodynamics of Materials

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Contents

1 314: Thermodynamics of Materials 4

2 Introduction 4

3 Big Ideas of Thermo 5
   3.1 Classification of Systems ................................. 5
   3.2 State Variables ............................................ 7
   3.3 Process Variables ........................................... 7
      3.3.1 Work Done by an External Force .................... 7
      3.3.2 Work Done by an Applied Pressure ................ 9
   3.4 Extensive and Intensive Props. ............................ 9

4 The Laws of Thermodynamics 10
   4.1 First Law .................................................. 10
   4.2 Second Law ................................................ 11
      4.2.1 Reversible and Irreversible Processes ............ 12
      4.2.2 Entropy and Heat .................................... 13
   4.3 Third Law ................................................ 13
   4.4 Differential Quantities .................................. 15

5 Thermodynamic Variables 16
   5.1 Enthalpy .................................................. 16
   5.2 Helmholtz Free Energy .................................... 17
   5.3 Gibbs Free Energy ......................................... 17
   5.4 Other Material Properties ................................ 18
      5.4.1 Volume thermal expansion coefficient ............ 18
      5.4.2 Isothermal Compressibility ....................... 18
      5.4.3 Heat Capacity ........................................ 18
   5.5 Coefficient Relations .................................... 19
      5.5.1 Internal Energy ........................................ 21
### CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5.2</td>
<td>Enthalpy</td>
<td>22</td>
</tr>
<tr>
<td>5.5.3</td>
<td>Helmholtz Free Energy</td>
<td>22</td>
</tr>
<tr>
<td>5.5.4</td>
<td>Gibbs Free Energy</td>
<td>22</td>
</tr>
<tr>
<td>5.6</td>
<td>Equation of State</td>
<td>22</td>
</tr>
<tr>
<td>5.6.1</td>
<td>Expression for $dS$</td>
<td>22</td>
</tr>
<tr>
<td>5.6.2</td>
<td>Expression for $dV$</td>
<td>23</td>
</tr>
<tr>
<td>5.6.3</td>
<td>Relationship between $C_P$ and $C_V$</td>
<td>23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>The Ideal Gas</td>
<td>24</td>
</tr>
<tr>
<td>6.1</td>
<td>Thermal Expansion Coefficient</td>
<td>24</td>
</tr>
<tr>
<td>6.2</td>
<td>Compressibility</td>
<td>25</td>
</tr>
<tr>
<td>6.3</td>
<td>Internal Energy</td>
<td>25</td>
</tr>
<tr>
<td>6.4</td>
<td>Specific Heat</td>
<td>26</td>
</tr>
<tr>
<td>6.5</td>
<td>Examples</td>
<td>26</td>
</tr>
<tr>
<td>6.5.1</td>
<td>Free expansion of an ideal gas</td>
<td>26</td>
</tr>
<tr>
<td>6.5.2</td>
<td>Isothermal Compression of an Ideal Gas</td>
<td>28</td>
</tr>
<tr>
<td>6.5.3</td>
<td>Reversibility requires work/heat</td>
<td>28</td>
</tr>
<tr>
<td>6.5.4</td>
<td>Some useful relations for heat flow</td>
<td>30</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Solids and Liquids</td>
<td>33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Conditions for Equilibrium</td>
<td>39</td>
</tr>
<tr>
<td>8.1</td>
<td>Finding equilibrium conditions</td>
<td>42</td>
</tr>
<tr>
<td>8.2</td>
<td>Energy Minima</td>
<td>43</td>
</tr>
<tr>
<td>8.3</td>
<td>Maxwell Relations</td>
<td>45</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>From Microstates to Entropy</td>
<td>46</td>
</tr>
<tr>
<td>9.1</td>
<td>Microstates and Macrostates</td>
<td>47</td>
</tr>
<tr>
<td>9.1.1</td>
<td>Postulate of Equal Likelihood</td>
<td>49</td>
</tr>
<tr>
<td>9.1.2</td>
<td>The Boltzmann Hypothesis (to be derived)</td>
<td>50</td>
</tr>
<tr>
<td>9.2</td>
<td>Conditions for equilibrium</td>
<td>50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Noninteracting (Ideal) Gas</td>
<td>53</td>
</tr>
<tr>
<td>10.1</td>
<td>Ideal gas Law</td>
<td>54</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Diatomic Gases</td>
<td>55</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>Einstein Model</td>
<td>56</td>
</tr>
<tr>
<td>12.1</td>
<td>Thermodynamic Properties</td>
<td>56</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>Unary Heterogeneous Systems</td>
<td>58</td>
</tr>
<tr>
<td>13.1</td>
<td>Phase Diagrams</td>
<td>59</td>
</tr>
<tr>
<td>13.2</td>
<td>Chemical Pot. Surfaces</td>
<td>59</td>
</tr>
<tr>
<td>13.3</td>
<td>$\mu(T, P)$ Surfaces</td>
<td>62</td>
</tr>
<tr>
<td>13.4</td>
<td>Clasius-Clapeyron Eq.</td>
<td>63</td>
</tr>
<tr>
<td>13.4.1</td>
<td>Step 1: Find $\Delta H(T, P)$</td>
<td>64</td>
</tr>
</tbody>
</table>
13.4.2  Step 2: Find $\Delta V^\alpha\to\beta(T, P) \equiv V^\beta(P, T) - V^\alpha(P, T)$ . . . . 65
13.4.3  Justification for Approximations ................................................. 66
13.4.4  Trouton’s Rule ................................................................. 66

14  Open Multicomponent Systems .................................................. 68
   14.1  Partial Molal Properties ......................................................... 68
   14.2  Gibbs-Duhem Eq. ................................................................. 69
   14.3  The Mixing Process ............................................................. 70
   14.4  Graphical Determination ....................................................... 72
   14.5  Relationships ..................................................................... 73
   14.6  Chemical Potential ............................................................. 74
   14.7  Activity ............................................................................. 74
   14.8  Ideal Solutions .................................................................. 75
   14.9  Dilute Solutions .................................................................. 76
   14.10 Excess Properties .............................................................. 78
   14.11 Regular Solutions .............................................................. 78
   14.11.1 Mixtures of Real Gases: Fugacity .......................................... 82

15  Multicomponent Heterogeneous Systems ...................................... 84
   15.1  Equilibrium ....................................................................... 85
   15.2  Gibbs Phase Rule ................................................................. 85

16  Phase Diagrams ............................................................................. 86
   16.1  Unary Phase Diagrams .......................................................... 87
   16.2  Alternative Representations .................................................. 87
   16.3  Binary Phase Diagrams .......................................................... 88
   16.4  Alternative Representations: $T$ vs. $X$ ..................................... 88
   16.5  Interpreting Phase Diagrams: Tie Lines .................................... 89
   16.6  The Lever Rule .................................................................... 90
   16.7  Applications of Phase Diagrams: Microstructure Evolution ...... 90
   16.8  Review .............................................................................. 91
   16.9  Types of $\alpha - L$ phase diagrams ........................................ 92

17  Phase Diagrams ............................................................................. 92
   17.1  Calculation of $\Delta G_{mix}$ ..................................................... 93
   17.2  Common Tangent Construction .............................................. 94
   17.3  A Monotonic Two-Phase Field .............................................. 96
   17.4  Non-monotonic Two-Phase Field .......................................... 96
   17.5  Regular Solutions ................................................................ 97
   17.6  Miscibility Gap ................................................................... 97
   17.7  Spinodal Decomposition ....................................................... 98

18  Summary of 314 .......................................................................... 101
   18.1  Chapters 2 and 3 ................................................................. 101
   18.2  Chapter 4 .......................................................................... 101
   18.3  Chapter 5 .......................................................................... 102
2 INTRODUCTION

Catalog Description

Classical and statistical thermodynamics; entropy and energy functions in liquid and solid solutions, and their applications to phase equilibria. Lectures, problem solving. Materials science and engineering degree candidates may not take this course for credit with or after CHEM 342 1. (new stuff)

Course Outcomes

1 314: Thermodynamics of Materials

At the conclusion of the course students will be able to:

1) articulate the fundamental laws of thermodynamics and use them in basic problem solving.

2) discriminate between classical and statistical approaches.

3) describe the thermal behavior of solid materials, including phase transitions.

4) use thermodynamics to describe order-disorder transformations in materials.

5) apply solution thermodynamics for describing liquid and solid solution behavior.

2 Introduction

The content and notation of these notes is based on the excellent book, “Thermodynamics in Materials Science”, by Robert DeHoff [2]. The notes provided
here are a complement to this text, and are provided so that the core curriculum of the undergraduate Materials Science and Engineering program can be found in one place (http://msecore.northwestern.edu/). These notes are designed to be self-contained, but are more compact than a full text book. Readers are referred to DeHoff’s book for a more complete treatment.

3 Big Ideas of Thermodynamics

The following statements sum up some of foundational ideas of thermodynamics:

- **Energy** is conserved
- **Entropy** is produced
- **Temperature** has an absolute reference at 0 - at which all substances have the same entropy

3.1 Classification of Systems

Systems can be classified by various different properties such as constituent phases and chemical components, as described below.

- Chemical components
  - **Unary system** has one chemical component
  - **Multicomponent system** has more than one chemical component

![Figure 3.1: Unary system (left) and multicomponent system (right).](image)

- Phases
  - **Homogeneous system** has one phase
  - **Heterogeneous system** has more than one phase

- Energy and mass transfer: closed and open systems:
3.1 Classification of Systems

An isolated system cannot change energy or matter with its surroundings.
Closed system can exchange energy but not matter with its surroundings.
Open system can exchange both energy and matter with its surroundings.

Figure 3.3: Open, closed and isolated thermodynamic systems.

- Reactivity
  - Non-reacting system contains components that do not chemically react with each other
  - Reacting system contains components that chemically react with each other

Another classification is between simple and complex systems. For instance, complex systems may involve surfaces or fields that lead to energy exchange.
3.2 Thermodynamic State Variables

Thermodynamic state variables are properties of a system that depend only on current condition, not history. Temperature, $T$, is an obvious example, since we know intuitively that the temperature in a room has the same meaning to us, no matter what the previous temperature history actually was. Other state variables include the pressure, $P$, and the system volume, $V$. For example, two states $A$ and $A'$, each with their own characteristic values of $P, V$ and $T$:

$$A \rightarrow A'$$

$$P, V, T \rightarrow P', V', T'$$

(3.1)

The values of the pressure difference $\Delta P = P' - P$ is independent of the path that the system takes to move from state $A$ to $A'$. The same is true for $\Delta V$ and $\Delta T$. Note that because state variables are often functions of other variables, they are often referred to as state functions of these other variables. For our purposes the terms ‘state function’ and ‘state variable’ can be used interchangeably.

3.3 Process Variables

Work and heat are examples of process variables.

Work ($W$) - Done on the system. Note that our sign convention here is that work done ON the system is positive.

Heat ($Q$) - Absorbed or emitted. The sign convention in this case is that heat absorbed by the system is positive.

Their values for a process depend on the path.

3.3.1 Work Done by an External Force

The work done by an external force is the force multiplied by distance over which the force acts. In other words, the force only does work if the body it is pushing against actually moves in the direction of the applied force. In differential form we have:

$$\delta W = \vec{F} \cdot d\vec{x}$$

(3.2)

Note that $\vec{F}$ and $d\vec{x}$ are vector quantities, but $W$ is a scalar quantity. As a reminder, the dot product appearing in Eq. 3.2 is defined as follows:
\[ \vec{A} \cdot \vec{B} = |\vec{A}| |\vec{B}| \cos \theta \] (3.3)

where \( \theta \) is the angle between the two vectors, illustrated in Figure 3.5.

![Figure 3.5: Definition of the angle \( \theta \) between two vectors.](image)

The total work is obtained by integrating \( \delta W \) over the path of the applied force:

\[ W = \int_{\text{path}} \vec{F} \cdot d\vec{x} \] (3.4)

For example, when we lift a barbell from the floor to the table as illustrated in Figure 3.6 we increase the gravitational potential energy, \( U \), of the barbell by an amount \( mgh \), where:

- \( m \) = the mass of the barbell
- \( g \) = the gravitational acceleration (9.8 m/s\(^2\))
- \( h_f \) = the final resting height of the barbell above the floor

Because the potential energy only depends only on the final resting location of the barbell, it is a state variable. The work we expend in putting the barbell there depends on the path we took to get it there, however. As a result this work is NOT a state function. Suppose, for example that we lift the barbell to a maximum height \( h_{\text{max}} \) and then drop it onto the table. The work, \( W \), we expended is equal to \( mgh_{\text{max}} \), which is greater than the increase in potential energy, \( \Delta U \). The difference between between \( W \) and \( \Delta U \) is the irreversible work and corresponds to energy dissipated as heat, permanent deformation of the table, etc. We’ll return to the distinction between reversible and irreversible work later.

![Figure 3.6: Work done on a barbell.](image)
3.3.2 Work Done by an Applied Pressure

Another important example of work is the work done by an external force in changing the volume of the system that is under a state of hydrostatic pressure. The easiest and most important example to describe is a gas that is being compressed by a piston as shown in Figure 3.7. Equation 3.2 still applies in this case, but the force in this case is given by the product of the area and pressure:

\[ \vec{F} = P \vec{A} \]  

(3.5)

It may seem strange to write the area as a vector, but it is just reminding us that the pressure acts perpendicular to the surface, so the direction of \( \vec{A} \) is perpendicular to the surface of the piston. Combining Eq. 3.5 with Eq. 3.2 gives:

\[ \delta W = P \vec{A} \cdot d\vec{x} \]  

(3.6)

The decrease in volume of the gas is given by \( \vec{A} \cdot d\vec{x} \), so we can replace \( \vec{A} \cdot d\vec{x} \) with \(-dV\) to obtain:

\[ \delta W = -P dV \]  

(3.7)

This result is an important one that we will use quite a bit later on.

Figure 3.7: Work done by force on a piston.

3.4 Extensive and Intensive Properties

Extensive properties depend on size or extent of the system. Examples include the volume \( (V) \), mass \( (m) \) internal energy \( (U) \) and the entropy \( (S) \). Intensive properties are defined at a point, with examples including the temperature \( (T) \) and the pressure \( (P) \) and the mass density, \( \rho \).

Extensive properties can be defined as integrals of intensive properties. For example the mass is obtained by integration of the mass density over the total volume:
Also, intensive properties can be obtained from combinations of extensive properties. For example, $C_k$, the molar concentration of component $k$, is the ratio of two extensive quantities: $n_k$ the total number of moles of component $k$ and the volume:

$$C_k \equiv \lim_{V \to 0} \frac{n_k}{V} \quad (3.9)$$

This approach works for the density as well, with the mass density, $\rho$, given by the ratio of the sample mass, $m$, to the sample volume, $V$:

$$\rho \equiv \lim_{V \to 0} \frac{m}{V} \quad (3.10)$$

## 4 The Laws of Thermodynamics

### Outcomes for this section:

1) State the first, second and third laws of thermodynamics.

2) Write a combined statement of the first and second laws in differential form.

3) Given sufficient information about how a process is carried out, describe whether entropy is produced or transferred, whether or not work is done on or by the system, and whether heat is absorbed or released.

4) Quantitatively relate differentials involving heat transfer/production, entropy transfer/production, and work.

### 4.1 First Law of Thermodynamics

The **first law of thermodynamics** is that energy is conserved. This means that the increase in the internal energy of the system is equal to the sum of the heat flow, the work done on the system and the heat flow into the system. In mathematical terms:

$$\Delta U = Q + W + W' \quad (4.1)$$

where:
4.2 Second Law

The second law of thermodynamics states that entropy can be transferred or produced, but not destroyed, so the total entropy change in the universe ($\Delta S_{uni}$) cannot be negative:

$$\Delta S_{uni} \geq 0$$ (4.2)

Here $\Delta S_{uni}$ includes the system of interest and its surroundings, as illustrated in Figure 4.2.

$$\Delta S_{uni} = [\Delta S_t + \Delta S'_p] + [\Delta S'_t + \Delta S_p]$$ (4.3)

We write the entropy this way to differentiate between entropy produced in the system and surroundings ($\Delta S_p$ and $\Delta S'_p$) and entropy that is transferred between the system and surroundings ($\Delta S_t$ and $\Delta S'_t$):

- $\Delta S_p$: entropy produced in the system
- $\Delta S'_p$: entropy produced in the surroundings
- $\Delta S_t$: entropy transferred to the system
- $\Delta S'_t$: entropy transferred to the surroundings
4.2 Second Law

The entropy change for a process can only be zero (for a reversible process) or positive (for an irreversible process) in the universe at large, which includes the systems and the surroundings. In mathematical terms:

\[ \Delta S_{uni} = \Delta S'_p + \Delta S_p \geq 0 \] (4.4)

For infinitesimal changes (very small \( \Delta \)), we replace \( \Delta \) with the differential, \( d \). We do this because we can always obtain the total change in a quantity, \( \Delta \), by integrating over the differential. For example, to calculate the entropy difference between state \( A \) and state \( B \) we have:

\[ \Delta S_{sys} [A \rightarrow B] = \int_A^B dS_{sys} \] (4.5)

That that while the overall entropy change (system + surroundings) cannot be negative, the system entropy change can be negative, if is compensated for by an appropriate increase in the entropy of the surroundings. In differential terms, \( dS_{sys} = dS_t + dS_p \) where \( dS_{sys} \) can be negative.

4.2.1 Reversible and Irreversible Processes

Irreversible processes produce entropy, whereas reversible processes (an idealization) do not. Entropy necessarily increases over time. The rate of entropy production is one measure of how far we are from equilibrium.

Processes carried out very slowly, and which remain very close to equilibrium approach the ideal of reversibility. A perfectly reversible process is extremely useful for calculations, and has the following characteristics.

- No entropy is produced
No permanent changes take place in the universe

To compute differences in state functions, for example the specific path between state $A$ and state $B$ in Eq. 4.5 one can chose the simplest path between the two states, which is the reversible path.

### 4.2.2 Entropy and Heat

The second law of thermodynamics is defined in terms of entropy, but we haven’t yet defined what entropy really is. The statistical approach described in Section 9 on page 46 will shed some light on entropy, but for now we will just introduce the following simple but remarkably important relationship between a differential change in the heat content and the differential change in the entropy:

$$dS = \frac{\delta Q}{T} \tag{4.6}$$

This equation a mathematical statement of the second law of thermodynamics. Qualitatively, it is easy to see that Eq. 4.6 is consistent with what know from common experience. For example, we know that a metal bar that is hot at one end and cold at the other end is not at equilibrium, since over time heat will flow from the hot end to the cold end. Consider a simplistic model of this where heat is flowing between one region at a temperature of $T_1$, and a second region at a temperature $T_2$, with $T_2 > T_1$. When a certain heat increment $\delta Q$ moves from region 1 to 2, the entropy in region 1 decreases by $\delta Q/T_1$, while the entropy in region 2 increases by $\delta Q/T_2$. The net change in entropy is given:

$$\delta S = \frac{\delta Q}{T_2} - \frac{\delta Q}{T_1} \tag{4.7}$$

This is positive whenever $T_1 > T_2$, which is consistent with our starting point where the heat was moving from region 1 to region 2. So when heat moves from a hot region to a cold region, the entropy increases, as we know it must for a non-equilibrium process.

### 4.3 Third Law of Thermodynamics

The third law of thermodynamics states that there is an absolute lower limit to the temperature of matter, and the entropy of all substances is the same at that temperature. In more practical terms, $S = 0$ at $T=0K$ (absolute zero) for all materials.

The fact that we can use absolute zero as a reference temperature for the entropy is quite useful in a variety of situations. It can be used, for example, to
provide information about the nature of a chemical reaction. Consider, for example, the following simple chemical reaction, where silicon reacts with carbon to form silicon carbide:

\[ \text{Si} + \text{C} \rightarrow \text{SiC} \]

Consider the following 4-step process, which begins and ends with Si and C as separate elements at T=0K (see Fig. 4.3):

- I: Heating Si and C from 0K to the reaction temperature, \( T_1 \).
- II: Reaction of Si and C to form SiC at \( T = T_1 \)
- III: Cooling the SiC from \( T_1 \) to 0K.
- IV: A (hypothetical) splitting of the SiC back into Si and C at 0K.

Because we start and end at the same place, and because entropy is a state function, the overall entropy for the cyclic process consisting of all 4 steps is equal to zero:

\[ \Delta S_{\text{cyc}} = \Delta S_I + \Delta S_{II} + \Delta S_{III} + \Delta S_{IV} = 0 \]  \hspace{1cm} (4.8)

We also know that \( \Delta S_{IV} = 0 \), since the reaction takes place at =0K, where all materials have \( S = 0 \). As a result we have:

\[ \Delta S_{II} = -\Delta S_I - \Delta S_{III} \] \hspace{1cm} (4.9)

Figure 4.3: Cyclic process involving formation of silicon carbide.
The quantity $\Delta S_I$ is the difference between the entropy of the starting compounds (Si and C) at $T_1$, compared to the value of the entropy of these compounds at 0K, so $\Delta S_I$ is simply $S_{Si} + S_C$. Similarly, $\Delta S_{III} = -S_{SiC}$, with the negative sign arising from the fact that process III corresponds to a reduction in the temperature from $T_1$ to 0K. Finally, $\Delta S_{II}$ is the entropy change associated the SiC-forming reaction, so we have:

$$\Delta S_{Si+C\rightarrow SiC} (T_1) = S_{SiC} (T_1) - S_{Si} (T_1) - S_C (T_1) \quad (4.10)$$

So $\Delta S$ for the reaction is simply the difference between the entropy of the products and reactants at the appropriate temperature. Entropies of different compounds are measurable quantities, as are other thermodynamic function state functions discussed later in the text.

### 4.4 Differential Quantities

In differential form the first law of thermodynamics (Eq. 4.1) is as follows:

$$dU = \delta Q + \delta W + \delta W' \quad (4.11)$$

We can combine this with the expression from the second law from $\delta Q$:

$$\delta Q = TdS \quad (4.12)$$

We also have the following expression for the work done by an external pressure, $P$, on changing the volume, $V$:

$$\delta W = -PdV \quad (4.13)$$

Combination of Eqs. 4.11-4.13 can be combined to give the following combined statement of the first and second laws:

$$dU = TdS - PdV + \delta W' \quad (4.14)$$

From this equation we see that at constant system entropy ($ds = 0$) and volume ($dv = 0$) the change in internal energy is equal to the non-mechanical reversible work done on the system. In general, entropy and volume are not constant, which is why we more commonly use other thermodynamic potentials as described in the following section.

Finally, if we will assume that there is no additional work done on the system apart from work done by the external pressure ($\delta W' = 0$), we have:

$$dU = TdS - PdV \quad (4.15)$$
5 Thermodynamic Variables and Relations

Outcomes for this section:
1) Derive differentials of state functions \((V, S, U, F, H, G)\) in terms of \(dP\) and \(dT\).

2) Using the Maxwell relations, relate coefficients in the differentials of state functions.

3) Define the coefficient of thermal expansion, compressibility, and heat capacity of a material.

4) Express the differential of any given state function in terms of the differentials of two others.

5) Define reversible, adiabatic, isotropic, isobaric, and isothermal processes.

6) Calculate changes in state functions by defining reversible paths (if necessary) and integrating differentials for (a) an ideal gas, and (b) materials with specified \(\alpha, \beta,\) and \(C_P(T)\). (Multiple examples are given for ideal gas, solids, and liquids.)

7) Special emphasis (Example 4.13): calculate the change in Gibbs free energy when one mole of a substance is heated from room temperature to an arbitrary temperature at constant pressure.

8) Describe the origin of latent heat, and employ this concept in the calculation of changes in Gibbs free energy \(G\).

5.1 Enthalpy

The enthalpy, \(H\), is defined in the following way:

\[
H \equiv U + PV
\]  
(5.1)

The total differential of the enthalpy is:

\[
dH = dU + PdV + VdP
\]  
(5.2)

Now we eliminate \(dU\) by using Eq. 4.14:

\[
dH = TdS + VdP + \delta W'\]  
(5.3)
5.2 Helmholtz Free Energy

For a process at constant \( P, dP = 0 \) (constant pressure, or \textit{isobaric}), and if no other work is done \( \delta W' = 0 \). Under these conditions we have:

\[
\begin{align*}
   dH_p &= TdS_p = \delta Q_p \\
\end{align*}
\]

where the \('p'\) subscripts indicate that the differential quantities are being evaluated at constant pressure. The enthalpy therefore measures the reversible heat exchange in an isobaric process.

\subsection{5.2 Helmholtz Free Energy}

The Helmholtz free energy is defined in the following way:

\[
F \equiv U - TS
\]

In differential form this becomes:

\[
\begin{align*}
   dF &= dU - TdS - SdT \\
\end{align*}
\]

\[
\begin{align*}
   dF &= -SdT - PdV + \delta W' \\
\end{align*}
\]

For a process carried out at constant \( T \) (isothermal), \( dT = 0 \)

\[
\begin{align*}
   dF_T &= -PdV_T + \delta W'_T = \delta W_T + \delta W'_T = \delta W_{T,tot} \\
\end{align*}
\]

\( F_T \) reports the total (reversible) work done on the system.

\subsection{5.3 Gibbs Free Energy}

The Gibbs free energy, \( G \), is defined in the following way.

\[
G \equiv U + PV - TS = H - TS
\]

\[
\begin{align*}
   dG &= dU + VdP + PdV - TdS - SdT \\
\end{align*}
\]

\[
\begin{align*}
   &= (TdS - PdV + \delta W') + VdP + PdV - TdS - SdT \\
\end{align*}
\]

\[
\begin{align*}
   dG &= -SdT + VdP + \delta W' \\
\end{align*}
\]
For processes carried out under isothermal and isobaric (constant \( P \)) conditions \((dT, dP = 0)\), then

\[
dG_{T,P} = \delta W'_{T,P} \tag{5.13}
\]

\( G \) reports the total work done other than mechanical work, e.g. chemical reactions and phase transformations.

### 5.4 Other Material Properties

#### 5.4.1 Volume thermal expansion coefficient

Here we define some material properties that relate different thermodynamic state variables to one one another. The first is the thermal expansion coefficient, \( \alpha \), which describes the temperature dependence of the volume:

\[
\alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P (K^{-1}) \tag{5.14}
\]

#### 5.4.2 Isothermal Compressibility

The isothermal compressibility, \( \beta \), gives the relationship between the pressure and the volume:

\[
\beta \equiv \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T (Pa^{-1}) \tag{5.15}
\]

#### 5.4.3 Heat Capacity

The heat capacity is the amount of energy needed to change temperature by some amount. Two different heat capacities are typically defined. The first of these, \( C_P \), corresponds to a process performed at a constant pressure:

\[
\delta Q_P \equiv C_P dT_P \tag{5.16}
\]

Here \( T_P \) indicates that the pressure is being held constant. If the process is reversible, then \( dQ_P = T dS \) (Eq. 4.12), and we have:

\[
TdS = C_P dT_P \tag{5.17}
\]
Because the process is happening at constant pressure, we can rewrite Eq. 5.17 in the following way:

\[
\frac{C_P}{T} = \left( \frac{\partial S}{\partial T} \right)_P
\]  

(5.18)

Empirically, \( C_P \) is described by four parameters, \( a, b, c \) and \( d \). These four parameters are a convenient way of tabulating the data.

\[
C_P(T) = a + bT + \frac{c}{T^2} + dT^2
\]  

(5.19)

The constant volume heat capacity, \( C_V \), is defined in a similar way, but with the volume held constant instead of the temperature:

\[
\delta Q_V \equiv C_V dT_V
\]  

(5.20)

The corresponding version of Eq. 5.18 is:

\[
\frac{C_V}{T} = \left( \frac{\partial S}{\partial T} \right)_V
\]  

(5.21)

Note that \( C_P \) is necessarily larger than \( C_V \). At constant \( P \), the volume increases with increasing temperature, so work is done on the surroundings. Therefore, more energy is needed to achieve the same \( \Delta T \). The relationship between \( C_P \) and \( C_V \) is obtained below in section 5.6.3.

5.5 Coefficient Relations

A variety of relationships exist between the different thermodynamic functions. These relationships are a consequence of some basic mathematical relationships. Suppose that we have a function, \( Z \) of two variables \( X \) and \( Y \):

\[
Z = Z(X, Y)
\]  

(5.22)

The differential of \( Z \) is given by:

\[
dZ = \left. \frac{\partial Z}{\partial X} \right|_Y dX + \left. \frac{\partial Z}{\partial Y} \right|_X dY
\]  

(5.23)
5.5 Coefficient Relations

The differential forms of $U$ (Eq. 4.15), $F$ (Eq. ), $H$ (Eq. ) and $G$ (Eq. ) all have the form of Eq. 5.23. The various relationships between the thermodynamic potentials ($U$, $F$, $G$, $H$) can be summarized by the thermodynamic square shown in Figure 5.1. Our description of how to use it is taken directly from the appropriate Wikipedia page (https://en.wikipedia.org/wiki/Thermodynamic_square)[3].

![Thermodynamic square](https://en.wikipedia.org/wiki/Thermodynamic_square)

**Figure 5.1**: Thermodynamic square used to help determine thermodynamic relations.

1) Start in the portion of the square corresponding the thermodynamic potential of interest. In our case we’ll use $U$.

2) The two opposite corners of the potential of interest represent the coefficients of the overall result. In our case these are $P$ and $T$. When the coefficient lies on the left hand side of the square, we use the negative sign that is shown in the diagram. In our example we have $dU = -P [\text{differential}] + T [\text{differential}]$. Now we just have to figure out what the two differentials are.

3) The differentials are obtained by moving to the opposite corner of the corresponding coefficient. In our case we have $V$ opposite $P$ and $S$ opposite $T$, so we end up with $dU = -PdV + TdS$, which is what we expect to get from Eq. 4.14. We can then use this same procedure to obtain the expressions given previously for $dH$, $dF$ and $dG$. Note that two variables on the opposite sides of the thermodynamic square are thermodynamically conjugate variables [1], with have units of energy when multiplied by one another.

We can also use the thermodynamic square of Fig. 5.1 to obtain a variety of expressions for the partial derivatives of the different thermodynamic potentials. The procedure is as follows:

1) Identify the potential you are interested in, just as before. We’ll again take $U$ as our example.

2) We can differentiate with respect to either of the variables adjacent to the potential we chose. For $U$ we can differentiate with respect to $S$ or $V$, with the other one of these two variables remaining constant during the differentiation.
The result of the differentiation is given by the variable that is conjugate to (diagonally across from) the variable we are differentiating by. For example, if we differentiate $U$ by $S$ we have, we have $(\partial U / \partial S)|_V = T$. The following 8 expressions are obtained in this way:

$$
T = (\frac{\partial U}{\partial S})_V, \quad -P = (\frac{\partial U}{\partial V})_S \\
T = (\frac{\partial H}{\partial S})_P, \quad V = (\frac{\partial H}{\partial S})_P, \\
-S = (\frac{\partial F}{\partial T})_V, \quad -P = (\frac{\partial F}{\partial V})_T, \\
-S = (\frac{\partial G}{\partial T})_P, \quad V = (\frac{\partial G}{\partial P})_T
$$

The thermodynamic square can be used to illustrate one more set of relationships, referred to as the Maxwell relationships. Consider a state variable $Z$, which is a function of two other variables, $X$ and $Y$. A property of state functions is that the order of differentiation doesn’t matter, so we have:

$$
\frac{\partial^2 Z}{\partial X \partial Y} = \frac{\partial^2 Z}{\partial Y \partial X} \quad (5.25)
$$

We can rewrite this as:

$$
\frac{\partial}{\partial X} \left( \frac{\partial Z}{\partial Y} \right)_X = \frac{\partial}{\partial Y} \left( \frac{\partial Z}{\partial X} \right)_Y \quad (5.26)
$$

Suppose the functions $M$ and $N$ are defined in the following way:

$$
M = \left( \frac{\partial Z}{\partial X} \right)_Y, \quad N = \left( \frac{\partial Z}{\partial Y} \right)_X \quad (5.27)
$$

By comparing Eqs. 5.26 and 5.27 we obtain the following expression.

$$
\left( \frac{\partial M}{\partial Y} \right)_X = \left( \frac{\partial N}{\partial X} \right)_Y \quad (5.28)
$$

The expressions for the differentials of the internal energy ($U$), Enthalpy ($H$), Helmoltz free energy ($F$), and Gibbs free energy ($G$) all have the form of Eq. 5.23, with values of $M$ and $N$ given in Eq. 5.24. Use of Eq. 5.28 in each of these four cases gives the following relationships between the appropriate partial derivatives:

### 5.5.1 Internal Energy

$$
dU = TdS - PdV \rightarrow \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V \quad (5.29)
$$
5.5.2 Enthalpy

\[ dH = TdS + VdP \rightarrow \left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P \] (5.30)

5.5.3 Helmholtz Free Energy

\[ dF = -SdT - PdV \rightarrow \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \] (5.31)

5.5.4 Gibbs Free Energy

\[ dG = -SdT + VdP \rightarrow -\left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P \] (5.32)

5.6 Equation of State Relationships

The ideal gas law is an example of an equation of state, where one thermodynamic variable (a dependent variable) is expressed in terms of two other thermodynamic variables (the independent variables). Equations of state can also be expressed in differential form, where differential changes in dependent variable are expressed in terms of differentials of the dependent variables. In general, once we know the equation of state for one combination of one independent and two dependent variables, we can express any thermodynamic function in terms of any two thermodynamic variables.

5.6.1 Expression for \( dS \)

It will be useful in many of our following derivations to have a general expression for \( dS \) in terms of \( dP \) and \( dT \). We begin by expressing \( dS \) in terms of the appropriate partial derivatives:

\[ dS = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP \] (5.33)

We can use Eq. 5.32 to replace \( \left( \frac{\partial S}{\partial P} \right)_T \) with \( -\left( \frac{\partial V}{\partial T} \right)_P \):

\[ dS = \left( \frac{\partial S}{\partial T} \right)_P dT - \left( \frac{\partial V}{\partial T} \right)_P dP \] (5.34)

Now we can use the definition of the thermal expansion coefficient, \( \alpha \), (Eq. 5.14) to replace \( \left( \frac{\partial V}{\partial T} \right)_P \) with \( V\alpha \):
\[ dS = \left( \frac{\partial S}{\partial T} \right)_P dT - V \alpha dP \]  

(5.35)

Finally, we use the definition of the constant pressure heat capacity, \( C_p \), (Eq. 5.18) to replace \( \left( \frac{\partial S}{\partial T} \right)_P \) with \( \frac{C_p}{T} \), which yields the following relationship expressing \( dS \) in terms of \( dT \) and \( dP \), and which involves the two material properties, \( \alpha \) and \( C_p \):

\[ dS = \frac{C_p}{T} dT - V \alpha dP \]  

(5.36)

### 5.6.2 Expression for \( dV \)

The differential of the volume in terms of \( dT \) and \( dP \) can also be obtained in a similar manner to the approach described above for obtaining \( dS \). We start with the following expression for \( dV \):

\[ dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP \]  

(5.37)

The two partial derivatives in this expression appear in the definitions of the volume thermal expansion coefficient, \( \alpha \), and the isothermal compressibility, \( \beta \). With \( \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \) and \( \beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \) we can rewrite Eq. 5.37 in the following way:

\[ dV = \alpha V dT - \beta V dP \]  

(5.38)

### 5.6.3 Relationship between \( C_P \) and \( C_V \)

In order to determine the relationship between the constant pressure heat capacity, \( C_P \) and its constant volume counterpart, \( C_V \), we need to get an expression for the \( dS \) with temperature and volume as the dependent variables instead of temperature and pressure. We do this by using Eq. 5.38 to get an expression for \( dP \):

\[ dP = \frac{\alpha}{\beta} dT - \frac{dV}{\beta V} \]  

(5.39)

This expression for \( dP \) can be substituted into Eq. 5.36 for \( dS \) to give:

\[ dS = \left( \frac{C_p}{T} - \frac{V \alpha^2}{\beta} \right) dT + \frac{\alpha}{\beta} dV \]  

(5.40)
From this we see that \((\frac{\partial S}{\partial T})_V = \frac{C_P}{T} - \frac{V\alpha^2}{\beta}\). We get the constant-volume heat capacity, \(C_V\), from it’s definition in Eq. 5.21:

\[
C_V = T \left(\frac{\partial S}{\partial T}\right)_V = C_P - \frac{TV\alpha^2}{\beta}
\]  

(5.41)

Note that \(C_V < C_P\), as mentioned earlier.

6 The Ideal Gas

We begin to apply these principles by considering an ideal gas, which obeys the following constitutive relationship:

\[
PV = nRT
\]  

(6.1)

Here \(n\) is the number of moles and \(R\) is the gas constant:

\[
R = 8.314 (\text{J/mol \cdot K}) = 1.987 (\text{cal/mol \cdot K}) = 0.08206 (\text{l-atm/mol \cdot K})
\]  

(6.2)

If \(n=1\), then \(PV = RT\), where \(V = V_m\), where \(V_m\) is the molar volume.

6.1 Thermal Expansion Coefficient of an Ideal Gas

We get the volume thermal expansion coefficient, \(\alpha\), by substituting the ideal gas constitutive law into Eq. 5.14:

\[
\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{P}{nRT} \frac{\partial}{\partial T} \left(\frac{nRT}{P}\right)_P = \frac{P}{nRT} \cdot \frac{nR}{P} = \frac{1}{T}
\]  

(6.3)

We see that the volume thermal expansion coefficient of an ideal gas is simply equal to the inverse of the absolute temperature.
6.2 Compressibility of an Ideal Gas

A very simple expression is also obtained for the isothermal compressibility of an ideal gas, in this case substituting the ideal gas constitutive equation into Eq. 5.15:

$$\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{P}{nRT} \left( nRT \frac{\partial}{\partial P} \left( \frac{nRT}{P} \right) \right)_T = -\frac{P}{nRT} \left( -\frac{nRT}{P^2} \right) = \frac{1}{P}$$  (6.4)

The isothermal also has a very simple form for an ideal gas, equal to the inverse of the pressure.

6.3 Internal Energy of Ideal Gas

To calculate the internal energy for an ideal gas, the first step is to rewrite the expression for $dU$ with $T$ and $P$ as the dependent variables. We begin with the following expression the first and second laws (Ex. 4.15):

$$dU = TdS - PdV$$  (6.5)

Using Eq. 5.36 for $dS$ and Eq. 5.38 for $dV$ gives:

$$dU = (C_p - PV \alpha) dT + V (P \beta - T \alpha) dP$$  (6.6)

This expression is general for any constitutive law. For an ideal gas, we also have $\alpha = 1/T$ and $\beta = 1/P$ (see previous sections), which gives:

$$dU = \left( C_p - \frac{PV}{T} \right) dT$$  (6.7)

We also have $PV = nRT$ for the ideal gas, so we have:

$$dU = (C_p - nR) dT$$  (6.8)
We see from this result that the internal energy of an ideal gas is independent of the pressure. From Eq. 5.41 we see that
\[ C_V = C_P - \frac{PV}{T} = C_P - nR \]  
(6.9)
\[ \therefore dU = C_V dT, \text{ and } C_V = \frac{3}{2} R \]

One can then integrate to find that
\[ \Delta U = \frac{3}{2} R (T_2 - T_1) \]

\( C_V \) is constant

For an ideal gas, the internal energy depends only on the temperature.

### 6.4 Specific Heat of Ideal Gas

\[ C_V = C_P - \frac{T (V \alpha)^2}{\beta} = C_P - R \]  
(6.10)

We will show that \( C_v = \frac{3}{2} R \) for a monatomic ideal gas. Therefore, \( C_P = \frac{3}{2} R + R = \frac{5}{2} R \).

### 6.5 Some Examples of Ideal Gas Behavior

#### 6.5.1 Free expansion of an ideal gas

![Figure 6.1: Free expansion of an ideal gas - the valve is opened at \( t_2 \) and fills both chambers](image)

Walls are rigid: \( \delta W = 0 \)

Walls are insulating: \( \delta Q = 0 \)
Example: Calculate the change in T when 1 mole of gas is compressed reversible and adiabatically (no heat flow) from $V_1$ to $V_2$.

Solution: In Example 4.6, we found that $dS = \frac{C_V}{T} dT + \frac{\alpha}{\beta} dV$, which simplifies to $dT_S = -\frac{T\alpha}{C_V \beta} dV_S$ for a reversible, iso-entropic process, for which $dS = 0$.

For an ideal gas, $\alpha = \frac{1}{T}$, $\beta = \frac{1}{P}$, so $dT_S = -\frac{R}{C_V} \frac{dV}{V}$. Evaluate by integrating.

\[ \int_{T_1}^{T_2} \frac{dT_S}{T} = -\frac{R}{C_V} \int_{V_1}^{V_2} \frac{dV_S}{V} \rightarrow \ln \left( \frac{T_2}{T_1} \right) = -\frac{R}{C_V} \ln \left( \frac{V_2}{V_1} \right) \]

\[ \ln \left( \frac{T_2}{T_1} \right) = \ln \left[ \left( \frac{V_2}{V_1} \right)^{-\frac{R}{C_V}} \right] \Rightarrow \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\frac{R}{C_V}} \]

\[ C_V = \frac{3}{2} R \]

\[ T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\frac{R}{C_V}} = T_1 \left( \frac{V_1}{V_2} \right)^{2/3} \]

\( \left( \frac{V_1}{V_2} \right) > 1 \) for compression, so T increases.

If the gas expands ($V_2 > V_1$), then T decreases. One can also derive T(P) and P(V).

System is closed.

\[ \Rightarrow \Delta S_t = 0, \Delta U = 0 \Rightarrow \Delta T = 0 \] (ideal gas)

The gas expands irreversibly.

Entropy is produced, but $\Delta S$ is not process dependent because $S$ is a state function.

What is $\Delta S$ when 1 mole of gas expands freely to twice its volume? (recall $\Delta T = 0$).

\[ dS = \frac{C_V}{T} dT + \frac{\alpha}{\beta} dV, \quad dT = 0 \]

\[ PV = RT \]

\[ \frac{P}{T} = \frac{R}{V} \]

\[ dS = \frac{\alpha}{\beta} dV_T = \frac{P}{T} dV_T = \frac{R}{T} dV_T \]

\[ \Delta S_T = \int_{V_1}^{V_2} \frac{R}{V} dV = R \ln \left( \frac{V_2}{V_1} \right) = R \ln \left( \frac{2V_1}{V_1} \right) = R \ln 2 \]
\[ \Delta S_T = 5.76 \text{J/mol-K} \]

This change for a reversible isothermal process is the same as for an irreversible free expansion in an isolated system. S is a state function.

### 6.5.2 Isothermal Compression of an Ideal Gas

How much heat is absorbed/released when 1 mole of gas is compressed isothermally from 1 to 25 bar at 300K?

To find heat, use S: \( \delta Q_{\text{rev,}T} = T dS_T \)

\[
dS = \frac{C_P}{T} dT - V^\alpha dP = -V^\alpha dP_T
\]

The volume change is unknown, so use \( V = \frac{RT}{P} \)

\[
dS_T = -\frac{RT}{P} \frac{1}{P} dP = -R d\left(\frac{P_f}{P_i}\right)
\]

\[
\Delta S_T = -R \int_{P_i}^{P_f} \frac{dP}{P} = -R \ln \left(\frac{P_f}{P_i}\right)
\]

\[ \rightarrow \Delta Q_{\text{rev,}T} = -RT \ln \left(\frac{P_f}{P_i}\right) = -(8.314 \text{J/mol-K})298K \ln\left(\frac{25}{1}\right) = -7.975 \text{kJ/mol} \]

### 6.5.3 Reversibility requires work/heat

The piston in Figure 6.2 below may be withdrawn very slowly to maintain equilibrium.

![Figure 6.2: Piston-cylinder device](image)

\[ \Delta U = 0 \rightarrow \Delta T = 0 \]
6.5 Examples

\[ \Delta S = \int_{V_i}^{V_f} \frac{nR}{V} dV = nR \ln \left( \frac{V_f}{V_i} \right) \]

But no entropy can be produced, so heat flow is needed to maintain T (for free expansion, T decreases).

So actually, \( \Delta U = Q + W = 0 \)

\[ \rightarrow W = -Q < 0 \]

The system does negative work! Heat flow is positive (inward).

![Figure 6.3: Irreversible Process (top) and reversible process (bottom)](image)

<table>
<thead>
<tr>
<th>Irreversible process</th>
<th>Reversible process</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta Q = 0 )</td>
<td>( \Delta Q \neq 0 )</td>
</tr>
<tr>
<td>( W=0 )</td>
<td>( W \neq 0 )</td>
</tr>
<tr>
<td>( \Delta U = 0 )</td>
<td>( \Delta U = 0 )</td>
</tr>
<tr>
<td>( \Delta T = 0 )</td>
<td>( \Delta T = 0 )</td>
</tr>
</tbody>
</table>

Table 6.1: Irreversible vs reversible process characteristics

\[ \Delta U = 0 \rightarrow W = -\Delta Q \]

\[ W < 0, \Delta Q > 0 \]

\[ \rightarrow \Delta S_t > 0 \]

What is the amount of heat required to raise the temperature to 1000K isobarically?

\[ \delta Q_{rev,P} = TdS_p \equiv C_p dT_p \]
\[ C_P = \frac{5}{2} R \]

\[ \Delta Q_{rev,P} = C_P \Delta T = \frac{5}{2} R \Delta T = \frac{5}{2} (8.314 \text{J/mol} - K) \times (1000 - 298) K \]

Note that \( dH = C_P dT + V(1 - T_\alpha) dP \). For \( dP = 0 \), \( dH = C_P dT \to \text{Enthalpy measures reversible heat flow in absence of work. This will be useful in the analysis of solids heated under conditions of constant pressure.} \]

### 6.5.4 Some useful relations for heat flow

\[ \delta Q_{rev,T} = T dS_T = dU_T - dF_T \]

\[ \delta Q_{rev,P} = T dS_P \equiv C_P dT_P = dH_P \ (\delta W' = 0) \]

\[ \delta Q_{rev,V} = T dS_V \equiv C_V dT_V = dU_V \ (\delta W' = 0) \]

Example 4.3: Relate \( S(P,V) \)

\[ dS = MdP + NdV \]

\[ dS = MdP + N(V^\alpha dT - V^\beta dP) = (M - NV^\beta)dP + NV^\alpha dT \]

\[ dS = -V^\alpha dP + \frac{C_P}{V^\alpha} dT \rightarrow N = \frac{C_P}{V^\alpha} T = \left( \frac{\partial S}{\partial V} \right)_P \]

\[ M - NV^\beta = -V^\alpha \]

\[ M = -V^\alpha + \frac{C_P}{V^\alpha} V^\beta \]

\[ M = \frac{C_P V^\beta}{\alpha T} - V^\alpha = \left( \frac{\partial S}{\partial P} \right)_V \]

\[ dS = \left( \frac{C_P V^\beta}{\alpha T} - V^\alpha \right) dP + \frac{C_P}{V^\alpha} dV \]

Luijten examples

1) \( Q \) for \( \Delta P \) at constant \( T \)

Reversible, \( \rightarrow \delta Q_{rev,T} = T dS \)

Use \( S(T, P) \) like 4.10(a)
2) Find $\Delta T$ given $\Delta P$ at constant $S$
   Use $S(T, V)$, also ideal gas law ($\sim 4.8$)

3) Free expansion of ideal gas, find $\Delta S$ for $\Delta V$
   $S(T, V)$ (4.9)

4) Adiabatic reversible compression of a solid.
   $T(S, P) \, dS = 0, \Delta P$ given (4.14)

5) Change in $G$ for heating at constant $P$
   $G(P, T), \, dP = 0$ (4.13)
   $dG = -SdT + VdP$, need to find $S(T)$

$$PV = RT$$

Problem: 1 mole of gas expands at an initial temperature of 300 K, from 1 l to
2 l at constant $S$. What is the final temperature?

Solution:

$$dS = MdT + NdP = 0$$

$$\left( \frac{C_P}{T} - \frac{(V^\alpha)^2}{\rho} \right) dT + \frac{\alpha}{\beta} dV = 0 \quad \alpha = \frac{1}{T}, \beta = \frac{1}{P}$$

$$C_P dT = -\frac{\alpha}{\beta C_V} dV$$

$$\frac{dT}{T} = -\frac{\alpha}{\beta C_V} dV$$

$$\frac{dT}{T} = -\frac{P}{T C_V} dU$$

$$dT = -\frac{P}{C_V} dV$$

Use $PV = RT$ to get to two variables

$$P = \frac{RT}{V}, \, C_V = \frac{3}{2} R$$

$$dT = -\frac{RT}{C_V V} dV =$$

$$\frac{dT}{T} = -\frac{R}{3/2 R V} dV = -\frac{2}{3} \frac{dV}{V}$$
\[
\int_{T_1}^{T_2} \frac{dT}{T} = -\frac{2}{3} \int_{V_1}^{V_2} \frac{dV}{V} \rightarrow \ln \left( \frac{T_2}{T_1} \right) = \ln \left( \frac{V_1}{V_2} \right)^{2/3}
\]

\[
\frac{V_1}{V_2} = \frac{1}{2}, \quad T_2 = T_1 \left( \frac{1}{2} \right)^{2/3} = 189K
\]

Note \( P_1 = \frac{300 \cdot R}{10^{-3} \text{m}^3} = 3 \times 10^5 R \)

\[
P_2 = \frac{189R}{2 \times 10^{-3} \text{m}^3} = 0.95 \times 10^5 R
\]

Pressure drops by threefold
\[
\downarrow PV \uparrow = RT \downarrow
\]

1 mole Fe is compressed reversibly. What is the change in \( T \)?
\( P_1 = 1 \text{atm}, P_2 = 10^5 \text{atm} \)

\[
dS = \frac{C_P}{T} dT - V^\alpha dP
\]

\[
\frac{dT}{T} = \frac{V^\alpha}{C_P} dP \quad \text{need exponential values}
\]

Does \( C_P \) vary with \( T \)?
If \( \frac{dC_P}{dT} \approx 0 \), then

\[
\ln \left( \frac{T_2}{T_1} \right) = \frac{V^\alpha}{C_P} \Delta P
\]

\[
\alpha = 36 \times 10^{-6} \text{K}^{-1}
\]

\[
C_P \approx 45.3 \text{J/mol} - \text{K}
\]

Otherwise, \( \int \frac{C_P}{T} dT = V^\alpha \Delta P \)

\[
V = \frac{3.1 \text{cm}^3}{\text{mol}} = 7.1 \times 10^{-6} \text{m}^3/\text{mole}
\]

\[
T_2 = T_1 \times 1.006 = 300K
\]
7 Solids and Liquids

Let’s begin with an example of the calculation of the free energy as a function of temperature for a substance

Compute $\Delta G$ when 1 mole of MgO is heated from 300K to temperature $T$ at constant pressure.

Solution:

\[
dG = -SdT + VdP
\]
\[
dP = 0
\]
\[
dG_P = -SdT_P = -S(T)dT_P
\]

But $C_P$ depends on temperature $\rightarrow$ so does $S$.

\[
dS = \frac{C_P}{T}dT - V^o dP = \frac{C_P}{T}dT
\]
\[
\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}
\]
\[
S = S_o + \int \frac{C_P(T)}{T}dT
\]
\[
C_P = a + bT, S_o = 26.8J/mol - K
\]
\[
S = S_o + \int_{T_1}^{T_2} dT \left(\frac{a}{T} + b\right)
\]

Evaluate expression, substitute data at the end

\[
S = S_o + \int \frac{C_P(T)}{T}dT = S_o + \int_{T_1}^{T_2} dT \left(\frac{a}{T} + b\right)
\]
\[
S = S_o + a \ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1)
\]
\[
T_1 = 300K, T_2 = T
\]
\[ S(T) = S(300K) + a \ln \left( \frac{T}{300} \right) + b(T - 300) \]

\[ \equiv a \ln T + bT + \left[ S_\circ - a \ln 300 - 300b \right] \quad \text{constant} \]

\[ C_P(T)_{MgO} = \frac{48.99}{a} + \frac{3.43 \times 10^{-3}}{b} T - \frac{11.34 \times 10^{-5}}{T^2} \left( \frac{J}{mol - K} \right) \quad \text{ignored} \]

\[ \Delta G = \int_{300}^{T} dG = - \int_{300}^{T_f} S(T) dT = - \int_{300}^{T_f} (a \ln T + bT + C) dT \]

\[ = [a(T \ln T - T) + \frac{1}{2} bT^2 + cT]_{T_f}^{300} \]

\[ \Delta G = aT \ln T + \frac{1}{2} bT^2 + (C - a)T = -300a \ln 300 - \frac{1}{2} b(300)^2 - (C - a)300 \]

\[ \uparrow \text{Check this, see also sec 7.3 p. 180} \]

\[ a = 48.99 \frac{J}{mol - K}, \quad b = 3.43 \times 10^{-3} \frac{J}{molK^2} \]

\[ C = 26.8 J/mol - K - a \ln 300 - 300b \]

Consider the following exothermic reaction (referred to as the Thermite reaction), where Aluminum reacts with iron oxide to form aluminum oxide and iron.

\[ 2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe \]

How hot will this system get as the reaction proceeds? We’ll do this in two parts. First, we’ll calculate the heat generated in the reaction, then we’ll figure out how much this heat will increase the temperature of the system.

Consider the change in enthalpy for each half-reaction:

\[ 2Al + \frac{3}{2} O_2 \rightarrow Al_2O_3 \quad \Delta H_1 = -1675.7 \text{kJ mol}^{-1} \]

\[ Fe_2O_3 \rightarrow 2Fe + \frac{3}{2} O_2 \quad \Delta H_2 = 823 \text{kJ mol}^{-1} \]
\[
2\text{Al} + \frac{3}{2}\text{O}_2 + \text{Fe}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe} + \frac{3}{2}\text{O}_2
\]

\[\Delta H = (-1675.1 + 823) \frac{\text{kJ}}{\text{mol}} = -852.3 \frac{\text{kJ}}{\text{mol}}\]

The minus sign implies that the reaction is exothermic. Now that we know how much heat is generated, we can figure out what the state of the system will be. Note that Fe melts at 1809 K and boils at 3343 K, and \(\text{Al}_2\text{O}_3\) melts at 2325 K. We need to determine to what temperature the system will rise assuming that all heat generated by the reaction is absorbed by the system.

**Step 1:** Heat \(\text{Fe}\) and \(\text{Al}_2\text{O}_3\) to the melting point of \(\text{Fe}\).

\[\Delta H_{\text{Al}_2\text{O}_3,1} = \int_{289}^{1809} C_P(T)dT = 183,649 \text{ J}\]

\(\Delta H_{\text{Fe},1}\) involves 3 sub-steps: (2 moles)

\[\uparrow \alpha \rightarrow \gamma : 2 \int_{289}^{1187} C_{P,\alpha}dT + \Delta H_{\alpha \rightarrow \gamma}\]

\[\uparrow \gamma \rightarrow \delta : 2 \int_{1187}^{1164} C_{P,\gamma}dT + \Delta H_{\gamma \rightarrow \delta}\]

\[\uparrow \delta \rightarrow l : 2 \int_{1164}^{1809} C_{P,\delta}dT + \Delta H_{\text{melt}}\]

\[C_{P,\delta} = C_{P,\alpha}\]

Considering the three integrals of \(T\) and three latent heats,

\[\Delta H_{\text{Fe},1} = 157,741 \text{ J (for 2 moles)}\]

So through step 1, we have \(\Delta H_{\text{Fe},1} + \Delta H_{\text{Al}_2\text{O}_3,1} = 341.390 \text{ J}\)

**Step 2:** Heat \(\text{Fe}\) and \(\text{Al}_2\text{O}_3\) to melting point of \(\text{Al}_2\text{O}_3\).

\[\Delta H_{\text{Al}_2\text{O}_3,2} = \int_{1809}^{2325} C_{P,\text{Al}}dT + \Delta H_{\text{Al}_2\text{O}_3}(S \rightarrow l) = (71,240 + 107,000) \text{ J}\]

\[\Delta H_{\text{Fe},2} = 2 \int_{1809}^{2325} C_{P,\text{Fe}(l)}dT = 43,178 \text{ J}\]
How much is left? 852, 300 − 341, 390 − 221, 418 = 289, 492 J

Step 3: How much energy is needed to get to the boiling point of Fe?

\[
\begin{align*}
272,600 \text{ J} & \left\{ \Delta H_{Fe,3} = 2 \int_{2325}^{3343} C_{P,Fe}(l) dT \right\} \\
& \left\{ \Delta H_{Al_2O_3,3} = \int_{2325}^{3343} C_{P,Al_2O_3}(l) dT \right\}
\end{align*}
\]

leaving 16.892 J

How much Fe evaporates?

\[
\frac{Q}{\Delta H_{Fe,(l\rightarrow g)}} = \frac{16.892 J}{340,159 J} = 0.05 \text{ moles or 5%}
\]

\[
\Delta H(T) = \Delta a T + \frac{\Delta b}{2} T^2 - \Delta C \frac{1}{T} + \frac{\Delta d}{3} T^3 - \Delta D
\]

\[
\Delta D = \Delta H(T_o) - [\Delta a T_o + \frac{\Delta b}{2} T_o^2 - \Delta C \frac{1}{T_o} + \frac{\Delta d}{3} T_o^3]
\]

\[
2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3 \quad \text{Exothermic}
\]

Compute the final state and temperature assuming adiabatic, reversible reaction at constant pressure.

\[
dT, Q = 0, dP = 0
\]

Need initial \( S, C_P \)

\[
T_F \quad \rightarrow \quad T_F
\]

\[
\begin{align*}
2Al + Fe_2O_3 & \quad \rightarrow \quad Al_2O_3 + 2Fe \\
\text{Ti} & \quad \rightarrow \quad \text{Ti}
\end{align*}
\]

\[
S @ 300
\]

\[
\text{Figure 7.1: Thermite reaction}
\]

Exothermic implies \( \Delta T \) from heat released.

\[
dS = MdT + N\delta P
\]

\[
dH = TdS + VdP + \delta W'
\]

\[
2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3 : \Delta H_1 = -1875 \text{kJ/mol}
\]
\[ 2Fe + \frac{3}{2}O_2 \rightarrow Fe_2O_3; \Delta H_2 = -823.4 \text{kJ/mol} \]

\[ 2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3 \]

\[ 2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3; \Delta H_1 \]

\[ Fe_2O_3 \rightarrow 2Fe + \frac{3}{2}O_2; -\Delta H_2 \]

\[ 2Al + Fe_2O_3 + \frac{3}{2}O_2 \rightarrow Al_2O_3 + 2Fe + \frac{3}{2}O_2 \]

\[ \Delta H_1 - \Delta H_2 = -852.3 \text{kJ/mol} \]

\[ \delta Q_{rev,P} = -TdS = dH \]

Heat is reversibly absorbed by the system.

\[ \Delta H_{Fe,1} = \int dH = \int_{298}^{1809} C_PdT = 157,741 \text{J for 2 mol} \]

Include \( \Delta H \) due to increasing \( T \) as well as due to phase transitions. For \( Al_2O_3 \), just \( \int C_PdT \)

\[ \Delta H_{Al_2O_3} = 183,649 \text{ J} \]

For a total change of 341,390 J

Now heat \( Al_2O_3 \) to melting point, and heat \( Fe(l) \)

\[ \int C_PdT + \Delta H_{melt} \]

Step 2 takes: 221,418 J

852,300 J is provided by the reaction: 852,300 \( = 221,418 - 341,390 \) = 289,492 J

\[ dS = \frac{C_V}{T}dT + \frac{\alpha}{\beta}dV = \frac{3}{2} \frac{R}{T}dT + \frac{P}{T}dV = \frac{3}{2} \frac{R}{T}dT + \frac{R}{V}dV \]

Good for constant \( V \): relate \( \Delta S \) to \( T \) change.

For constant \( T \): relate \( \Delta S \) to volume change.

For constant \( S \), \( dS=0 \)

\[ \left( \frac{T_2}{T_1} \right)^{3/2} = \left( \frac{V_1}{V_2} \right)^{2/3} \]

\[ \frac{T_2}{T_1} = \frac{V_2}{V_1} \frac{P_2}{P_1} \]
Figure 7.2: Changes in enthalpy in Fe and $Al_2O_3$

\[ \left( \frac{P_2}{P_1} \right)^{3/2} \left( \frac{V_2}{V_1} \right)^{3/2} = \frac{V_1}{V_2} \rightarrow \left( \frac{P_2}{P_1} \right)^{3/2} = \left( \frac{V_1}{V_2} \right)^{5/2} \]

\[ \frac{P_2}{P_1} = \left( \frac{V_1}{V_2} \right)^{5/3} \]

\[ T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1} \]

\[ T_1^{\frac{\gamma}{1 - \gamma}} P_1 = T_2^{\frac{\gamma}{1 - \gamma}} P_2 \]

\[ P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \]

\[ \gamma = \frac{C_p}{C_V} = \frac{5/2}{3/2} = 5/3 \]

\[ \frac{5/3}{1 - 5/3} = \frac{5/3}{2/3} = 5/2 \]

\[ \gamma - 1 = 2/3 \]

\[ dU = (C_P - PV^\alpha) dT + V(\rho \beta - T_0) dP \]
\[ dU = \left( \frac{5}{2} R - R \right) dT + V (1 - 1) dP = \frac{3}{2} RT \]

\[ dS = \frac{C_P}{T} dT - V^\alpha dP = \frac{5}{2} R \frac{dT}{T} - \frac{V}{T} dP \]

\[ dS = \frac{5}{2} R \frac{dT}{T} - \frac{R}{P} dP \]

\[ dS = \frac{C_V}{T} dT + \frac{\alpha}{\beta} dV = \frac{3}{2} R \frac{dT}{T} + \frac{P}{T} dV = \frac{3}{2} R \frac{dT}{T} + \frac{R}{V} dV \]

Constant P: \( \Delta S = \frac{5}{2} R \ln \left( \frac{T_2}{T_1} \right) \)

Constant T: \( \Delta S = -R \ln \left( \frac{P_2}{P_1} \right) \)

\( \Delta S = -R \ln \left( \frac{V_2}{V_1} \right) \)

Constant V: \( \Delta S = \frac{3}{2} R \ln \left( \frac{T_2}{T_1} \right) \)

Constant S: \( \frac{P_1}{P_2} = \left( \frac{T_2}{T_1} \right)^{5/2} = \left( \frac{V_1}{V_2} \right)^{5/3} \)

\[ dU = -P dV + T dS \]

\[ dU = \left( -\frac{\partial U}{\partial V} \right)_S dV + \left( \frac{\partial U}{\partial S} \right)_V dS \Rightarrow \left[ \frac{\partial}{\partial S} \left( -\frac{\partial U}{\partial V} \right)_V \right]_S = \left[ \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right)_V \right]_S \]

Note that these are second derivatives of the internal energy, so they should be negative for equilibrium.

### 8 Conditions for Equilibrium

**Outcomes for this section:**

1) Derive the condition for equilibrium between two phases.

2) Show that at constant temperature and pressure, the equilibrium state corresponds to that which minimizes the Gibbs free energy \( G \).

3) Explain why the evolution to a state of lower Gibbs free energy occurs spontaneously.
For an isolated system ($\delta Q = 0, \delta W = 0, \text{n fixed}$), equilibrium corresponds to the state of maximum entropy. So if we maximize $S$, which is a function of multiple variables, we will have determined the equilibrium state, regardless of the past history.

How do we recognize that a system has reached equilibrium? We need to be able to answer ‘yes’ to the following questions:

1) Is the system in a stationary state (i.e. not changing)?

2) If the system is isolated from its surroundings, will no further changes occur?

A useful example of the application of these systems is the copper rod in contact with hot and cold surfaces, shown in Figure 8.1. When the rod is first put into contact with the hot and cold surfaces, the system is clearly not in equilibrium because the temperature profile is changing and we answer ‘no’ to question 1. At long times a steady state temperature profile is reached, but the system is not at equilibrium because we would answer ‘no’ to question 2.

**Figure 8.1:** Illustration of a copper rod in contact with hot and cold surfaces. The temperature reaches a steady state profile at long times ($t = t_\infty$), but the system is not at equilibrium because the this temperature profile will change to a uniform value if the bar is isolated from its surroundings where it is no longer in contact with the hot and cold surfaces.

$z$ varies monotonically with $x,y$ - there is no global maximum. Constraints such as $y = y(x)$ may define a maximum in $z(x,y)$ subject to $y = y(x)$.
Example 5.1

\[ z = xu + yv \]

For simple cases, eliminate dependent variables. In general, use Lagrange Multipliers.

Challenge: minimize a function of several variables when relationships (constraints) exist between those variables.

Approach: Lagrange Multipliers

<table>
<thead>
<tr>
<th>Minimize: (will be S)</th>
<th>Given these constraints (other state functions, vars)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ f(x_1, x_2, \ldots x_n) ]</td>
<td>[ \Phi_1(x_1, x_2, \ldots x_n) = 0 ]</td>
</tr>
<tr>
<td>function of n variables</td>
<td>[ \Phi_2(x_1, x_2, \ldots) = 0 ]</td>
</tr>
<tr>
<td>degrees of freedom=n-m</td>
<td>[ \vdots ]</td>
</tr>
<tr>
<td></td>
<td>[ \Phi_m(x_1, x_2, \ldots) = 0 ]</td>
</tr>
</tbody>
</table>

m constraints.

Define: \( df + \lambda_1 d\Phi_1 + \lambda_2 d\Phi_2 + \ldots + \lambda_m d\Phi_m = 0 \)

\( \lambda_m \): Lagrange multiplier

\[ dF = \frac{\partial F}{\partial x_1} dx_1 + \frac{\partial F}{\partial x_2} dx_2 + \ldots + \frac{\partial F}{\partial x_n} dx_n \]

In general, \( dF = \frac{\partial F}{\partial x_1} dx_1 + \frac{\partial F}{\partial x_2} dx_2 + \ldots + \frac{\partial F}{\partial x_n} dx_n \).

To guarantee that \( dF=0 \) for all \( x_1, x_2, \ldots x_n \), the coefficients \( \frac{\partial F}{\partial x_i} \) must all be zero.

i.e. \( \frac{\partial F}{\partial x_i} + \sum_{k=1}^{m} \lambda_k \frac{\partial \Phi_k}{\partial x_i} = 0 \)

Example 5.1

\[ z = xu + yv \]

Constraints

- \( u = x + y + 12 \rightarrow \Phi_1 = x + y + 12 - u = 0 \)
- \( v = x - y - 8 \rightarrow \Phi_2 = x - y - 8 - v = 0 \)

\( u, v \): dependent

\( x, y \): independent

\[ dz + \lambda_1 d\Phi_2 + \lambda_2 d\Phi_2 = 0 \]

Minimize \( z \) subject to constraints

\[ = xdu + udx + ydv + vdy + \lambda_1(dx + dy - du) + \lambda_2(dx - dy - dv) = 0 \]
8.1 Finding equilibrium conditions

A unary 2-phase system is in equilibrium when the $T$, $P$ and $\mu$ for both phases are equal.

Consider 2 phases $\alpha$ and $\beta$ of one component.

$U = U^\alpha + U^\beta$, $V = V^\alpha + V^\beta$, $S = S^\alpha + S^\beta$ because these are extensive properties.

So $U^\alpha(S^\alpha, T^\alpha, n^\alpha)$ where $n^\alpha$ is the number of moles of $\alpha$ phase.

Then $dV^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \mu^\alpha d n^\alpha$, where $\mu \equiv \left(\frac{\partial V^\alpha}{\partial n^\alpha}\right)_{V^\alpha, T^\alpha}$

$\mu^\alpha$ is the chemical potential of the $\alpha$ phase. To find the equilibrium condition, maximize $S$.

$$
dS^\alpha = \frac{dU^\alpha}{T^\alpha} + \frac{P^\alpha}{T^\alpha} dV^\alpha - \frac{\mu^\alpha}{T^\alpha} d n^\alpha, \quad dS^\beta = \frac{dV^\beta}{T^\beta} + \frac{P^\beta}{T^\beta} dV^\beta - \frac{\mu^\beta}{T^\beta} d n^\beta
$$

If the entropy is maximized, then no changes will occur if the system is isolated (rigid walls, insulated).

$$
dU = dU^\alpha + dV^\beta = 0 \rightarrow dU^\alpha = -dU^\beta \quad \text{(no heat is exchanged)}
$$

$$
dV = dV^\alpha + dV^\beta = 0 \rightarrow dV^\alpha = -dV^\beta \quad \text{(no work is done)}
8.2 Energy Minima

Consider first the internal energy $U$ in an $m$-component system.

$dU = TdS + PdV + \sum_i^m \mu_i dn_i$ where $i$ : index of components

$dU = \delta Q + \delta W + \delta W'$

Consider a reversible process in an isolated system

$\delta Q_{\text{rev}} = TdS \delta W_{\text{rev}} = -PdV \Rightarrow \delta W' = \sum_i \mu_i d\mu_i$ "chemical" work associated with reversible reactions

Claim: For a system of constant $S, V, n, \lambda$, the equilibrium state is a state of minimum internal energy $U$.

If this is not true, then work can be extracted and reinserted as heat. But then $S$ would increase while nothing else changes. Therefore, energy cannot be extracted from a system under these conditions (unchanging/maximized $S, V, n$).

1) Derive conditions for equilibrium again $dU = 0$ (minimize $U$)

$dS = 0 \Rightarrow dS^\alpha = -dS^\beta$

$dV = 0 \Rightarrow dV^\alpha = -dV^\beta$

$dn = 0 \Rightarrow dn^\alpha = -dn^\beta$

$dU^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \mu^\alpha dn^\alpha$

$dU^\beta = T^\beta dS^\beta - P^\beta dV^\beta + \mu^\beta dn^\alpha$

$dU = (T^\alpha - T^\beta) dS^\alpha - (P^\alpha - P^\beta) dV^\alpha + (\mu^\alpha - \mu^\beta) dn^\alpha = 0$

$\Rightarrow T^\alpha = T^\beta, P^\alpha = P^\beta, \mu^\alpha = \mu^\beta$ (Additional condition: second derivative)

$\Rightarrow$ Thermal, mechanical, and chemical equilibrium

$U$ will decrease spontaneously if a system of constant $S$ and $V$ is not in equilibrium.

Enthalpy $H = U + PV$
Hemholtz Free Energy $F = U - TS$

Gibbs Free Energy $G = U + PV - TS$

The equilibrium conditions for different situations (constant $S$, $P$; constant $T$, $V$; etc) are outlined below in table xx

<table>
<thead>
<tr>
<th>Variables Held Constant</th>
<th>Equilibrium Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S, P$</td>
<td>$dH = 0$</td>
</tr>
<tr>
<td>$T, V$</td>
<td>$dF = 0$</td>
</tr>
<tr>
<td>$T, P$</td>
<td>$dG = 0$</td>
</tr>
<tr>
<td>$S, V$</td>
<td>$dU = 0$</td>
</tr>
</tbody>
</table>

Table 8.1: Equilibrium conditions.

If $T$ and $P$ are held constant, a system will seek to minimize the Gibbs free energy, $G$. Consider two states connected by an isothermal and isobaric path:

\[
G_1 = U_1 + PV_1 - TS_1 \\
G_2 = U_2 + PV_2 - TS_2 \\
\Delta G = \Delta U + P\Delta V - T\Delta S, \text{ and } \Delta U = Q + W + W' \\
\]

Consider first a reversible path:

$W_{rev,T} = -P\Delta V$ and $Q_{rev,P} = T\Delta S$

For any path:

\[
\Delta G = (Q - Q_{rev}) + (W - W_{rev}) + W' < 0
\]

In a system at constant $T$ and $P$ that is not in equilibrium, $G$ will tend to decrease spontaneously to approach chemical equilibrium.

2) Example for two component system

Two isolated systems are defined - each in equilibrium with separate environments.

\[
\begin{align*}
P_1V_1 &= n_1RT_1 \\
P_2V_2 &= n_2RT_2
\end{align*}
\]

Let them come to equilibrium in isolation

\[
\Delta U_1 + \Delta U_2 = 0
\]

\[
\frac{3}{2}n_1R(T_f - T_i) + \frac{3}{2}n_2R(T_f - T_i) = 0
\]

\[
\Rightarrow n_1T_f - n_1T_1 = -n_2T_f + n_2T_2 \Rightarrow T_f = \frac{n_1T_1 + n_2T_2}{n_1 + n_2}
\]
We can also solve for $P_f, V_i$

$$P_f = \frac{(n_1 + n_2)RT_f}{V_1 + V_2} = \frac{R(n_1T_1 + n_2T_2)}{V_1 + V_2}$$

and

$$V_1 = \frac{n_1RT_f}{P_f}, V_2 = \frac{n_2RT_f}{P_f}$$

$$V_1 + V_2 = \frac{n_1RT_f}{P_f} + \frac{n_2RT_f}{P_f}$$

8.3 Maxwell Relations

For free energies:

- coefficients in opposite corners
- derivatives in adjacent corners
- minus signs apply to coefficients

For Maxwell Relations:

$$\therefore = \therefore \text{ i.e. } - \left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P$$

Note: This does not include the chemical potential. $\delta W' = \sum_i^m \mu_i dn_i$

3) Useful relations between $S, T, P, V$ for an ideal monatomic gas

$$dS = C_v dT - V^\alpha dP = \frac{5}{2} R dT - \frac{V}{T} dP = \frac{5}{2} R dT - \frac{R}{T} dP$$

$$dS = C_v dT + \frac{\alpha}{\beta} dV = \frac{3}{2} R dT + \frac{P}{T} dV = \frac{3}{2} R dT + \frac{R}{V} dV$$

Constant $P$: $\Delta S = \frac{5}{2} R \ln \left( \frac{T_2}{T_1} \right)$

Constant $T$: $\Delta S = -R \ln \left( \frac{P_2}{P_1} \right)$

Constant $V$: $\Delta S = \frac{3}{2} R \ln \left( \frac{T_2}{T_1} \right)$

Constant $S$: $\frac{P_2}{P_1} = \left( \frac{T_2}{T_1} \right)^{5/2} = \left( \frac{V_1}{V_2} \right)^{5/3}$
Figure 8.3

\[ dS = C_v dT + \alpha \beta dV = \frac{3}{2} R dT + \frac{P}{T} dV = \frac{3}{2} R dT + \frac{P}{V} dV \]

\[ 0 = \frac{3}{2} \frac{R}{T} dT + \frac{R}{V} dV \rightarrow \frac{3}{2} \ln \left( \frac{T_2}{T_1} \right) = - \ln \left( \frac{V_2}{V_1} \right) \]

\[ \left( \frac{T_2}{T_1} \right)^{3/2} = \frac{V_1}{V_2}, \left( \frac{T_2}{T_1} \right)^{5/2} = \left( \frac{V_1}{V_2} \right)^{5/3} = \frac{P_2}{P_1} \]

One can show this using \( \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \) and substituting.

9 From Microstates to Entropy

Outcomes for this section:
1) Express the entropy \( S \) of the system in terms of equivalent microstates in the equilibrium (most probable) macrostate.

2) Given the energy levels of a system of particles, calculate the partition function.

3) Given the partition function, calculate the Helmholtz free energy, the entropy, the internal energy, and the heat capacity.

Destination: \( S = k_B \ln \Omega \)

where \( k_B \) = Boltzmann’s constant, \( 8.317 \times 10^{-5} \text{eV}/K, 1.38 \times 10^{-23} \text{J}/K \) and \( \Omega = \) number of equivalent microstates in (equilibrium) macrostate.

Matter is composed of atoms, and is therefore discrete. Continuum thermodynamics arises from interactions between discrete components and interactions with the environment.
A statistical description is needed to connect the microscopic and macroscopic descriptions.

### 9.1 Microstates and Macrostates

**Microstate**: Specification of the state (e.g., energy level) of every atom at a particular point in time.

Example: 4 identical particles in 2 levels, pour 4 balls in 2 boxes.

If balls are placed randomly, which configuration is more likely?

![Figure 9.1](image)

<table>
<thead>
<tr>
<th># Microstates</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(4,0)</td>
</tr>
<tr>
<td>6</td>
<td>(2,2)</td>
</tr>
<tr>
<td>4</td>
<td>(1,3)</td>
</tr>
</tbody>
</table>

**Table 9.1**: Microstates and distribution of balls

**Macrostate**: collection of equivalent microstates. Equivalent means the same numbers of particles within each of the levels.

Example: the macrostate with 1L, 3R - (1,3)

We will use combinatorics to calculate:

1) The distribution function specifies the occupation of atomic states by identical particles, and thus the macrostate.
2) Number of macrostates \ll \text{number of microstates}

3) If all microstates are equally likely, then some macrostates are much more likely. (e.g. (2,2))
   ⇒ How do we see this?

1) How many microstates correspond to a given macrostate? \( N_0 : \# \text{ of balls, } r : \# \text{ of boxes, } n_i : \text{balls in } i^{th} \text{ box} \)

\[
\Omega = \frac{N_0!}{n_1!n_2!n_3!...n_r!}
\]

\[
n! \equiv n(n-1)(n-2)...3 \cdot 2 \cdot 1
\]

\[
= \frac{N!}{\Pi_{i=1}^r n_i!}
\]

<table>
<thead>
<tr>
<th>Number of Microstates</th>
<th>Distribution</th>
<th>( \Omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(4,0)</td>
<td>( \Omega_{4,0} = \frac{4!}{4!} = 1 )</td>
</tr>
<tr>
<td>6</td>
<td>(2,2)</td>
<td>( \Omega_{2,2} = \frac{4!}{2!2!} = 3 \cdot 2 \cdot 1 = 6 )</td>
</tr>
<tr>
<td>4</td>
<td>(1,3)</td>
<td>( \Omega_{1,3} = \frac{4!}{1!3!} = \frac{4 \cdot 3 \cdot 2 \cdot 1}{3 \cdot 2 \cdot 1} = 4 )</td>
</tr>
</tbody>
</table>

Table 9.2: Microstates corresponding to given macrostates

Total number of possibilities is \( r^{N_0} \), or \( 2^4 = 16 \). There are 5 macrostates: (4,0) (1,3) (2,2) (3,1) (4,0)

Example: Four atoms in volume V. How many microstates are there, and how many macrostates?

- Divide each side into M compartments.
- Compartments are so small that \( M \gg 4 \) and occupation is 0 or 1.
9.1 Microstates and Macrostates  9  FROM MICROSTATES TO ENTROPY

Figure 9.3

How many ways can we distribute 4 indistinguishable particles over 2M compartments?

Case I: \( \Omega_I \)

\[
\binom{2M}{4} = \frac{(2M)!}{4!(2M - 4)!} = \frac{2M \cdot (2M - 1)(2M - 2)(2M - 3)}{4!} \approx \frac{(2M)^4}{4!}
\]

Case II: How many configurations have all the particles on one side, i.e. M boxes?

\[
\Omega_{II} = \binom{M}{4} \approx \frac{M^4}{4!}
\]

Note that \( \frac{\Omega_{II}}{\Omega_I} \approx \frac{1}{2^4} = \frac{1}{16} \), \( \Omega_{II} \) is much less likely.

For N atoms, we would find \( \frac{\Omega_{II}}{\Omega_I} = \frac{1}{2^N} \ll 1 \)

Even a state with 51% on the left would be highly improbable. \( \frac{(1.98M)^N}{(2M)^N} \) for \( N \sim N_A \) is vanishingly small. (Try plotting this).

100 - 3.790
1000 - 4 \times 10^{-5}
10000 - 2 \times 10^{-44}

9.1.1 Postulate of Equal Likelihood

All allowable microstates (energetically equivalent configurations) are equally likely.

\[
P_j = \frac{\Omega_j}{\Omega} \] is the probability of finding the system in macrostate j. The most probable macrostate is the one that represents the most microstates in \( \Omega \).
9.2 Conditions for equilibrium

9.1.2 The Boltzmann Hypothesis (to be derived)

\[ S = k_B \ln \Omega \]

\[ k_B = 1.38 \times 10^{-23} \text{J/K} \]

Maximum in \( \Omega \) corresponds to a maximum in \( S \).

How do we determine the most probable macrostate?

What are the conditions of equilibrium?

9.2 Conditions for equilibrium

We aim to minimize \( S \), where \( S = k \ln \Omega \), or

\[ S = k_B \left( \frac{N_o!}{\prod_{i=1}^{r} n_i!} \right) \]

What tools do we need to do so?

\[ \ln \left( \frac{x}{y} \right) = \ln x - \ln y, \ln(xy) = \ln x + \ln y \]

\[ d \ln x = \frac{dx}{x} \]

Stirling’s Approximation: \( \ln x! \approx x \ln x - x \)

This is very accurate for large \( x \). How large?

1) Express \( \Omega \) as a sum over logarithms of occupation numbers.

\[ \Omega = \frac{N!}{\prod_{i=1}^{r} n_i!} \rightarrow \ln \Omega = \ln N! - \ln \left( \prod_{i=1}^{r} n_i! \right) \]
Apply Stirling’s Approximation, \( \ln(\Pi x_i) = \sum \ln x_i \)

\[
\ln \Omega = \approx N \ln N - N - \sum_{i=1}^{r} (n_i \ln n_i - n_i)
\]

Note also that \( N = \sum_{i=1}^{r} n_i \) (summing occupation numbers gives the total particle number).

So

\[
\ln \Omega \approx N \ln N - \sum_{i=1}^{r} n_i \ln n_i + \sum_{i=1}^{r} n_i \ln n_i
\]

\[
\ln \Omega \approx \sum_{i=1}^{r} n_i (\ln N - n_i) \text{ Not too bad}
\]

2) Differentiate

\[
d \ln \Omega = \sum_{i=1}^{r} \left[ dn_i (\ln N - \ln n_i) + n_i \left( \frac{dN}{N} - \frac{dn_i}{n_i} \right) \right]
\]

\[
= \sum_{i=1}^{r} (\ln N - \ln n_i) dn_i + \sum_{i=1}^{r} \left( \frac{n_i}{N} \right) dN - \sum_{i=1}^{r} \frac{dn_i}{dN}
\]

\[
d \ln \Omega = - \sum_{i=1}^{r} \ln \left( \frac{n_i}{N} \right) dn_i
\]

3) Impose constraints

For an isolated system, the total particle number and energy are constant as \( \ln \Omega \) is maximized.

\[
N = n_1 + n_2 + ... + n_r = \sum_{i=1}^{r} n_i, \quad dN = 0
\]

\[
U = n_1 \Sigma_1 + n_2 \Sigma_2 + ... + n_r \Sigma_r = \sum_{i=1}^{r} n_i \Sigma_i, \quad dU = 0
\]

To impose constraints, we use Lagrange Multipliers.

\[
d \ln \Omega + \lambda_1 dN + \lambda_2 dU = 0
\]

\[
- \sum_{i=1}^{r} \ln \left( \frac{n_i}{N} \right) dn_i + \lambda_1 \sum_{i=1}^{r} dn_i + \lambda_2 \sum_{i=1}^{r} \Sigma_i dn_i = 0
\]

\[
- \sum_{i=1}^{r} \left[ \ln \left( \frac{n_i}{N} \right) dn_i + \lambda_1 - \lambda_2 \Sigma_i \right] dn_i = 0 \Rightarrow \text{Gives } r \text{ equations, e.g.}
\]

\[
\ln \left( \frac{n_i}{N} \right) - \lambda_1 - \lambda_2 \Sigma_i = 0 \Rightarrow \frac{n_i}{N} = e^{\lambda_1} e^{\lambda_2 \Sigma_i}, \quad i = 1, 2, ..., r
\]

4) Use constraints to eliminate \( \lambda_1, \lambda_2 \)
\[ \frac{n_i}{N} = e^{\lambda_1} e^{\lambda_2 \Sigma_i} \]
\[ \sum_{i=1}^{r} \frac{n_i}{N} = 1 \rightarrow \sum_{i=1}^{r} e^{\lambda_1} e^{\lambda_2 \Sigma_i} = 1 \]
\[ e^{\lambda_1} = \frac{1}{\sum_{i=1}^{r} e^{\lambda_2 \Sigma_i}} \frac{n_i}{N} \]
\[ \frac{e^{\lambda_2 \Sigma_i}}{Z} \]

The fractional occupation number of the \( i^{th} \) level.

So
\[ \ln \Omega_i = -\sum_{i=1}^{r} n_i \left( \frac{n_i}{N} \right) = -\sum_{i=1}^{r} n_i \ln \left( \frac{e^{\lambda_2 \Sigma_i}}{Z} \right) \]
\[ = -\sum_{i=1}^{r} n_i \left( \lambda_2 \Sigma_i - \ln Z \right) \]

\[ \ln \Omega = -\lambda_2 \sum_{i=1}^{r} n_i \Sigma_i + \ln Z \sum_{i=1}^{r} n_i = -\lambda_2 U + N \ln Z \]

What is \( \lambda_2 \)?

Consider response of system to the reversible absorption of an infinitesimal amount of heat \( \delta Q \).

\[ d \ln \Omega = -\lambda_2 dU + d(N \ln Z) \]
\[ dU = \delta Q_{rev} = TdS \]
\[ d \ln \Omega = -\lambda_2 TdS \]

So
\[ S \propto \ln \Omega \]

\[ S = -\frac{1}{\lambda_2 T} \ln \Omega = k_B \ln \Omega \rightarrow \lambda_2 = -\frac{1}{k_B T} \]

\[ \frac{n_i}{N} = \frac{e^{-\Sigma_i/kT}}{Z} \sum_{i=1}^{r} e^{-\Sigma_i/kT} \]

We can calculate macroscopic properties from the partition function.

Recall \( \ln \Omega = -\lambda_2 U + N \ln Z \), \( S = k \ln \Omega \)

\( (k \ln \Omega =) \)
\[ S = -\frac{U}{T} + k_B N \ln Z \]

\[-kT \ln Z = U - TS \equiv F \text{ Hemholtz Free Energy!} \]
So

\[ F = -kTN \ln Z \]

\[ \frac{F}{N} = -kT \ln Z \]

Also, \( S = -\left( \frac{\partial F}{\partial T} \right)_V = Nk \ln Z + NkT \left( \frac{\partial \ln Z}{\partial T} \right)_V \)

Then

\[ U = F + TS = NkT^2 \left( \frac{\partial \ln Z}{\partial T} \right)_V \]

\[ C_V = \left( \frac{\partial U}{\partial T} \right)_V = 2NkT \left( \frac{\partial \ln Z}{\partial T} \right)_V + NkT^2 \left( \frac{\partial^2 \ln Z}{\partial T^2} \right)_V \]

Note that the pressure dependence of \( Z \) is needed to calculate \( V, H, G, C_P \).

## 10 Noninteracting (Ideal) Gas

The definition of an ideal gas is that there are no interactions between the molecules, they only have kinetic energy. The total kinetic energy for an ideal gas of molecules, each with mass, is as follows:

\[ \sum \frac{1}{2} mv^2 = \sum \frac{m}{2} (v_x^2 + v_y^2 + v_z^2) \quad (10.1) \]

- The energy distribution of free particles is continuous.

\[ \sum \rightarrow \int \]

- For convenience, assume box of dimensions \( L \times L \times L = V \)

\[ Z = \int_0^L \int_0^L \int_0^L dx dy dz \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{1}{2kT} (v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z \]

Gaussians

\[ = V \int_{-\infty}^{\infty} e^{-\frac{1}{2kT}mv_x^2} dv_x \int_{-\infty}^{\infty} e^{-\frac{1}{2kT}mv_y^2} dv_y \int_{-\infty}^{\infty} e^{-\frac{1}{2kT}mv_z^2} dv_z \]

\[ \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}} \quad (\text{for } \alpha > 0) \]
10.1 Ideal gas Law

\[ \frac{\alpha}{e^{\frac{1}{2kT}mv^2}} \]

\[ \therefore Z = V \left( \frac{2\pi kT}{m} \right)^{3/2} \]

Now we can easily derive many functions.

\[ \ln Z = \ln V + \frac{3}{2} \ln \left( \frac{2\pi k}{m} \right) + \frac{3}{2} \ln T \]

\[ \frac{\partial \ln Z}{\partial T} = \frac{3}{2} \frac{1}{T} \]

\[ \Rightarrow F = -NkT \ln Z = -NkT \left[ \ln V + \frac{3}{2} \ln \left( \frac{2\pi kT}{m} \right) \right] \]

\[ U = NkT^2 \left( \frac{\partial \ln Z}{\partial T} \right)_V = NkT^2 \left( \frac{3}{2} \frac{1}{T} \right) = \frac{3}{2} NkT \]

\[ U = \frac{3}{2} kT \quad \text{Energy per particle} \]

\[ C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{3}{2} NK = \frac{3}{2} \left( \frac{N}{N_A} \right) kN_A = \frac{3}{2} nR \]

\[ \frac{C_V}{n} = \frac{3}{2} R \quad \text{n: moles} \]

10.1 Ideal gas Law

\[ dF = -SdT - PdV + \delta W' \]

\[ -P = \left( \frac{\partial F}{\partial V} \right)_T \]

\[ P = -NkT \left( \frac{\partial \ln Z}{\partial V} \right)_T = NkT \left[ \frac{\partial}{\partial V} \left( \ln V + \frac{3}{2} \ln \left( \frac{2\pi k}{m} \right) + \frac{3}{2} \ln T \right) \right]_T \]

\[ P = NkT \cdot \frac{1}{V} = \frac{\mu}{V} \]
• Note that we have ignored interactions between particles/atoms. Attractive interactions lead to, e.g. condensation.

• We have also ignored repulsive interactions, i.e. atoms occupy finite volumes.

Including these leads to the van der Waals equation:

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT$$

11 Diatomic Gases

Diatomic gases possess rotational and vibrational degrees of freedom. The kinetic energy of a gas molecule with $p$ degrees of freedom is

$$\Sigma = \sum_{j=1}^{P} b_j v_j^2,$$

and

$$Z = \prod_{j=1}^{P} \sqrt{\frac{\pi kT}{b_j}}$$

(e.g. $b = \frac{m}{2}$ for translations) For rotations $v \rightarrow \omega$, $M \rightarrow I$

Surprisingly, $U$ and $C_V$ do not depend on $b_j$:

$$\left( \frac{\partial \ln Z}{\partial T} \right)_V = \frac{P}{2T} \rightarrow U = NkT^2 \left( \frac{P}{2T} \right) = \frac{P}{2} NkT$$

Get $\frac{1}{2}RT$ for each degree of freedom

$$C_V = \frac{P}{2} Nk = \frac{P}{2} nR$$

Observations:

Heat capacity measurement reveals the number of degrees of freedom.

• Monatomic: 3 translational

• Heteronuclear Diatomic: 3 translational + 2 rotational + 2 vibrational

Figure 11.1: Diatomic gas
12 The Einstein Model of a Crystal

How is the discrete nature of matter manifested in easily observable quantities?

Consider atoms in a simple cubic lattice

- Bounded to six nearest neighbors (vibrating in harmonic potential) \( F = -kx \)
  \[ \omega = \sqrt{\frac{k}{m}} \]

Figure 12.1: Vibration of atoms in harmonic potential

- 3 bonds/atom, 3N bonds in crystal

Figure 12.2: Binding to six nearest neighbors

By solving the Schrödinger equation for the harmonic oscillator potential, one can show that

\[ \sum_i = \left( i + \frac{1}{2} \right) \hbar \omega = \left( i + \frac{1}{2} \right) \hbar v \]  
\( i = 0, 1, 2... \)

\( h \): Planck’s constant, \( v \): frequency, \( h : \frac{h}{2\pi} \)

Energy is stored in vibration of atoms. To analyze, calculate the partition function for the vibrations:

\[ Z = \sum_{i=0}^{n} e^{-\Sigma_i / kT} = \sum_{i=0}^{n} e^{-\left(i + \frac{1}{2}\right) \hbar v / kT} = e^{-\frac{1}{2} \frac{\hbar v}{kT}} \sum_{i=0}^{n} e^{-i \hbar v / kT} \]

Here \( n \) is the number of energy levels. If \( n \) is large, we can take the limit \( n \to \infty \) and use

\[ \sum_{i=0}^{\infty} e^{-i \hbar v / kT} = \frac{1}{1 - e^{-\hbar v / kT}}, \quad Z = e^{-\frac{1}{2} \frac{\hbar v}{kT}} \frac{1}{1 - e^{-\hbar v / kT}} \]

12.1 Thermodynamic Properties of a Crystal

Vibrations along each of three bonding axes contribute to energy:
\[ F = -3NkT \ln Z = 3NkT \left[ \frac{hv}{2kT} + \ln(1 - e^{-hv/kT}) \right] \]
\[ = \frac{3}{2} Nhv + 3NkT \ln(1 - e^{-\frac{hv}{kT}}) \]

Note that the crystal has energy even at zero T!

\[ U = -\frac{\partial}{\partial \beta} \ln Z = kT^2 \frac{\partial}{\partial T} \ln Z \quad (\beta = kT) \quad \text{(per particle?)} \]
\[ U = 3NkT^2 \frac{\partial}{\partial T} \ln Z \]
\[ = 2NkT^2 \frac{\partial}{\partial T} \left[ -\frac{1}{2} \frac{hv}{kT} - \ln(1 - e^{-\frac{hv}{kT}}) \right] \]

\[ U = \frac{3}{2} Nhv \left[ \frac{1 + e^{-\frac{hv}{kT}}}{1 - e^{-\frac{hv}{kT}}} \right] \]

How does this change with temperature?

The heat capacity, \( C_V = \frac{\partial U}{\partial T} \)

\[ C_V = \frac{3}{2} Nhv \cdot \frac{hv}{kT} e^{-\frac{hv}{kT}} \times \left( \frac{1 - e^{-\frac{hv}{kT}} + (1 + e^{-\frac{hv}{kT}})}{(1 - e^{-\frac{hv}{kT}})^2} \right) \]

\[ C_V = 2Nk \left( \frac{hv}{kT} \right)^2 \frac{e^{-\frac{hv}{kT}}}{(1 - e^{-\frac{hv}{kT}})^2} \]

![Figure 12.3: Heat capacity in an atom as a function of temperature](image)

Classical limit \( (3R \frac{J}{mol\cdot K}) \)

The Einstein model captures the qualitative behavior of the heat capacity very well. (But something is missing).

Note here regarding information derived from heat capacity.
Outcomes for this section:

1) State the differential of the Gibbs free energy $G$ as a function of $S$, $T$, $V$, and $P$.

2) State the conditions for two phases to coexist in equilibrium.

3) Explain how isobaric section of the chemical potential $\mu(T, P)$ as a function of temperature and pressure can be calculated from knowledge of the heat capacity and the entropy at room temperature.

4) Given $\mu(T, P)$ for multiple phases, determine the equilibrium phase at a given temperature.

5) Derive the Clausius-Clapeyron relation: express the general condition for determining the region of two-phase coexistence.

6) Calculate the $\Delta H$ given the $C_P(T)$, assuming a negligible contribution from thermal expansion.

7) Calculate $\Delta V^{\alpha \rightarrow \beta}$ assuming ideal gas behavior.

8) Integrate $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$ with the assumption that $\Delta S$ and $\Delta V$ depend only weakly on the temperature.

9) Given the $P - T$ diagram, qualitatively sketch $G(T)$ for a specified region.

10) Given the $P - T$ diagram, specify the sign of $\Delta V^{\alpha \rightarrow \beta}$.

11) State Trouton’s rule and justify its validity qualitatively.

12) Sketch the $P - T$ diagram for a one-component system.

- Unary material: single chemical component
- Homogeneous: 1 phase
- Heterogeneous: 2 phase
- Phases: Gas, Liquid, Solid; allotropes are distinct solid phases
- Phase boundary: limit of phase stability
  - multiple phases co-exist in equilibrium at a phase boundary
  - Boundary defined by Clasius - Clapeyron Equation
- Phase transformation: solid $\rightarrow$ liquid, liquid $\rightarrow$ vapor, allotropic process of phase transformation determines microstructure
13.1 Phase Diagrams

Phase Diagram of Unary Heterogeneous System

The phase boundary defines the limits of phase stability. Phases co-exist at a phase boundary. A phase transformation occurs when crossing phase boundaries i.e. \( s \rightarrow \ell, \ell \rightarrow v, s \rightarrow v \).

13.2 Chemical Potential Surfaces

To find \( \mu(T, P) \), integrate \( d\mu = dG = -SdT + VdP \)
knowns: \( C_P \), expansion coefficient, compressibility depends on phase
Then repeat for each phase (solid \( \alpha \), solid \( \beta \), liquid, etc.)

\[ \mu^L(T, P) \text{ and } \mu^S(T, P) \] (two surfaces) intersect at a line defined by \( \mu^L = \mu^S \).

- \( \mu^L \) and \( \mu^S \) must be computed from same reference state (e.g. \( \mu^S(T_o, \ell_o) \))
- Equilibrium conditions are met at intersection
- \( T^\alpha = T^L, P^\alpha = P^L, \mu^\alpha = \mu^L \)

AB: solid + liquid
COD: solid + gas
EOF: liquid + gas
O: triple point S+ℓ+S

Relation between chemical potential and the Gibb’s free energy (for unary systems).

G: intensive molar Gibbs free energy

\[ G' = nG \text{ : Extensive} \]

\[ dU' = TdS' - PdV' + \mu dn \]

\[ G' = U' + PV' - TS' \]

\[ dG' = dU' + PdV' + V'dP - TdS' - S'dT \]

Substitute \( dU' \)

\[ dG' = TdS' + PdV' + \mu dn + PdV' + V'dP - TdS' - S'dT \]

\[ dG' = -S'dT + V'dP + \mu dn \]

\[ \mu = \left( \frac{\partial G'}{\partial n} \right)_{T,P} \]

\[ \mu = \left( \frac{\partial G'}{\partial n} \right)_{T,P} = \left( \frac{\partial}{\partial n} (nG) \right)_{T,P} = G \left( \frac{\partial}{\partial n} \right)_{T,P} = G \]
13.3 $\mu(T, P)$ Surfaces

\[ d\mu^\alpha = dG^\alpha = -S^\alpha dT + V^\alpha dP \]

Approach: compute isobaric sections by integrating $-S^\alpha dT$.

\[ dS_P^\alpha = \frac{C_P^\alpha}{T} dT \Rightarrow S^\alpha(T) = S^\alpha(298) + \int_{298}^{T} \frac{C_P^\alpha(T')}{T'} dT' \]

\[ \mu^\alpha(T) = \mu^\alpha(298) - \int_{298}^{T} S^\alpha(T')dT' \]

\[ \mu^\alpha(T) = \mu^\alpha(298) - \int_{298}^{T} \left[ S^\alpha(T') + \int_{298}^{T} \frac{C_P^\alpha(T')}{T'} dT' \right] dT'' \]

To compare $\mu^\alpha$ with $\mu^L$, we need to calculate $\mu^L$ from the same reference point.

Connecting $\mu^\alpha$ with $\mu^L$ at the melting point $T_m$:

\[ \mu^L(T) - \mu^\alpha(298) = \left[ \mu^L(T) - \mu^L(T_m) \right] + \left[ \mu^\alpha(T_m) - \mu^\alpha(298) \right] \]

integral of $-S_L$ from $T_m$ to $T$ (already calculated this integral)

\[ \mu^L = \mu^L(T_m) - \int_{T_m}^{T} \left[ S_L(T_m)^* + \int_{T_m}^{T} \frac{C_L^P(T')}{T'} dT' \right] dT'' \]

Plot $G(T) - G^\alpha(298)$ versus $T$ for each phase $\alpha, L$ i.e. plot of $G^\alpha$ begins at 0, do example where $P=1$ bar.

* Note the entropy changes with the phase change

\[ S_L(T_m) = S^\alpha(T_m) + \Delta S^{\alpha \rightarrow L}(T_m) \]

$\Delta S$ : latent heat

\[ S_L(T_m) = S^\alpha(T_m) + \int_{298}^{T_m} \frac{C_P^\alpha(T)}{T} dT + \Delta S^{\alpha \rightarrow L}(T_m) \]

\[ G^L(T) - G^\alpha(298) = G^L(T) - G^L(T_m) + G^\alpha(T_m) - G^\alpha(298) = \]

\[ = \int_{T_m}^{T} \left\{ S^\alpha(T_m) + \int_{298}^{T_m} \frac{C_P^\alpha(T')}{T'} dT' + \Delta S^{\alpha \rightarrow L}(T_m) \right\} + \int_{T_m}^{T} \frac{C_L^P(T')}{T'} dT' \]
13.4 Clasius-Clapeyron Eq.

Goal: Determine two-phase coexistence lines in order to complete the P-T phase diagram

Areas: single phase

Lines: 2-phase

Intersections: 3 phases (triple point)

Consider co-existence of two phases in equilibrium:

\[ T^\alpha = T^\beta, \quad P^\alpha = P^\beta, \quad \mu^\alpha = \mu^\beta \]

Phase changes change the amounts of two phases:

\[ d\mu^\alpha = -S^\alpha dT^\alpha + V^\alpha dP^\alpha \]
\[ d\mu^\beta = -S^\beta dT^\beta + V^\beta dP^\beta \]

But we require equilibrium:

\[ dT^\alpha = dT^\beta \quad dP^\alpha = dP^\beta \quad d\mu^\alpha = d\mu^\beta \]

\[ -S^\alpha dT + V^\alpha dP = -S^\beta dT + V^\beta dP \]

\[ (S^\beta - S^\alpha) dT = (V^\beta - V^\alpha) dP \]

\[ \Delta S^{\alpha \rightarrow \beta} dT = \Delta V^{\beta \rightarrow \alpha} dP \]
\[
\Delta S^{\alpha \rightarrow \beta} : \text{difference in molar entropy}
\]
\[
\Delta V^{\alpha \rightarrow \beta} : \text{difference in molar volume}
\]

\[
\frac{dP}{dT} = \frac{\Delta S^{\alpha \rightarrow \beta}}{\Delta V^{\alpha \rightarrow \beta}} \quad \text{Classius-Claperyon Equation}
\]

\[
\text{Slope} = \frac{\text{Entropy Change}}{\text{Volume Change}}
\]

**But how do we measure entropy change?**

Instead, we measure the heat of fusion of vaporization isobarically under reversible conditions.

So, \(Q^{\alpha \rightarrow \beta} = \Delta H^{\alpha \rightarrow \beta}\)

In equilibrium,

\[
G^\alpha = G^\beta \quad H^\alpha - TS^\alpha = H^\beta - TS^\beta \quad (T^\alpha = T^\beta)
\]

So \(\Delta S^{\alpha \rightarrow \beta} = \frac{\Delta H^{\alpha \rightarrow \beta}}{T}\), and

\[
\frac{dP}{dT} = \frac{\Delta H^{\alpha \rightarrow \beta}}{T \Delta V^{\alpha \rightarrow \beta}}
\]

Can be integrated to get \(P(T)\) for 2-phase coexistence.

We need \(\Delta H(P, T)\), \(\Delta V(P, T)\) from Chapter 4.

**13.4.1 Step 1: Find \(\Delta H(T, P)\)**

\[
d(\Delta H^{\alpha \rightarrow \beta}) = d(H^\beta - H^\alpha) = dH^\beta - dH^\alpha
\]

\[
dH = C_P dT + V (1 - T^\alpha) dP
\]

\[
d\Delta H^{\alpha \rightarrow \beta} = \Delta C_P dT + \Delta [V (1 - T^\alpha)] dP
\]

negligible for pressures up to \(\sim 10^{-5}\) bar

To find \(\Delta H\), we need the temperature dependence of the heat capacity. \(C_P(T)\) is often given empirically as

\[
C_P = a + bT + \frac{c}{T^2} + dT^2 \quad \text{(See Appendix B,E)}
\]

\[
\Delta C_P = \Delta a + \Delta bT + \frac{\Delta c}{T^2} + \Delta dT^2
\]

Now we can integrate to get \(\Delta H\).
Step 2: Find $\Delta V^{\alpha \to \beta}(T, P) \equiv V^{\beta}(P, T) - V^{\alpha}(P, T)$

First consider the case of $\beta$ as a vapor phase, and $\alpha$ as liquid or solid.

- $V^{\beta} \gg V^{\alpha}$
- Assume ideal gas behaviour.

$$\Delta V^{\alpha \to \beta} = V^{\beta} - V^{\alpha} \approx V^{\beta} = \frac{RT}{P}$$

Then for sublimation or vaporization to phase $\beta$,

$$\frac{dP}{dT} = \frac{\Delta H^{\alpha \to \beta}}{T \Delta V^{\alpha \to \beta}} = \frac{\Delta C_P}{T} \frac{dT}{dP} = \Delta C_P \frac{P}{RT^2} dT \text{ small, positive slope}$$

Phase boundaries can be calculated based on knowledge of $C_P$. (or vice versa, as we will see)

For solid $\to$ solid transformations, ($\beta$ is the stable phase at high T)

- Positive ($\Delta H, \Delta S > 0$)
- \[\frac{dP}{dt} = \frac{\Delta C_P^{\alpha \to \beta}(T)}{T \Delta V} dT\]

$\Delta V$ determines sign of slope

$\Delta V$ is usually positive but can be negative (e.g. $H_2O$)

$\Delta V \sim$ constant over few 10's of atmosphere.

An approximate analysis of solid-solid phase boundary:

$\Delta S, \Delta H, \Delta V$ are determined by $C_P, \alpha, \beta$, but suppose the variation with temperature is weak.

Since \[\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \text{constant}, \quad P - P_o \approx \frac{\Delta S}{\Delta V} (T - T_o) \approx \frac{\Delta H}{\Delta V} \left( \frac{T - T_o}{T_o} \right)\]

The slope $\frac{dP}{dT}$ is generally large since $\Delta V$ is small.

$$\frac{dP}{dT} \approx \frac{\Delta H}{T \Delta V} \approx \frac{\Delta H}{RT^2} \cdot P$$

$$\frac{dP}{P} \approx \frac{\Delta H(T)}{RT^2} dT$$

If we assume $\frac{d}{dT} \Delta H = 0$,

$$\ln \left( \frac{P}{P_o} \right) = -\frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right)$$

$$|\frac{dP}{dT}|^{S \to L} > |\frac{dP}{dT}|^{S \to V}$$
13.4.3 Justification for Approximations

Consider the enthalpy of transformation
\[ d\Delta H^{\alpha \rightarrow \beta}(T) = \Delta C_p(T)dT, \]
and integrate
\[ \Delta H(T) = \Delta H(T_o) + \int_{T_o}^{T} \Delta C_p(T)dT \]

Typically ~ 100kJ
\[ \int_{T_o}^{T} \Delta C_p(T)dT \]
Typically few kJ over few 100K

\[ \Delta H(T_o): \text{enthalpy change at the transformation temperature.} \]

Heat to drive phase change is larger than that needed to change the temperature.

Thus, \[ \Delta H(T) \approx \Delta H(T_o) \]

For vaporization,
\[ \ln \left( \frac{P}{P_o} \right) \approx -\frac{\Delta H(T_o)}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right) \]

13.4.4 Trouton’s Rule

\[ \Delta S_{vap} \] is approximately the same for all materials. \[ \Delta S = \frac{\Delta H}{T} \rightarrow \text{materials with high boiling points have larger } \Delta H_{vap}. \]

\[ \ln \left( \frac{P}{P_o} \right) = -\left( \frac{\Delta H}{R} \right) \frac{1}{T} + \left( \frac{\Delta H}{RT_o} \right) \]
Figure 13.9
14 Open Multicomponent Systems

Outcomes for this section:

1) Given sufficient information about the dependence of a total property $B$ or $\Delta B$ versus composition, find the partial molal properties as a function of composition via calculations of derivatives $dB$ or $d\Delta B$.

2) Given the partial molal properties as a function of composition, calculate the total properties of the system via integration of the derivatives.

3) Given the differentials of state functions, write partial derivatives that define the partial molal properties.

4) What is $B_k^0$?

5) What is $\mu_k - \mu_k^0$ for (a) a component behaving ideally, and (b) in general?

6) Define the activity of a component.

7) Given $\mu_k(T, P, X_k)$, calculate changes in the partial molal properties.

8) State and justify/explain Raoult’s law.

9) State and justify/explain Henry’s law.

10) Explain how the activity coefficient $\gamma$ can be used to describe the departure from ideal behavior in terms of “excess” quantities.

11) Define a “regular” solution and calculate the partial molal properties and total properties versus composition for binary mixtures.

12) Describe the driving forces for mixing and their origins in statistical mechanics.

13) Interpret changes in state functions with mixing in terms of ideal behavior and departures from ideality.

14.1 Partial Molal Properties of Open Multicomponent Systems

Volume $V'$ is an extrinsic quantity that depends on amount of each component: $V' = V'(T, P, n_1, n_2, \ldots, n_c)$

$C : \# \text{ components} \quad x_c : \text{mole fraction} \quad n_k : \# \text{ moles of component } k$
Then
\[ dV' = \left( \frac{\partial V'}{\partial T} \right)_{P,n} dT + \left( \frac{\partial V'}{\partial P} \right)_{T,n} dP + \sum_{k=1}^{c} \left( \frac{\partial V'}{\partial n_k} \right)_{T,P,n_0 \neq n_k} dn_k \]

We previously defined coefficients of \( dP, dT \)

For convenience, define \( \bar{V}_K \equiv \left( \frac{\partial V'}{\partial n_k} \right)_{T,P,n_0 \neq n_k} \) as partial molal volumes.

We can do the same for any other extensive property \( B'(U', S', F', G', H') \)

\[ dB' = MdT + NdP + \sum_{k=1}^{r} \bar{B}_k dn_k \]

\( \bar{B}_K \equiv \left( \frac{\partial B'}{\partial n_k} \right)_{T,P,n_0 \neq n_k} k = 1, 2, \ldots < \)

Consider a system (or sample) that we create by adding various amounts of the components sequentially (holding others constant).

If \( dT = dP = 0 \), \( dK'_{T,P} = \sum_{k=1}^{C} \bar{V}_k dn_k \), which we could integrate.

But \( \bar{V}_k \) depends on the composition, which changes continuously.

However, we can calculate changes in state functions using the simplest possible path: add all components simultaneously and in the proportions of the final mixture. \( \rightarrow \) Intensive properties \( (T, P, X_k) \) are constant

\[ V' = \sum_{k=1}^{C} \bar{V}_k dn_k = \sum_{k=1}^{C} \bar{V}_k \int_{n_0}^{n_k} dn_k = \sum_{k=1}^{C} \bar{V}_k n_k \]

and

\[ B' = \sum_{k=1}^{C} \bar{B}_k n_k \]

Interpretation: We can calculate how much each component contributes to a given extensive quantity.

### 14.2 Gibbs - Duhem Equation: Evaluating Differentials

\[ dB' = d \left[ \sum_{k=1}^{C} (\bar{B}_k n_k) \right] = \sum_{k=1}^{c} d(\bar{B}_k n_k) \]

Apply product rule:
14.3 The Mixing Process

\[ dB' = \sum_{k=1}^C \bar{B}_k dn_k + \sum_{k=1}^C n_k d\bar{B}_k, \]
but \( dP, dT \) are held constant, and

\[ dB' = \frac{MdT + N dP}{0} + \sum_{k=1}^C \bar{B}_k dn_k \]

\[ \rightarrow \sum_{k=1}^C n_k d\bar{B}_k = 0 \]

Gibbs Duhem equation relates the different partial molal properties. To be shown: given one, the others can be computed. For two components:

\[ n_1 \bar{B}_1 + n_2 \bar{B}_2 = 0 \]

14.3 The Mixing Process: Calculating changes in energy

Reference and Final States have the same T and P.

\[ B^o_k : \text{value of property B for pure component, per mole.} \]

\[ B^{to} = \sum_{k=1}^C B^o_k n_k : \text{total value of B} \]

\[ \Delta B'_{mix} - B'_{soln} - B'^o \]

\[ \Delta B'_{mix} = \sum_{k=1}^C \bar{B}_k n_k - \sum_{k=1}^C B^o_k n_k = \sum_{k=1}^C (\bar{B}_k - B^o_k) n_k \]

\[ \Delta B'_{mix} = \sum_{k=1}^C \Delta \bar{B}_k n_k \]

per mole

\[ \Delta B = \frac{\Delta B'}{n_T} = \sum_{k=1}^C \Delta \bar{B}_k \frac{n_k}{n_T} = \sum_{k=1}^C \Delta \bar{B}_k X_k \]

How does this vary with changes in composition?
\[ \Delta B_{mix}' = \sum_{k=1}^{C} \Delta \bar{B}_k n_k \]

\[ d(\Delta B') = \sum_{k=1}^{C} (\bar{B}_k d n_k - B^o_k d n_k) = \sum_{k=1}^{C} \Delta \bar{B}_k d n_k \]

Alternatively, we could have written

\[ d(\Delta B') = \sum_{k=1}^{C} (\Delta \bar{B} d n_k + n_k d \Delta \bar{B}_k) \rightarrow \sum_{k=1}^{C} n_k d \Delta \bar{B}_k = 0 \]

We can also express these per mole:

\[ d \Delta B_{mix} = \sum_{k=1}^{C} \Delta \bar{B}_k d X_k \]

\[ \sum_{k=1}^{C} X_k d \Delta \bar{B}_k = 0 \]

How do we find molal properties?

1) Measurement of total property \( B \) or \( \Delta B \) versus composition.

2) Measurements of PMP \( \bar{B}_k \) versus composition.

We will first apply to two component systems.

\[ B = \bar{B}_1 x_1 + \bar{B}_2 x_2, \quad dB = \bar{B}_1 d x_1 + \bar{B}_2 d x_2 \]

\[ dx_1 = -d x_2 \]

\[ x_1 + x_2 = 1, \quad x_2 = 1 - x_1 \]

\[ dB = (\bar{B}_1 - \bar{B}_2) d X_1 \]

\[ \frac{dB}{dX_1} = \bar{B}_1 - \bar{B}_2 \]

\[ B = \bar{B}_1 x_1 + \left( \bar{B}_1 - \frac{dB}{dX_1} \right) (1 - X_1) = \bar{B}_1 - \frac{dB}{dX_1} + \frac{dB}{dX_1} X_1 \]

71
14.4 Graphical Determination of Partial Molal Properties

\[ \Delta \bar{B}_2 = \Delta B_{\text{mix}} + (1 - X_2) \frac{d\Delta B_{\text{mix}}}{dX_2} \]

\[ \Delta B_2 = AB + PB \cdot \frac{BC}{PB} = AB + BC = AC \]

Evaluations of PMPs: given \( \bar{B}_1(X) \rightarrow \bar{B}_2(X_1) \), \( B \)

Gibbs - Duhem: \( X_1 d\bar{B}_1 + X_2 d\bar{B}_2 = 0, \quad d\bar{B}_1 = -\frac{X_2}{X_1} d\bar{B}_2 \)

\[ \bar{B}_1 = \bar{B}_1(x = 0) + \int_0^{X_2} d\bar{B}_1 = B_1^0 + \int_0^{X_2} \left( \frac{X_2}{X_1} d\bar{B}_2 \right) \]

\[ d\bar{B}_2 = \frac{dB}{dX_2} dX_2 \]

.: Given \( \bar{B}_2(X_2) \), we can compute \( \bar{B}_1(X_2) \).

Then we can find \( B = \bar{B}_1 X_1 + \bar{B}_2 X_2 \)
Example 8.2:
Given $\Delta \bar{H}_2$, find $\Delta \bar{H}_1$ and $\Delta H$.

$\Delta \bar{H}_2 = aX_1^2$ Compute total derivative:

$$\frac{d\Delta \bar{H}_2}{dX_2} = 2aX_1 \frac{dX_1}{dX_2} = -2aX_1$$

$$X_1 + X_2 = 1dX_1 + dX_2 = 1$$

$$dX_1 = -dX_2$$

$$\Delta \bar{H}_1 = - \int_{X_2=0}^{X_2} \frac{X_2}{X_1} \frac{d\Delta \bar{H}_2}{dX_2} dX_2 = - \int_{X_2=0}^{X_2} \frac{X_2}{X_1} (-2aX_1) dX_2$$

$$\Delta \bar{H}_1 = 2a \int_{0}^{X_2} X_2 dX_2 = aX_2^2$$

$$\Delta H = X_1 \Delta \bar{H}_1 + X_2 \Delta \bar{H}_2 = X_1(aX_2^2) + X_2(aX_1^2) = aX_1X_2 (X_1 + X_2)$$

$$\Delta H = aX_1X_2$$

14.5 Relationships between partial molal properties:

(F', G', H', S', U', their derivative, and coefficient relations)

Apply differential operator $\left( \frac{\partial}{\partial n_k} \right)_{P,T,n_j}$ to an extensive quantity:

Example: Hemholtz free energy $F' = U' - TS'$

Differentiating,

$$\left( \frac{\partial F'}{\partial n_k} \right)_{T,P,n_j} = \left( \frac{\partial U'}{\partial n_k} \right)_{T,P,n_j} - T \left( \frac{\partial S'}{\partial n_k} \right)_{T,P,n_j}$$

By definition,

$$\bar{F}_k = \bar{U}_k - T\bar{S}_k$$

See De Hoff for more examples and for coefficient an Maxwell relations.
14.6 Chemical Potential in Multicomponent Systems

Given \( \mu_k(T, P, X_k) \), one can find \( B, B', \bar{B}(T, P, X) \)

The thermodynamic state is specified by \( C+2 \) variables:
\[
dU' = TdS' - PdV' + \sum_{k=1}^C \mu_k dn_k , \quad \text{so} \quad \mu_k \equiv \left( \frac{dU'}{dn_k} \right)_{S,V,n_j}
\]

From Chapter 4 then, \( \delta W' = \sum_{k=1}^C \mu_k dn_k \) (necessary in open systems)

Examining \( dH', dF' \) and \( dG' \), we find that

Given \( \mu_k(T, P) = \bar{G}_k \), we can express all PMP’s in terms of \( \mu_k \):
\[
\bar{S}_k, \bar{V}_k, \bar{H}_k, \bar{U}_k, \bar{F}_k
\]

\[
\bar{S}_k = - \left( \frac{\partial \bar{G}_k}{\partial T} \right)_{P,n_k} = - \left( \frac{\partial \mu_k}{\partial T} \right)_{P,n_k}
\]

\[
\bar{V}_k' = \left( \frac{\partial \bar{G}_k}{\partial P} \right)_{T,n_k} = \left( \frac{\partial \mu_k}{\partial P} \right)_{T,n_k}
\]

So
\[
\bar{H}_k = \bar{G}_k + T\bar{S}_k = \mu_k - T \left( \frac{\partial \mu_k}{\partial T} \right)_{P,n_k} - P \left( \frac{\partial \mu_k}{\partial P} \right)_{T,n_k}
\]

\[
\bar{F}_k = \bar{U}_k - T\bar{S}_k = \mu_k - P \left( \frac{\partial \mu_k}{\partial P} \right)_{T,n_k}
\]

\( \mu_k \) is not measured directly

\( \Rightarrow \) measurement of \( \mu_k(P, T) \) enables PMPs to be determined. Note that \( \Delta \bar{B}_k \) can also be determined by substituting \( \mu_k \to \Delta \mu_k = \mu_k - \mu^0_k \)

14.7 Activity and Activity Coefficient

We found that \( \mu_k(T, P) = \left( \frac{\partial G'}{\partial n_k} \right)_{P,T,\mu_j} \equiv \bar{G}_k(T, P) \) but we do not know how to measure directly.

Define \( \mu_k - \mu^0_k = \Delta \mu_k \equiv RT \ln a_k \), where \( a_k \) is the activity of component \( k \).

Further we define the activity coefficient \( \gamma_k \) in \( a_k = \gamma_k X_k \), where \( X_k \) is the mole fraction.

So
\[
\Delta \mu_k = RT \ln(Y_k X_k)
\]

Next step: derive this for an ideal solution.
14.8 Properties of ideal solutions (e.g. ideal gas mixtures)

Imagine removing the partitions in Figure 14.3 below and allowing the gases to mix while keeping \( T, P \) constant. The process is analogous to free expansion.

![Figure 14.3: Mixture of ideal gases](image)

Each component experiences a decrease in pressure from \( P \) to \( P_k \). Each gas exerts, through collisions, a partial pressure on the wall of \( P_k = X_k P \). The total pressure \( P \) is

\[
P = \sum_{k=1}^{C} P_k = \sum_{k=1}^{C} X_k P = P \sum_{k=1}^{C} X_k = P
\]

Consider the change in chemical potential for the component, \( K \) which we can find by integrating \( d\mu_K \):

\[
d\mu_k = -\bar{S}_k dT + \bar{V}_k dP = \bar{V}_k dP \text{ since expansion is isothermal.}
\]

For an ideal gas,

\[
V' = n_T \frac{RT}{P} = \frac{RT}{P} \sum_{k=1}^{C} n_k,
\]

for which we can find \( \bar{V}_k = \left( \frac{\partial V'}{\partial n_k} \right)_{T,P,n_j} = \frac{RT}{P} \)

So

\[
\Delta \mu_k = \mu_k - \mu_k^0 = \int_{P}^{P_k} \bar{V}_k dP = \int_{P}^{P_k} \frac{RT}{P} dP = RT \ln \frac{P_k}{P} = RT \ln X_k
\]

Since the activity \( a_k = X_k \), we conclude that the activity coefficient \( \gamma_k = 1 \) for an ideal gas. (no interactions)

How do the partial molal quantities vary?

\[
\Delta G_k = RT \ln X_k
\]

\[
\Delta \bar{V}_k = \left( \frac{\partial \Delta \mu_k}{\partial P} \right)_{T,n_k} = 0
\]

\[
\Delta \bar{S}_k = \left( \frac{\partial \Delta \mu_k}{\partial T} \right)_{P,n_k} = -R \ln X_k
\]

\[
\Delta H_k = \Delta \mu_k + T \Delta \bar{S}_k = RT \ln X_k + T(-R \ln X_k) = 0
\]

\[
\Delta \bar{U}_k = \Delta \bar{H}_k - P \Delta \bar{V}_k = 0
\]
$\Delta F_k = \Delta U_k - T \Delta S_k = RT \ln X_k$

The change in total volume, enthalpy, and internal energy is 0, as the changes in partial molal quantities is zero. However, entropy is produced, leading to decreases in the free energies $\Delta G_{mix}, \Delta F_{mix}$.

![Figure 14.4: Properties of an ideal solution including $\Delta G_{mix}, \Delta S_{mix}, \Delta H_{mix}, \Delta V_{mix}, \Delta U_{mix}$ and $\Delta F_{mix}$. Maximum temperature shown is 1400 K.](image)

### 14.9 Behavior of Dilute Solutions

Add a few atoms of component 2 (solute) to a large volume of component 1 (solvent).

The solvent atoms still behave as though they are in an ideal solution, regardless of interactions.

**Raoult’s Law:** $\lim_{X_1 \to 1} a_1 = X_1$

The solute atoms interact primarily with solvent atoms, so the average properties will be proportional to $X_2$ for small $X_2$. (However, properties depend on solvent-solute combination.)

**Henry’s Law:** $\lim_{X_2 \to 0} a_2 = \gamma_0^0 X_2 : \gamma_0^0 (T, P)$ is Henry’s Law constant (in particular range), the solute activity coefficient for a dilute solution.

Consider Solute A in Solvent B

$\gamma_2 = e^{a_2 X_2^2 / RT}$ for $X_1 \to 1$, $\gamma_1^0 = e^{a_0^0 / RT}$

**Example: HW 8.4**

One mole of solid $Cr_2O_3$ at 2500K is dissolved in a large volume of a liquid Raoultian solution (at 2300K) of $Al_2O_3$ and $Cr_2O_3 (20\%)$.

Calculate the resulting $\Delta H$ and $\Delta S$ given

$T_{m, Cr_2O_3} = 2538K$, $\Delta H_{m, Al_2O_3} = 107, 500 \sigma/mol - K$ at $T_m (2324K)$

$\Delta S_{m, Al_2O_3} = \Delta S_{m, Cr_2O_3}$
Recall that under isobaric, reversible conditions, \( \Delta S^{a \rightarrow \beta} = \frac{\Delta H^{a \rightarrow \beta}}{T} \)

\[
\frac{\Delta H_{m,1}}{T_{m,1}} = \frac{\Delta H_{m,2}}{T_{m,2}} \Rightarrow \Delta H_{m,\text{Cr}_2\text{O}_3} = \Delta H_{m,\text{Al}_2\text{O}_3} = \Delta H_{m,\text{Al}_2\text{O}_3} \left( \frac{T_{m,\text{Cr}_2\text{O}_3}}{T_{m,\text{Al}_2\text{O}_3}} \right)
\]

\[
\Delta H_{m,\text{Cr}_2\text{O}_3} = 107,500 \frac{J}{mol - K} \times \frac{2538K}{2324K} = 117,400 \frac{J}{mol - K}
\]

Note: \( \Delta H = \Delta H^{S \rightarrow L} + \Delta H_{mix} \), but for ideal solution, \( \Delta H_{mix} = 0 \)

Note: if heating of \( \text{Cr}_2\text{O}_3 \) were required we read \( C_P(T) \).

Next calculate the change in entropy due to 1) melting and 2) mixing.

"Large" liquid volume \( \rightarrow \) no change in \( X_{\text{Cr}_2\text{O}_3} \) \( \rightarrow \) \( \Delta \overline{H}_{\text{Al}_2\text{O}_3} = 0 \)

Focus on change in 1 mole of solid \( \text{Cr}_2\text{O}_3 \).

\[
\Delta S = \Delta S_m + \Delta S_{mix}
\]

\[
\Delta S_m = \frac{\Delta H_m}{T_m} = \frac{117500}{2538} = 46.26 \frac{J}{K}
\]

\[
\Delta S_{mix} = -R \ln X^F - (-R \ln X^T), \text{ where } X_{\text{Cr}_2\text{O}_3}^i = 1 \text{ (assume } \gamma^0 = 1) \]

\[
\Delta S_{mix} = -R \ln(0.2)
\]

\[
\Delta S = 46.26 + 13.38 = 59.64 \frac{J}{K}
\]
14.10 Excess Properties, relative to ideal

\[ \Delta \mu_k = RT \ln(a_k) = RT \ln(Y_k X_k), \] so we can write

\[ \Delta \bar{G}_k = RT \ln \gamma_k + RT \ln X_k = \Delta \bar{G}^X_S + \Delta \bar{G}^{id}_k \]

If \( \gamma_k > 1 \), the excess free energy is positive.
If \( \gamma_k > 1 \), the excess free energy is negative.

Temperature and pressure derivatives of \( \mu(P, T) \) give the remaining properties in terms of \( \gamma_k \). (See table 8.5)

\[
\Delta H_k = \Delta \bar{G}_k - T \Delta S_k = \Delta \mu_k - T \left( \frac{\partial \mu_k}{\partial T} \right)_{P, \mu_k} = -RT^2 \left( \frac{\partial \ln \gamma_k}{\partial T} \right)_{P, n_k} \\
\Delta V_k = \left( \frac{\partial \Delta G_n}{\partial P} \right)_{T, n_k} = \frac{\partial}{\partial P} \left( [RT \ln \gamma_k + RT \ln X_R] \right)_{T, n_k} = RT \left( \frac{\partial \ln \gamma_k}{\partial P} \right)_{T, n_k} \\
= 0 \text{ for an ideal gas.}
\]

14.11 Beyond the ideal solution: the “regular” solution

1) The entropy of mixing is the same as for an ideal solution
2) The enthalpy of mixing is not zero, but depends on composition

Partial Molar \( \Delta \bar{G}_k = \Delta \mu_k = \Delta \bar{H}_k - T \Delta \bar{S}_k \)

Total Molar \( \Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \)
For ideal solution, $\Delta H_{\text{mix}} = 0$. For regular: $\Delta H_{\text{mix}} = \Delta H_{\text{mix}}^{XS} (X_2, X_3, \ldots X_c)$

For a regular solution, $\Delta S_{\text{mix}}^{\text{reg}} = \Delta S_{\text{mix}}^{\text{id}}$, so $\Delta S_{\text{mix}}^{XS} = 0$

$\Delta G_{\text{mix}}^{XS} = \Delta H_{\text{mix}}^{XS} - T \Delta S_{\text{mix}}^{XS}$

So $\Delta G_{\text{mix}}^{XS} = \Delta \tilde{H}_k = RT \ln \gamma_k$

We see that $\gamma_k$ can be evaluated from the heat of mixing: $\gamma_k = e^{\frac{\Delta \tilde{H}_k}{RT}}$ (check in eq 8.102)

Let’s look at the simplest binary example:

Let $\Delta H_{\text{mix}} = a_o X_1 X_2 = \Delta G_{\text{mix}}^{XS}$, where $a_o$ is constant. This corresponds to example 8.1. The change in Gibbs Free energy.

$\Delta G_{\text{mix}} = \Delta G_{\text{mix}}^{XS} + \Delta G_{\text{mix}}^{id} = a_o X_1 X_2 + RT X_1 \ln X_1 + RT X_2 \ln X_2$

$a_o$ determines the departure from ideal behavior arising from interactions between components.

A more realistic model (not symmetric and temperature dependent) of a binary system is

$\Delta H_{\text{mix}} = X_1 X_2 [\alpha_o(T) X_1 + \alpha_1(T) X_2] = \Delta G_{\text{mix}}^{XS}$

Let’s examine the impact of interactions on $\Delta H_{\text{mix}}, \Delta S_{\text{mix}},$ and $\Delta G_{\text{mix}},$ starting with the simpler regular solution.

Figure 14.7: Properties of an ideal solution

$\Delta \tilde{S}_k = -R \ln \gamma_k - R \ln X_k - RT \left( \frac{\partial \ln \gamma_k}{\partial T} \right)_{P,n_k}$

$\Delta \tilde{U}_k = RT^2 \left( \frac{\partial \ln \gamma_k}{\partial T} \right)_{P,n_k} - PRT \left( \frac{\partial \ln \gamma_k}{\partial P} \right)_{T,n_k}$
14.11 Regular Solutions

**Figure 14.8**: Properties of a regular solution

\[
\Delta F_k = RT \ln \gamma_k + RT \ln X_k - PRT \left( \frac{\partial \ln \gamma_k}{\partial P} \right)_{T,n_k}
\]

For reference, not lecture

Gibbs Duhem Equations

\[
X_1 d\Delta \mu_1 + X_2 d\Delta \mu_2 = 0
\]

\[
\Delta \mu_k = RT \ln (a_k)
\]

\[
X_1 d\ln \gamma_1 + X_2 d\ln \gamma_2 = 0
\]

\[
a_k = \gamma_k X_k
\]

\[
\Delta \mu = - \int_0^{X_2} \frac{X_2'}{X_1} \frac{d\Delta \mu_2}{dX_2'} dX_2'
\]

\[
\ln \gamma_1 = - \int_{X_1}^{X_2} \frac{X_2'}{X_1} \frac{d\ln \gamma_2}{dX_2'} dX_2'
\]
\[
\ln a_1 = - \int_0^{X_2} \frac{X_2'}{X_1} \frac{d \ln a_2}{dX_2'} dX_2'
\]

\[
\Delta \bar{S}_k = - \left( \frac{\partial \Delta \mu_k}{\partial T} \right)_{P,n_k}
\]

\[
\Delta \bar{H}_k = \Delta \mu_k + T \left( \frac{\partial \Delta \mu_k}{\partial T} \right)_{P,n_k}
\]

\[
\Delta \bar{G}_k = \Delta \mu_k = \Delta \bar{H}_k - T \Delta \bar{S}_k
\]

\[
\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}
\]

For an ideal solution, \(\Delta H_{mix} = 0\), for a regular solution \(\Delta S_{mix}^{reg} = \Delta S_{mix}^{id}\)

\[
\Delta G_{mix}^{XS} = \Delta H_{mix}^{XS} - T \Delta S_{mix}^{XS}
\]

\[
\Delta S_{mix}^{XS} = 0
\]

The entropy of mixing for a regular solution is the same as for an ideal solution (hence \(\Delta S_{mix}^{XS} = 0\))

The enthalpy of mixing for a regular solution deciates from that of an ideal solution \((\Delta H_{id} = 0, \Delta H_{mix}^{XS} \neq 0)\).

1) Example: HW 8.4 One mole of solid \(Cr_2O_3\) at 2500 K is dissolved in a large column of a liquid Raoultian solution (2300 K) of \(Al_2O_3\) and \(Cr_2O_3\) (20%).

Calculate the resulting \(\Delta H\) and \(\Delta S\) given

\[
T_{m, Cr_2O_3} = 2538 K
\]

\[
\Delta H_{m, Al_2O_3} = 107,500 J/mol-K @ T_m (= 2324 K)
\]

\[
\Delta S_{m, Al_2O_3} = \Delta S_{m, Cr_2O_3}
\]
Recall that under isobaric, reversible conditions, \( \Delta S^\alpha \rightarrow \beta = \frac{\Delta H^\alpha \rightarrow \beta}{T} \)

\[
\frac{\Delta H_{m,1}}{T_{m,1}} = \frac{\Delta H_{m,2}}{T_{m,2}} \Rightarrow \Delta H_{m,Cr_2O_3} = \Delta H_{m,Al_2O_3} \times \frac{T_{m,Cr_2O_3}}{T_{m,Al_2O_3}}
\]

\[
\Delta H_{m,Cr_2O_3} = 107,500 \frac{J}{mol - K} \times \frac{2538K}{2324K} = 117,400 \frac{J}{mol - K}
\]

Note: if heating of \( Cr_2O_3 \) were required, we need \( C_P(T) \). Next calculate changes in entropy due to 1) melting and 2) mixing.

“Large” liquid volume \( \rightarrow \) no change in \( X_{Cr_2O_3} \rightarrow \Delta H_{Al_2O_3} = 0 \)

Focus on change in 1 mole of solid \( Cr_2O_3 \)

\[
\Delta S = \Delta S_m + \Delta S_{mix}
\]

\[
\Delta S = \frac{\Delta H_m}{T_m} = \frac{117400}{2538} = 46.26 J/K
\]

\[
\Delta S_{mix} = -RT \ln X^F - (-RT \ln X^i), \text{ where } X_{Cr_2O_3}^i = 1
\]

\[
\Delta S_{mix} = -RT \ln(0.2)
\]

\[
\Delta S = 46.26 + 13.38 = 59.64 J/K
\]

14.11.1 Mixtures of Real Gases: Fugacity

Describe “real” gases in terms of their deviation from ideal behavior, starting with molar volume \( \bar{V}_k \)

Define \( \alpha_k = \bar{V}_k - \frac{RT}{P} \) (note that \( \alpha_k = 0 \leftrightarrow \text{ideal} \))

The change in chemical potential with mixing is then

\[
\Delta \mu_k = \int_P^{P_k} (\alpha_k + \frac{RT}{P'})dP' = \int_P^{P_k} \alpha_k dP' + RT \ln \left( \frac{P_k}{P} \right)
\]

Introduce fugacity \( f_k \) in

\[
\Delta \mu_k \equiv RT \ln \left( \frac{f_k}{P} \right)
\]
Note: \( a_k = \frac{f_k}{P} \)

Taking the exponential, we get

\[
f_k = P_k \exp \left[ \int_P^{P_\mu} \alpha_k dP \right]
\]

As \( \alpha_k \to 0 \), \( f_k \to P_k \)

Determination of fugacity (or \( a_k \)) \( \leftrightarrow \) finding \( \mu(P, T) \)

**Key goal of 314-316 Sequence: Predict Microstructure**

**Figure 14.9:** Calculated and observed microstructures

**Figure 14.10:** Multicomponent heterogeneous (multi-phase) system
15 Multicomponent Heterogeneous Systems

Outcomes for this section:
1) Write a combined statement of the first and second law of thermodynamics for multiple phases.
2) State the conditions for equilibrium for an arbitrary number of phases and components.
3) State the Gibbs phase rule and apply it to the description of unary and binary phase diagrams.
4) Given a single component phase diagram in terms of pressure and temperature, construct alternative representations that enable determination of phase fractions in terms of volume of mole fraction.
5) Given a two-component phase diagram in terms of pressure, temperature, and activity, construct alternative representations that enable determination of phase fractions in terms of volume or mole fraction.
6) Use the lever rule to compute phase fractions from temperature versus composition diagrams.

1) Define conditions for equilibrium
2) Derive Gibbs Phase Rule
3) Structure of 1 and 2 component phase diagrams
4) The Lever Rule

Consider $PV = RT$ (ideal gas)

There are two degrees of freedom: E.g. choose $P, T$ (independent) $\rightarrow V$ (dependent) is determined

Equilibrium between 2 phases implies that the system is in equilibrium.

Homogeneous system: $dU' = TdS' - PdT + \sum_{k=1}^{C} \mu_k dn_k$

Heterogeneous System: $dU'_{sys} = \sum_{\alpha=1}^{P} \left[ T^\alpha dS'_{\alpha} - P^\alpha dV' + \sum_{k=1}^{C} \mu^\alpha_k dn^\alpha_k \right]$
15.1 Conditions for Equilibrium

\[ T^\alpha = T^\beta \quad P^\alpha = P^\beta \quad \mu^\alpha = \mu^\beta \]

likewise for all pairs of phases \( \beta / \gamma, \gamma, \ldots, P \), where \( P \) = number of phases

\[ T^I = T^{II} = \ldots = T^P \quad P - 1 \text{ independent equations} \]

\[ P^I = P^{II} = \ldots = P^P \quad P - 1 \text{ independent equations} \]

\[
\begin{align*}
  \mu_1^I &= \mu_1^{II} = \ldots = \mu_1^P \\
  \mu_2^I &= \mu_2^{II} = \ldots = \mu_2^P \\
  \vdots \\
  \mu_C^I &= \mu_C^{II} = \ldots = \mu_C^P \\
\end{align*}
\]

Equilibrium conditions generate \((C + 2)(P - 1) = n\) equations. These are constraints on the variables

15.2 Gibbs Phase Rule

\[ F = C - P + 2 \]
\(F = m - n\) is the number of degrees of freedom

For \(n\) equations relating \(m\) variables. What is \(m\)?

\[
\begin{align*}
T^I, P^I, X^I_2, X^I_3 \ldots X^I_C & \quad 2 + C - 1 = C + 1 \\
T^{II}, P^{II}, X^{II}_2, X^{II}_3 \ldots X^{II}_C & \\
\vdots & \quad \vdots \\
T^P, P^P, X^P_2, X^P_3 \ldots X^P_C & \quad \text{P sets of C+1 variables}
\end{align*}
\]

\[
\therefore m = P(C + 1)
\]

\[
m - n = P(C + 1) - (C + 2)(P - 1) = P(C + 1) + P(C + 1) - 2P + C + 2
\]

\[m-n=C-P+2\]

Gibbs Phase Rule

16 Phase Diagrams

Outcomes for this section:

1) Apply a common tangent construction to define the regions of phase stability in a \(G\) versus \(X\) diagram.

2) Use a single component \(G - T\) diagram to compute \(\Delta G_k^{0, \alpha \rightarrow \beta}\).

3) Given \(G\) versus \(X\) at different \(T\), construct a phase diagram in terms of \(T\) and \(X\).

4) Describe the influence of interactions (in a simple regular solution model) on the features of a phase diagram, including phase boundaries, their curvature, and regions of two-phase coexistence.

5) Describe the origins and consequences of a miscibility gap.
16.1 Unary Phase Diagrams

\[ C = 1 \]
\[ F = C - P + 2 \]

In single phase regions \((P = 1)\), there are two degrees of freedom (e.g. \(T, P\))

1) \(P \) and \(T\) required to specify state in single-phase region.
2) For 2-phase region, \(P\) fixes and \(T\) (and vice versa)
   1 degree of freedom \((F = 1 - 2 + 2 = 1)\)
3) For triple point, \(F = 0\)

Only three phases are possible for a single component diagram.

16.2 Alternative Representations

\(P - V, T - X\), etc.

Not all useful variables (e.g. \(V, X\)) are thermodynamic potentials
2-phase coexistence lines \(\rightarrow\) areas

To describe:

1) Increasing \(T\), which increases \(V\)
2) Mixture of phases in regions with tie lines, average molar volume.
3) Triple points
4) Changes in enthalpy and phase fraction upon heating.
16.3 Binary Phase Diagrams

$C = 2$

There are 5 possible phases: $\alpha, \epsilon, \beta, L, V$

$F = C - P + 2$

For a single phase region, $f = 3 \rightarrow$ Plot in $P, T, a_2$ space. 2-phase regions are planes, 3-phase regions are lines, and 4-phase regions are points.

16.4 Alternative Representations: $T$ vs. $X$

In Figure 16.4 below, the 2-phase coexistence lines are areas.
16.5 Interpreting Phase Diagrams: Tie Lines

For plots with two degrees of freedom, a point on the diagram corresponds to a state of the system.

1) Which phases are present (and #) in equilibrium
2) The state of the phases (P, T, or other variables).
3) For plots with V or X, the relative amounts.

Example:
State P with average composition $X_o$ at temperature T. The phase $\Sigma$ is in equilibrium with the liquid ($T^\Sigma \neq T^L$).

$$n_T X_o^2 = n^\Sigma X_2^\Sigma + n^L X_2^L \rightarrow X_2^o = \frac{n^\Sigma}{n_T} X_2^\Sigma + \frac{n^L}{n_T} X_2^L = f^\Sigma X_2^\Sigma + f^L X_2^L$$

where $n =$ # of moles and $f =$ fraction

In terms of $X_2$,

$$X_o^2 = f^\Sigma X_2^\Sigma + (1 - f^\Sigma) X_2^L = X_2^L + f^\Sigma (X_2^\Sigma - X_2^o)$$

$$\therefore f^\Sigma = \frac{X_2^o - X_2^L}{X_2^\Sigma - X_2^L}$$

and

$$f^L = \frac{X_2^o - X_2^\Sigma}{X_2^L - X_2^\Sigma}$$

These fractions can be derived from the lengths of segments of a tie line.
16.6 The Lever Rule

\[ f^L = \frac{X_2^o - X_2^\Sigma}{X_2^L - X_2^\Sigma} = \frac{AP}{AB} \]

\[ f^\Sigma = \frac{X_2^o - X_2^L}{X_2^\Sigma - X_2^L} = \frac{PB}{AB} \]

\[ X_2^\Sigma - X_2^L = AB \]

\[ X_2^\Sigma - X_2^o = AP \]

\[ X_2^o - X_2^L = PB \]

X-T diagrams gives temperature, compositions, and amounts.

16.7 Applications of Phase Diagrams: Microstructure Evolution

Following an isotherm in the X-T diagram of Figure shows the following microstructures:

- \( T_o \): homogeneous melt
- \( T_1 : \alpha + L \) (nucleation)
- \( T_2 \): increase in \( \alpha \) phase
- \( T_3 \): solidification - \( \alpha + \beta \)
16.8 Review

\[ \Delta G_{mix} = \Delta H_{mix} - T S_{mix}^{id} \]

\[ \Delta G_{mix} = \Delta G_{mix}^{XS} + RT(X_1 \ln X_1 + X_2 \ln X_2) \]

\[ \Delta G_{mix}^{ideal} = RT(X_1 \ln X_1 + X_2 \ln X_2) \]

**Figure 16.7:** Gibbs free energy of mixing for ideal vs real mixtures

\( \Delta H_{mix} \neq 0 \): interactions change Gibbs free energy of mixing

\( T \uparrow \): particle kinetic energy increases, influence of interactions decreases, behavior is more ideal.
16.9 Types of $\alpha - L$ phase diagrams

$\Delta H_{\text{mix}} = a_o X_1 X_2$

Note the curvature of the phase boundary in Figure 16.8 below - the sign follows that of $a_o^2$.

Figure 16.8: Patterns of phase diagrams can be generated by only two phases, $\alpha$ and $L$, with the simplest regular solution model

17 Thermodynamics of Phase Diagrams

**Goal:** Generate phase diagrams from $\Delta G$ vs. $X$ curves

**Observe:** how interactions (changing potential energy) and temperature (changing kinetic energies) influence characteristics of phase diagrams.

**Approach:** find common tangent lines between $\Delta G_{\alpha}^{\text{mix}}$ and $\Delta G_{L}^{\text{mix}}$ to determine regions of phase stability.

**Needed:** comparison of solid and liquid reference states
17.1 Calculation of $\Delta G_{\text{mix}}$ from pure component reference states

We can plot $\Delta G_{\text{mix}}$ for a solid ($\alpha$) or liquid (L) solution using solid or liquid reference states for components 1,2 (4 possibilities).

One cannot directly compare the following:

Need to change reference states

$$\Delta G_{\text{mix}}^\alpha = X_1^\alpha \left( \bar{G}_1^\alpha - G_1^{\alpha \alpha} \right) + X_2^\alpha \left( \bar{G}_2^\alpha - G_2^{\alpha \alpha} \right)$$

$$\Delta G_{\text{mix}}^L = X_1^L \left( \bar{G}_1^L - G_1^{\alpha L} \right) + X_2^L \left( \bar{G}_2^L - G_2^{\alpha L} \right)$$

Indicate choice of reference states with brackets:

Reference states the same for $\alpha$ and L phases

$$\Delta G_{\text{mix}}^\alpha = X_1^\alpha \left( \bar{G}_1^\alpha - G_1^{\alpha \alpha} \right) + X_2^\alpha \left( \bar{G}_2^\alpha - G_2^{\alpha \alpha} \right)$$

Rewrite:

$$\Delta G_{\text{mix}} = X_1^\alpha \left( \bar{G}_1^\alpha - G_1^{\alpha \alpha} \right) + X_2^\alpha \left( \bar{G}_2^\alpha - G_2^{\alpha \alpha} \right) - X_2^\alpha \left( G_2^{\alpha L} - G_2^{\alpha} \right)$$

$$\Delta G_{\text{mix}}^\alpha (\alpha, L) = X_1^\alpha \left( \bar{G}_1^\alpha - G_1^{\alpha \alpha} \right) + X_2^\alpha \left( G_2^{\alpha \alpha} - G_2^{\alpha L} \right)$$

Similarly,

$$\Delta G_{\text{mix}}^L (\alpha, L) = \Delta G_{\text{mix}}^L (L, L) + X_1^L \Delta G_2^{\alpha \rightarrow \alpha}$$

What do these look like?

$$\Delta G_{\text{mix}}^\alpha (\alpha, L) = \Delta G_{\text{mix}}^\alpha (\alpha, \alpha) + X_2^\alpha \Delta G_2^{\alpha \rightarrow \alpha}$$

Next step: plot $\Delta G_{\text{mix}}^\alpha$, $\Delta G_{\text{mix}}^L$ together and find common tangent to determine regimes of phase stability.
17.2 Common Tangent Construction

The common tangent construction is a graphical representation of two phase equilibrium for a given P,T. An example is illustrated in Figure 17.3. At this T and P, a solid of composition $X_2^\alpha$ can be in equilibrium with a liquid of composition $X_2^L (T^\alpha = T^L, P^\alpha = P^L, \mu_1^\alpha = \mu_1^L, \mu_2^\alpha = \mu_2^L)$.

The intercepts reflect the conditions for chemical equilibrium.

A: $\frac{\Delta \mu_1^\alpha}{\Delta \mu_1^L} = \frac{\mu_1^\alpha (X_2^\alpha) - \mu_1^{\alpha L}}{\mu_1^L (X_2^L) - \mu_1^{\alpha L}} \quad \mu_1^\alpha (X_2^\alpha) = \mu_1^L (X_2^L)$

Chemical equilibrium of component 1 between $\alpha, L$

B: $\frac{\Delta \mu_2^\alpha}{\Delta \mu_2^L} = \frac{\mu_2^\alpha (X_2^\alpha) - \mu_2^{\alpha L}}{\mu_2^L (X_2^L) - \mu_2^{\alpha L}} \quad \mu_2^\alpha (X_2^\alpha) = \mu_2^L (X_2^L)$

Chemical equilibrium of component 2 between $\alpha, L$.

When are two-phase regions $(\alpha+L, \alpha+\beta)$ stable at intermediate compositions?
17.2 Common Tangent Construction

\[ X_2 < D : \alpha \]
\[ X_2 > F : \beta \]

\( \{ \) homogeneous mixtures of 1 and 2

\( D < X_2 < F : \alpha + \beta \) has lower energy than homogeneous mixture of 1 and 2

\( B : \Delta G \) for 1 & 2 in \( \beta \) phase

\( A : \Delta G \) for 1 & 2 in \( \alpha \) phase

\( M : \Delta G \) for \( \frac{EF}{DP} \) of \( \alpha \) and \( \frac{DE}{DP} \) of \( \beta \)

\( \Delta G_M < \Delta G_A < \Delta G_B \)

Sequential transitions between multiple two-phase regions 3 solid phases, 1 liquid phase

How are the single and two phase regions represented on a phase diagram?

We need \( \Delta G(X) \) for many temperature. Examine \( G^\alpha(T) \) and \( G^P(T) \).

To generate \( \Delta G_{mix} \) vs. \( X \) curves, we need \( G(T) \) of pure components to establish “hanging points” (the \( \Delta G^{\alpha \rightarrow \beta} \))
Next, examine changes in $\Delta G^{\alpha}_{\text{mix}}$ and $\Delta G^{L}_{\text{mix}}$ versus $T$ to establish which phases are present.

### 17.3 A Monotonic Two-Phase Field

- $a_0^\alpha = 1000 \text{J/mol}$
- $a_0^L = -6000 \text{J/mol}$

- $\Delta H_{\text{mix}} = a_0 X_1 X_2$

### 17.4 Non-monotonic Two-Phase Field

- $a_0^\alpha = 6000 \text{J/mol}$
17.5 Properties of a regular solution

Recall: Regular - $\Delta G_{mix}^{id} + \Delta G_{mix}^{XS}$

17.6 Miscibility Gap: Appearance Upon Cooling

$\Delta H_{mix} = 13.7X_1X_2kJ/mol$: below critical T, mixture is driven towards phase separation

$\alpha_o = 13,700 J/mol$
17.7 Spinodal Decomposition

Spinodal decomposition: concave down region in $\Delta G$ drives unmixing and “uphill” diffusion
Figure 17.10: Variation of mixing properties with composition and temperature for the simplest regular solution model. Maximum temperature is 1200 K, and $a_{\alpha} = 12,500 J/mol$

Figure 17.11: Miscibility gap
Figure 17.12: Spinodal decomposition
18 Summary of 314

The summary is presented in terms of a set of detailed learning outcomes, coupled to the chapters in Dehoff. These are things you should be able to do after completing 314.

18.1 Chapters 2 and 3

1) State the first, second and third laws of thermodynamics.
2) Write a combined statement of the first and second laws in differential form.
3) Given sufficient information about how a process is carried out, describe whether entropy is produced or transferred, whether or not work is done on or by the system, and whether heat is absorbed or released.
4) Quantitatively relate differentials involving heat transfer/production, entropy transfer/production, and work.

18.2 Chapter 4

1) Derive differentials of state functions \( (V, S, U, F, H, G) \) in terms of \( dP \) and \( dT \).
2) Using the Maxwell relations, relate coefficients in the differentials of state functions.
3) Define the coefficient of thermal expansion, compressibility, and heat capacity of a material.
4) Express the differential of any given state function in terms of the differentials of two others.
5) Define reversible, adiabatic, isotropic, isobaric, and isothermal processes.
6) Calculate changes in state functions by defining reversible paths (if necessary) and integrating differentials for (a) an ideal gas, and (b) materials with specified \( \alpha, \beta \), and \( C_P(T) \). (Multiple examples are given for ideal gas, solids, and liquids.)
7) Special emphasis (Example 4.13): calculate the change in Gibbs free energy when one mole of a substance is heated from room temperature to an arbitrary temperature at constant pressure.
8) Describe the origin of latent heat, and employ this concept in the calculation of changes in Gibbs free energy \( G \).
18.3 Chapter 5

1) Derive the condition for equilibrium between two phases.

2) Show that at constant temperature and pressure, the equilibrium state corresponds to that which minimizes the Gibbs free energy $G$.

3) Explain why the evolution to a state of lower Gibbs free energy occurs spontaneously.

18.4 Chapter 6

1) Express the entropy $S$ of the system in terms of equivalent microstates in the equilibrium (most probable) macrostate.

2) Given the energy levels of a system of particles, calculate the partition function.

3) Given the partition function, calculate the Helmholtz free energy, the entropy, the internal energy, and the heat capacity.

18.5 Chapter 7

1) State the differential of the Gibbs free energy $G$ as a function of $S, T, V,$ and $P$.

2) State the conditions for two phases to coexist in equilibrium.

3) Explain how isobaric section of the chemical potential $\mu(T, P)$ as a function of temperature and pressure can be calculated from knowledge of the heat capacity and the entropy at room temperature.

4) Given $\mu(T, P)$ for multiple phases, determine the equilibrium phase at a given temperature.

5) Derive the Clausius-Clapeyron relation: express the general condition for determining the region of two-phase coexistence.

6) Calculate the $\Delta H$ given the $C_P(T)$, assuming a negligible contribution from thermal expansion.

7) Calculate $\Delta V^{\alpha \rightarrow \beta}$ assuming ideal gas behavior.

8) Integrate $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$ with the assumption that $\Delta S$ and $\Delta V$ depend only weakly on the temperature.

9) Given the $P - T$ diagram, qualitatively sketch $G(T)$ for a specified region.
10) Given the $P - T$ diagram, specify the sign of $\Delta V^{\alpha \rightarrow \beta}$.

11) State Trouton’s rule and justify its validity qualitatively.

12) Sketch the $P - T$ diagram for a one-component system.

### 18.6 Chapter 8

1) Given sufficient information about the dependence of a total property $B$ or $\Delta B$ versus composition, find the partial molal properties as a function of composition via calculations of derivatives $dB$ or $d\Delta B$.

2) Given the partial molal properties as a function of composition, calculate the total properties of the system via integration of the derivatives.

3) Given the differentials of state functions, write partial derivatives that define the partial molal properties.

4) What is $B^0_k$?

5) What is $\mu_k - \mu^0_k$ for (a) a component behaving ideally, and (b) in general?

6) Define the activity of a component.

7) Given $\mu_k(T, P, X_k)$, calculate changes in the partial molal properties.

8) State and justify/explain Raoult’s law.

9) State and justify/explain Henry’s law.

10) Explain how the activity coefficient $\gamma$ can be used to describe the departure from ideal behavior in terms of “excess” quantities.

11) Define a “regular” solution and calculate the partial molal properties and total properties versus composition for binary mixtures.

12) Describe the driving forces for mixing and their origins in statistical mechanics.

13) Interpret changes in state functions with mixing in terms of ideal behavior and departures from ideality.

### 18.7 Chapter 9

1) Write a combined statement of the first and second law of thermodynamics for multiple phases.

2) State the conditions for equilibrium for an arbitrary number of phases and components.
3) State the Gibbs phase rule and apply it to the description of unary and binary phase diagrams.

4) Given a single component phase diagram in terms of pressure and temperature, construct alternative representations that enable determination of phase fractions in terms of volume of mole fraction.

5) Given a two-component phase diagram in terms of pressure, temperature, and activity, construct alternative representations that enable determination of phase fractions in terms of volume or mole fraction.

6) Use the lever rule to compute phase fractions from temperature versus composition diagrams.

18.8 Chapter 10

1) Apply a common tangent construction to define the regions of phase stability in a $G$ versus $X$ diagram.

2) Use a single component $G - T$ diagram to compute $\Delta G^0_{k, \alpha \rightarrow \beta}$.

3) Given $G$ versus $X$ at different $T$, construct a phase diagram in terms of $T$ and $X$.

4) Describe the influence of interactions (in a simple regular solution model) on the features of a phase diagram, including phase boundaries, their curvature, and regions of two-phase coexistence.

5) Describe the origins and consequences of a miscibility gap.
19 314 Problems

Contents

Phases and Components

1) (2014) For each of the following thermodynamic systems, indicate the number of components, the number of phases, and whether the system is open or closed.

1) An open jar of water at room temperature (assume that the jar defines the boundaries of the system). Assume that the water molecules do not dissociate.

2) A sealed jar of water at room temperature.

3) A sealed jar of water with ice.

4) An open jar of water with NaCl entirely dissolved within.

5) If the jar is left open, in what ways might your description change?

6) How would your answer to (a) change if you take into account equilibrium between water, protons, and hydroxyl ions?

Intensive and Extensive Properties

2) (2014) Classify the following thermodynamic properties are intensive or extensive:

1) The mass of an iron magnet.

2) The mass density of an iron magnet.

3) The concentration of phosphorous atoms in a piece of doped silicon.

4) The volume of the piece of silicon.

5) The fraction by weight of copper in a penny.

6) The temperature of the penny in your pocket.

7) The volume of gas in a hot air balloon.
Differential Quantities and State Functions

3) (2014) Consider the function \( z = 6x^2 y^3 \cos^2 u \).

1) Write down the total differential of \( z \). Identify the coefficients of the three differentials in this expression as partial derivatives.

2) Demonstrate that three Maxwell relations (see section 2.3) hold between the coefficients identified under (a).

4) (2014) Why are state functions so useful in calculating the changes in a thermodynamic system?

5) (2014) Derive equation 4.41 starting from 4.34 and 4.31. Note that other equations listed in table 4.5 can be derived in a similar fashion.

Entropy

6) (2015) Following Section 3.6, compute the change in entropy in the formation of one mole of \( \text{SiO}_2 \) from \( \text{Si} \) and \( \text{O} \) at room temperature.

7) (2015) Consider an isolated system consisting of three compartments A, B, and C. Each compartment has the same volume \( V \), and they are separated by partitions that have about. Initially, the valves are closed and volume A is filled with an ideal gas to a pressure \( P_0 \) at 298 K. Volumes B and C are under vacuum.

1) Calculate the change in entropy when the valve between compartment A and B is opened.

2) Calculate the change in entropy when the valve between compartment B and compartment C is opened.

3) Without considering the calculations above, how would you know that the overall change in entropy is positive?

4) What would you need to do to the system to restore the initial condition?
Thermodynamic Data

8) (2015) This problem requires you to find sources to look up the values of important materials parameters that will be used to compute thermodynamic functions.

1) Find values of the coefficient of thermal expansion for a metal, a semiconductor, an insulator, and a polymer. Provide the information below in your answer.

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Specific Material</th>
<th>$\alpha$</th>
<th>Source (include page or link info)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental Metal</td>
<td>e.g. Gold</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Semiconductor</td>
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<td>Insulator</td>
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<tr>
<td>Polymer</td>
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</tbody>
</table>

2) What is a common material with a negative $\alpha$?

3) How is the coefficient of compressibility related to the bulk modulus?

4) Which metal has the highest bulk modulus at room temperature, and what is the value?

5) The heat capacity is an extensive quantity. Define the related intensive quantity.

6) What trend do you observe in elemental solids?

7) What is the smallest value you can find for a solid material? (Explain your search method, and cite your sources.)

9) (2014) The density of silicon carbide at 298 K and 1 atm is ~3.2 g/cm$^3$. Estimate the molar volume at 800 K and a pressure of 1000 atm. See tables 4.1 and 4.2 on page 61 of DeHoff for useful materials parameters.

10) (2015) The density of aluminum at 298 K and 1 atm (or “bar”) is 2.7 g/cm$^3$. Estimate the molar volume at 1000 K and a pressure of 1000 atm. See tables 4.1 and 4.2 on page 61 of DeHoff, and Appendix B, for useful materials parameters. Hint: break the problem into two steps, each corresponding to a path.
11) (2015) Use the car mileage dataset provided to do the following:

1) Create a second order polynomial fit to determine the coefficients for the mileage dataset online. Use the systems of equations we developed during discussion to help you solve for the coefficients. Write your polynomial coefficients down in your submitted assignment.

2) Using your curve of best fit, determine the optimal speed for driving that maximizes your mileage.

3) Identify an obvious failure of your model and comment on it below.

12) (2015) Answer the following questions using the heat capacity dataset and the following model:

\[ C_p = a + bT + c/T^2 + dT^2 \]

1) Use the system of equations derived in class to determine the coefficients a, b, c, d.

2) Give a possible Gibbs free energy function for bulk silicon using your heat capacity fit. The Gibbs free energy is related to the heat capacity through the following equation:

\[ C_p = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_p \]

13) (2015) Compare the change in entropy for the specific examples below of isothermal compression and isobaric heating of gases and solids.

1) One mole of nitrogen (N\textsubscript{2}) at 1000 K is compressed isothermally from 1 to 105 bar.

2) One mole of silicon at 300 K is compressed isothermally from 1 to 105 bar.

3) One mole of oxygen (O\textsubscript{2}) at 300 K is heated isobarically from 300 to 1200 K.

4) One mole of tungsten at 300 K is heated isobarically from 300 to 1200 K.
14) (2015) For each of the following processes carried out on one mole of a monatomic ideal gas, calculate the work done by the gas, the heat absorbed by the gas, and the changes in internal energy, enthalpy, and entropy (of the gas). The processes are carried out in the specified order.

1) Free expansion into the vacuum to twice the volume, starting from 300 K and 4 bar. Then,

2) Heating to 600 K reversibly with the volume held constant. Then,

3) Reversible expansion at constant temperature to twice the volume of the previous state. Then,

4) Reversible cooling to 300 K at constant pressure.


1) Under isobaric conditions, the gas absorbs 5000 J of heat in the entropy of the gas increases by 12.0 J/K. What are the initial and final temperatures of the gas?

2) Under isothermal conditions, 1600 J of work is performed, resulting in an entropy increase of 5.76 J/K and a doubling of the volume. At what temperature was this expansion performed?

16) (2015) In class we learned that the change in entropy of a material with temperature is given by:

\[ S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT \]  \hspace{1cm} (19.1)

In a prior homework, we fit the heat capacity to a polynomial, which we could then integrate. Now, we will numerically integrate the data points using the Trapezoid Rule discussed in class:

\[ \int_{T_1}^{T_2} f(x) \approx (T_2 - T_1) \left[ \frac{f(T_1) + f(T_2)}{2} \right] \] \hspace{1cm} (19.2)

where the function \( f(T) \) in our case is the right hand side of Equation 19.1, is simply the right hand side of Equation 19.1. Do this by creating a “FOR” loop in MATLAB that sums up all the trapezoids in the temperature range. Email your MATLAB script to the TA by the due date.
1) What is the difference in entropy at 300 K and 1300 K?
2) Previously, we determined that the heat capacity is given by:

\[ C_p = 22.83 + 3.826 \times 10^{-3}T - \frac{3.533 \times 10^5}{T^2} + 2.131 \times 10^{-8}T^2 \] (19.3)

b) Use Equation 19.1 to analytically solve for the change in entropy using Equation 19.3. Which method do you think is more accurate? Explain your reasoning.

Temperature Equilibration

17) (2015) 100 g of ice at 250 K is added to 100 g of water at 300 K, and the mixture is allowed to come to equilibrium in an isolated container at constant pressure. You may assume that \( C_p \) is constant for this problem (though it is not the same for water and ice) and that the melting point is 273 K.

1) What is the final temperature?
2) How much liquid is present?
3) How would your answer change if the initial liquid was 40% ethanol?

18) (2015) A square block of Al, initially at a uniform temperature of 300 K, is brought into contact with another block of aluminum, initially at a uniform temperature of 600 K. Both blocks are of equal mass, and they are isolated at constant pressure while they come to equilibrium. The questions below assume equilibrium has been reached.

1) What do you know about the final temperatures of the Al blocks?
2) Will the final temperature(s) be 450 K? Justify your answer.
3) Find the final temperature.

Statistical Thermodynamics

19) (2015) DeHoff 6.3: Consider a system of two particles (A and B) that may each occupy any of the four energy levels \( (\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4) \).

1) How many distinct microstates are there for this system?
2) List each of the microstates and indicate which microstates have the same energy.

3) How many macrostates are there?

4) List the most probable macrostates.

20) (2015) DeHoff 6.5 Variant: Consider the system consisting of 9 identical but distinguishable particles, each of which can be in any of three states. The respective energy levels of the states are $\epsilon_0 = 0, \epsilon_1 = \epsilon, \epsilon_2 = 2\epsilon$. The system has a temperature $T$.

1) Write the partition function for a single particle.

2) Calculate the average number of particles in each state.

3) Determine the number of configurations that have the following occupation numbers for the three states: $n_0 = 4, n_1 = 3, n_2 = 2$.

4) Calculate the entropy of the macrostate described by the occupation numbers above.

5) Calculate the internal energy.

6) Choose a different set of occupation numbers to give the same internal energy (e.g., $(3,5,1)$) and repeat your calculation of the entropy. Which macrostate is more likely?

21) (2015) DeHoff 6.7 variant: A System containing 500 particles and 15 energy levels is in the following macrostate: {14, 18, 27, 38, 51, 78, 67, 54, 32, 27, 23, 20, 19, 17, 15}. Estimate the change in entropy when the system undergoes a process leading to the following changes in occupation numbers: {0, 0, -1, -1, -2, 0, 1, 0, 3, 2, -1, 1, -1, 0, -1}.

Single Component Thermodynamics

22) (2015) DeHoff 6.10: Compute the change in entropy when one mole of a monatomic ideal gas is compressed from an initial condition at 273K and 1 bar to 500K at 3.5 bar.

1) Calculate using the phenomenological thermodynamics of Chapter 4.

2) Calculate using the results of statistical thermodynamics. Hint: first calculate the initial and final volumes.
23) (2015) DeHoff 7.5: Sketch $G(T)$ for an element that the pressure corresponding to the triple point. Repeat the sketch for a pressure slightly above and slightly below the triple point.

\[ P \]
\[ T \]
\[ \alpha \]
\[ \beta \]
\[ \gamma \]


25) (2015) DeHoff 7.7 variant: At what pressure will ice melt at -2°C?

26) (2015) DeHoff 7.8: At 1 atm pressure and below 1155 K, the $\varepsilon$ form of titanium is stable; above 1155 K, the $\beta$ form is the stable phase ($\varepsilon$ becomes metastable). Given the following data:

- $\Delta S_{\varepsilon \rightarrow \beta} = 3.43 \text{ J/mol} \cdot \text{K}$ (This is the difference in molar entropy 3 between the phases).
- The change in molar entropy upon melting is $9.02 \text{ J/mol} \cdot \text{K}$.
- $T_{\beta m} = 1940 \text{ K}$.

1) Sketch $G_{\varepsilon}, G_{\beta}$ and $G_{\ell}$ in the temperature range of interest.
2) What is $T_{\varepsilon m}$?
3) There is a database of the Gibbs free energy of 78 pure elements as a function of temperature. The database can be found here: [http://www.crct.polymtl.ca/sgte/unary50.tdb](http://www.crct.polymtl.ca/sgte/unary50.tdb)

   a) Find the $\varepsilon$ phase of titanium (labeled as GHSERTI), the $\beta$ phase (labeled as GBCCTI), and the liquid phase (labeled as GLIQTI) and repeat a and b using the empirical formulas. Compare your answers and comment on the accuracy of your assumptions.

NOTE: The formula is written so that a program called Thermocalc can read them. Each free energy curve is a piecewise formula. The “;” separates the parts of the function over different temperature ranges. In addition, a “***” is the same as an exponent or “^”. 
Mulitcomponent Thermodynamics

27) (2015) DeHoff 8.1: Titanium metal is capable of dissolving up to 30 atomic percent oxygen. Consider a solid solution in the system Ti–O containing an atom fraction, $X_0 = 0.12$. The molar volume of this alloy is 10.68 cc/mol. Calculate the following:

1) The weight percent of O in the solution.

2) The molar concentration (mol/cc) of O in the solution.

3) The mass concentration (gm/cc) of O in the solution.

4) Use these calculations to deduce general expressions for weight percent, molar, and mass concentrations of a component in a binary solution in terms of the atom fraction, $X_2$, the molar volume, $V$, and the molecular weights, $MW_1$ and $MW_2$, of the elements involved.

28) (2015) DeHoff 8.4: Use the partial molal volumes computed in Problem 8.3 (worked out in class) to demonstrate that the Gibbs – Duhem equation holds for these properties in this system.

29) (2015) DeHoff 8.6: For an ideal solution it is known that, for component 2, $\Delta G_2 = RT \ln X_2$. Use the Gibbs – Duhem integration to derive corresponding relation for component 1.

30) (2015) One mole of solid $\text{Cr}_2\text{O}_3$ at 2500 K is dissolved in a large volume of a liquid Raoultian solution (also at 2500 K) of $\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$ with $X_{\text{Cr}_2\text{O}_3} = 0.2$. Calculate the resulting changes in the total enthalpy and entropy given the following:

$$T_{m,\text{Cr}_2\text{O}_3} = 2538 \text{ K}; \Delta H_{m,\text{Al}_2\text{O}_3} = 107,500 \text{ J/mol at } T_{m,\text{Al}_2\text{O}_3} = 2324 \text{ K}$$

$$\Delta S_{m,\text{Al}_2\text{O}_3} = \Delta S_{m,\text{Cr}_2\text{O}_3}$$

314 Computational Exercises

31) (2015) For this problem, you will be using MATLAB’s symbolic solver (fzero) and function handles to find the zero of an equation. On last week’s quiz we found that 89.1 grams of ice were necessary to cool a 1 kg block of Pb down to 300 K from 600 K. We will be plotting the change in temperature for both the Pb and ice. You will need the following parameters:
\[ C_p^{Pb} = 0.1169 + 4.2 \times 10^{-5} T \text{ kg kg }^{-1} \text{ K }^{-1} \]
\[ C_p^{H_2O} = 4.2 \text{ kJ kg }^{-1} \text{ K }^{-1} \]
\[ \Delta H_{\text{fus}}^{H_2O} = 344 \text{ kJ kg }^{-1} \]
\[ \frac{dT}{dt} = a \Delta T \]

Here \( a \) is a coefficient that controls the heat transfer in conduction, which we will assume to be \( 3.33 \times 10^{-3} \text{ kJ/K s} \), and \( \Delta T \) is the temperature difference between the two materials.

32) Use the equations derived in class to plot the change in temperature for \( H_2O \) and \( Pb \). Assume \( dt=1 \text{ s} \) and calculate the first 200 time steps. How do you know when the system is at equilibrium?

1) Create a plot that shows the amount of water in the system as a function of time. At what time is all the ice gone?

2) Create a plot that shows the total heat transfer occurring between the Pb and \( H_2O \). How can you tell when equilibrium is reached from this plot?

33) (2015) We will be putting together a program to help calculate phase diagrams of all sorts piece by piece. The first step is to create a MATLAB script that solves a system of two equations. The system is below:

\[ G_s - X_s \frac{dG_s}{dX_s} = G_\ell - X_\ell \frac{dG_\ell}{dX_\ell} \]
\[ \frac{dG_s}{dX_s} = \frac{dG_\ell}{dX_\ell} \]

where \( G_s \) and \( G_\ell \) are given by the following expressions:

\[ G_s (X_s) = \Omega_s X_s (1 - X_s) + RT [X_s \ln X_s + (1 - X_s) \ln (1 - X_s) + 200X_s - 400 (1 - X_s)] \]
\[ G_\ell (X_\ell) = \Omega_\ell X_\ell (1 - X_\ell) + RT [X_\ell \ln X_\ell + (1 - X_\ell) \ln (1 - X_\ell)] \]

Here \( G_s \) is the Gibbs energy of the solid phase, \( G_\ell \) the Gibbs free energy of the liquid phase, \( R \) the gas constant (8.314 J/K), \( T \) the absolute temperature, \( X_s \) and \( X_\ell \) are the compositions of the solid and liquid phase respectively, and \( \Omega_s, \Omega_\ell \) are parameters to be defined later. We can rewrite Eqs. 19.4 and 19.5 as follows:
\[ G_s - X_s \frac{dG_s}{dX_s} - G_\ell + X_\ell \frac{dG_\ell}{dX_\ell} = 0 \]  
(19.6)

\[ \frac{dG_s}{dX_s} - \frac{dG_\ell}{dX_\ell} = 0 \]  
(19.7)

Create a MATLAB function that takes \( X_s, X_\ell, T, \Omega_s \) and \( \Omega_\ell \) as inputs and then create a script that uses the MATLAB command fsolve to calculate \( X_s \) and \( X_\ell \) for \( T=700 K, \Omega_\ell = 1500 \text{ cal/mol} \) and \( \Omega_s = 3000 \text{ cal/mol} \).

34) (2015) Now that we are able to solve for the composition of the solid and liquid at one point, we will improve our script to calculate it over a range of temperatures. Start with an initial guess for both the solid and liquid near zero and a temperature of 900 K. Determine the composition of the liquid and solid down to 1 K for each temperature using a for loop. Make sure to update your guess with the correct answer for the previous temperature to help your program converge. Repeat again starting from 600 down to 1 K, this time starting with an initial guess near 1, and plot your results. Use the following parameters to make the Gibbs energy more physical:

\[ T^\alpha_m = 900 \text{ K} \]

\[ T^\beta_m = 600 \text{ K} \]

\[ \Delta H^\beta_f = 2000 \text{ cal/mol} \]

\[ \Delta H^\beta_f = 1300 \text{ cal/mol} \]

The liquid and solid free energies are given by the following expressions.

(Note that the Gibbs energy for the solid phase has changed slightly and should be adjusted in your code. In these units \( R = 1.987 \text{ cal/mol} \cdot \text{K} \))

\[ G_s (X_s) = \Omega_s X_s (1 - X_s) + RT + 
\[ X_s \ln X_s + (1 - X_s) \ln (1 - X_s) + X_s \Delta G^\ell \rightarrow s_\beta + (1 - X_s) \Delta G^{\ell \rightarrow s}_\alpha \]

\[ G_\ell (X_\ell) = \Omega_\ell X_\ell (1 - X_\ell) + RT \left[ X_\ell \ln X_\ell + (1 - X_\ell) \ln (1 - X_\ell) \right]. \]

As a reminder, the free energy change for the melting transition can be written in terms of the enthalpic and entropic contributions to the free energy:

\[ \Delta G^{s \rightarrow \ell} = \Delta H^{s \rightarrow \ell} - T \Delta S^{s \rightarrow \ell} \]
Our phase diagram calculation is almost complete! We only have to find the equilibrium between the two solid phases left. To do that, we simply take the derivative of the Gibbs free energy of the solid phase and set it equal to zero. The equation becomes:

\[ RT \ln \left( \frac{X_s}{1 - X_s} \right) - \Omega_s (2X_s - 1) \]

Again, assume that \( \Omega_s = 3000 \text{ cal/mol} \). This is easily done by creating a for loop that solves for the temperature at each composition between .01 and .99. Plot your results on the same figure from the previous homework and voila, your first phase diagram!

Now with your working code, replot the diagrams for the following interaction coefficients. You will have to change the range of temperatures for one of the sets below. You can figure out which one it is, if you think of the physical significance of the parameters.

1) \( \Omega_s = 3000 \text{ cal/mol} : \Omega_\ell = 0 \)
2) \( \Omega_s = 0 : \Omega_\ell = 3000 \text{ cal/mol} \)
3) \( \Omega_s = 0; \Omega_\ell = 0 \)
4) \( \Omega_s = 3000 \text{ cal/mol} : \Omega_\ell = 3000 \text{ cal/mol} \)

For each phase diagram, plot your results and describe how the changing interaction parameters changed the shape of the plot.
References


Index

Closed system, 6
dependent variable, 22
equation of state, 22
Extensive properties, 9
First law of thermodynamics, 10
gas constant, 24
Heat Capacity, 18
Heat flow, 10
Heterogeneous system, 5
Homogeneous system, 5

Ideal gas, 24
thermal expansion coefficient, 24
independent variable, 22
Intensive properties, 9
Internal energy, 10
Irreversible processes, 12
Isobaric, 17
Isolated system, 5
Isothermal, 17
Isothermal Compressibility, 18

Macrostate, 47
Maxwell relationships, 21
Microstate, 47
Multicomponent system, 5

Non-reacting system, 6

Open system, 6

Process variables, 7

Reacting system, 6
Reversible mechanical work, 11
Reversible processes, 12

second law of thermodynamics, 11
State Variables, 6

Temperature

Thermite reaction, 34
Thermodynamic laws
first law, 10
second law, 11
third law, 13
Third law of thermodynamics, 13
Unary system, 5