314: Thermodynamics of Materials

Northwestern MSE Faculty

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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

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.

1 Introduction

The content and notation of these notes is based on the excellent book, "Thermodynamics in Materials Science", by Robert DeHoff [?]. The notes provided here are a complement to this text, and are provided so that the core curriculum of the undergradaute 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.

2 Big Ideas of Thermodynamics

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

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

2.1 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 2.1: Unary system (left) and multicomponent system (right).

- \diamond Phases
 - Homogeneous system has one phase
 - Heterogeneous system has more than one phase



Figure 2.2: Homogeneous system (left) and heterogeneous system (right).

- ♦ Energy and mass transfer: closed and open 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 2.3: Open, closed and isolated thermodynamic systems.

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



Figure 2.4: Non-reacting system (left) and reacting system (right).

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

2.2 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, now 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:

$$\begin{array}{ccc} A & \to & A' \\ P, V, T & & P', V', T' \end{array}$$
(2.1)

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 ΔV and ΔT . 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.

2.3 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.

2.3.1 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:

$$\delta W = \vec{F} \cdot d\vec{x} \tag{2.2}$$

Note that \vec{F} and \vec{x} are vector quantities, but W is a scalar quantity. As a reminder, the dot product appearing in Eq. 2.2 is defined as follows:

$$\vec{A} \cdot \vec{B} = \left| \vec{A} \right| \left| \vec{B} \right| \cos \theta \tag{2.3}$$

where θ is the angle between the two vectors, illustrated in Figure 2.5.



Figure 2.5: Definition of the angle θ between two vectors.

The total work is obtained by integrating δW over the path of the applied force:

$$W = \underbrace{\int}_{path} \vec{F} \cdot d\vec{x} \tag{2.4}$$

For example, when we lift a from the floor to the table as illustrated in Figure 2.6 we increase the gravitational potential energy, U, of the barbell by an amount mgh, where:

- $\diamond m =$ the mass of the barbell
- $\diamond g =$ the gravitational acceleration (9.8 m/s²)
- $\diamond h_f$ = 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_{max} and then drop it onto the table. The work, W, we expended is equal to mgh_{max} , which is greater than the increase in potential energy, ΔU . The difference between between W and ΔU 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 2.6: Work done on a barbell.

2.3.2 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 2.7. Equation 2.2 still applies in this case, but the force in this case is given by the product of the area and pressure:

$$\vec{F} = P\vec{A} \tag{2.5}$$

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. 2.5 with Eq. 2.2 gives:

$$\delta W = P\vec{A} \cdot d\vec{x} \tag{2.6}$$

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:

$$\delta W = -PdV \tag{2.7}$$

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



Figure 2.7: Work done by force on a piston.

2.4 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, ρ .

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:

$$m = \int_{V} \rho\left(\vec{r}\right) d\vec{r} \tag{2.8}$$

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:

$$C_k \equiv \lim_{V \to 0} \frac{n_k}{V} \tag{2.9}$$

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

$$\rho \equiv \lim_{V \to 0} \frac{m}{V} \tag{2.10}$$

3 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.

3.1 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:

$$\Delta U = Q + W + W' \tag{3.1}$$



Figure 3.1: Conservation of energy

where:

- $\diamond \Delta U =$ **Internal energy** change of the system
- $\diamond Q =$ **Heat flow** into the system
- $\diamond W =$ Mechanical work done by surroundings on the system (P_{ext})
- $\diamond W' =$ All other reversible work done on the system

3.2 Second Law of Thermodynamics

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

$$\Delta S_{uni} \ge 0 \tag{3.2}$$

Here ΔS_{uni} includes the system of interest and its surroundings, as illustrated in Figure 3.2.

$$\Delta S_{uni} = [\Delta S_t' + \Delta S_p] + [\Delta S_t + \Delta S_p]$$
(3.3)

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

- $\diamond \ \Delta S_p$: entropy produced in the system
- $\diamond \Delta S'_p$: entropy produced in the surroundings
- $\diamond \Delta S_t$: entropy transferred to the system
- $\diamond \ \Delta S_t':$ entropy transferred to the surroundings

Surroundings



Figure 3.2: Transfer of entropy

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:

$$\Delta S_{uni} = \Delta S'_p + \Delta S_p \ge 0 \tag{3.4}$$

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

$$\Delta S_{sys} \left[A \to B \right] = \int_{A}^{B} dS_{sys} \tag{3.5}$$

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.

3.2.1 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
- \diamond 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. 3.5 one can chose the simplest path between the two states, which is the reversible path.

3.2.2 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 section 8 on page 39 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:

$$dS = \frac{\delta Q}{T} \tag{3.6}$$

This equation a mathematical statement of the second law of thermodynamics. Qualitatively, it is easy to see that Eq. 3.6 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 δQ 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:

$$\delta S = \delta Q/T_2 - \delta Q/T_1 \tag{3.7}$$

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.

3.3 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:

$$\mathrm{Si} + \mathrm{C} \to \mathrm{SiC}$$

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

- ♦ I: Heating Si and C from 0K to the reaction temperature, T_1 .
- $\diamond\,$ II: Reaction of Si and C to form SiC at $T=T_1$
- ♦ III: Cooling the SiC from T_1 to 0K.
- \diamond 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:

$$\Delta S_{cyc} = \Delta S_I + \Delta S_{II} + \Delta S_{III} + \Delta S_{IV} = 0 \tag{3.8}$$

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:

$$\Delta S_{II} = -\Delta S_I - \Delta S_{III} \tag{3.9}$$

The quantity ΔS_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 ΔS_I is simply $S_{\rm Si}+S_{\rm C}$. Similarly, $\Delta S_{III} = -S_{\rm SiC}$, with the negative sign arising from the fact that process III corresponds to a reduction in the temperature from T_1 to 0K. Finally, ΔS_{II} is, the entropy change associated the SiC-forming reaction, so we have:

$$\Delta S_{\rm Si+C\to SiC}(T_1) = S_{\rm SiC}(T_1) - S_{\rm Si}(T_1) - S_{\rm C}(T_1)$$
(3.10)

So ΔS 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.



Figure 3.3: Cyclic process involving formation of silicon carbide.

3.4 Differential Quantities

In differential form the first law of thermodynamics (Eq. 3.1) is as follows:

$$dU = \delta Q + \delta W + \delta W' \tag{3.11}$$

We can combine this with the expression from the second law from δQ :

$$\delta Q = T dS \tag{3.12}$$

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

$$\delta W = -PdV \tag{3.13}$$

Combination of Eqs. 3.11-3.13 can be combined to give the following combined statement of the first and second laws:

$$dU = TdS - PdV + \delta W' \tag{3.14}$$

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:

$$dU = TdS - PdV \tag{3.15}$$

4 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 α , β , 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.

4.1 Enthalpy

The enthalpy, H, is defined in the following way:

$$H \equiv U + PV \tag{4.1}$$

The total differential of the enthalpy is:

$$dH = dU + PdV + VdP \tag{4.2}$$

Now we eliminate dU by using Eq. 3.14:

$$dH = TdS + VdP + \delta W' \tag{4.3}$$

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

$$dH_p = TdS_p = \delta Q_p \tag{4.4}$$

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.

4.2 Helmholtz Free Energy

The Helmholtz free energy is defined in the following way:

$$F \equiv U - TS \tag{4.5}$$

In differential form this becomes:

$$dF = dU - TdS - SdT \tag{4.6}$$

$$dF = -SdT - PdV + \delta W' \tag{4.7}$$

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

$$dF_T = -PdV_T + \delta W'_T = \delta W_T + \delta W'_T = \delta W_{T,tot}$$
(4.8)

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

4.3 Gibbs Free Energy

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

$$G \equiv U + PV - TS = H - TS \tag{4.9}$$

$$dG = dU + VdP + PdV - TdS - SdT (4.10)$$

$$= (\mathcal{F}d\mathcal{S} - \mathcal{P}d\mathcal{V} + \delta W') + VdP + \mathcal{P}d\mathcal{V} - \mathcal{F}d\mathcal{S} - SdT$$
(4.11)

$$dG = -SdT + VdP + \delta W' \tag{4.12}$$

For processes carried out under isothermal and isobaric (constant P) conditions (dT,dP=0) , then

$$dG_{T,P} = \delta W'_{T,P} \tag{4.13}$$

 ${\cal G}$ reports the total work done other than mechanical work, e.g. chemical reactions and phase transformations.

4.4 Other Material Properties

4.4.1 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**, α , which describes the temperature dependence of the volume:

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (\mathbf{K}^{-1}) \tag{4.14}$$

4.4.2 Isothermal Compressibility

The **isothermal compressibility**, β , gives the relationship between the pressure and the volume :

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \text{ (Pa}^{-1} \text{)}$$
(4.15)

4.4.3 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:

$$\delta Q_P \equiv C_P dT_P \tag{4.16}$$

Here T_P indicates that the pressure is being held constant. If the process is reversible, then $dQ_P = TdS$ (Eq. 3.12), and we have:

$$TdS = C_P dT_p \tag{4.17}$$

Because the process is happening at constant pressure, we can rewrite Eq. 4.17 in the following way:

$$\frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P \tag{4.18}$$

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

$$C_P(T) = a + bT + \frac{c}{T^2} + dT^2$$
(4.19)

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

$$\delta Q_V \equiv C_V dT_V \tag{4.20}$$

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The corresponding version of Eq. 4.18 is:

$$\frac{C_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V \tag{4.21}$$

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 ΔT . The relationship between C_P and C_V is obtained below in section 4.6.3.

4.5 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:

$$Z = Z(X, Y) \tag{4.22}$$

The differential of Z s given by:

$$dZ = \left. \frac{\partial Z}{\partial X} \right|_{Y} dX + \left. \frac{\partial Z}{\partial Y} \right|_{X} dY \tag{4.23}$$

The differential forms of U (Eq. 3.15), F (Eq.) H (Eq.) and G (Eq.) all have the form of Eq. 4.23. The various relationships between the thermodynamic potentials (U, F, G, H) can be summarized by the thermodynamic square shown in Figure 4.1. Our description of how to use it is taken directly from the appropriate Wikipedia page (https://en.wikipedia.org/wiki/Thermodynamic_square)[?].

-S	U	V
Н		F
-P	G	Т

Figure 4.1:	Thermodynamic	square	used t	o help	determine	thermodynamic	rela-
tions.							

- 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 [differential] + T [differential]. Now we just have to figure out what the two differentials are.

4 THERMODYNAMIC VARIABLES

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. 3.14. 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 [?], with have units of energy when multiplied by one another.

We can also use the thermodynamic square of Fig. 4.1 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.
- 3. 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:

$$T = \begin{pmatrix} \frac{\partial U}{\partial S} \end{pmatrix}_{V}, \quad -P = \begin{pmatrix} \frac{\partial U}{\partial V} \end{pmatrix}_{S}$$

$$T = \begin{pmatrix} \frac{\partial H}{\partial S} \end{pmatrix}_{P}, \quad V = \begin{pmatrix} \frac{\partial H}{\partial P} \end{pmatrix}_{S}$$

$$-S = \begin{pmatrix} \frac{\partial F}{\partial T} \end{pmatrix}_{V}, \quad -P = \begin{pmatrix} \frac{\partial F}{\partial V} \end{pmatrix}_{T}$$

$$-S = \begin{pmatrix} \frac{dG}{\partial T} \end{pmatrix}_{P}, \quad V = \begin{pmatrix} \frac{\partial G}{\partial P} \end{pmatrix}_{T}$$
(4.24)

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:

$$\frac{\partial^2 Z}{\partial X \partial Y} = \frac{\partial^2 Z}{\partial Y \partial X} \tag{4.25}$$

We can rewrite this as:

$$\frac{\partial}{\partial X} \left(\frac{\partial Z}{\partial Y} \right)_X = \frac{\partial}{\partial Y} \left(\frac{\partial Z}{\partial X} \right)_Y \tag{4.26}$$

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

$$M = \left(\frac{\partial Z}{\partial X}\right)_Y, N = \left(\frac{\partial Z}{\partial Y}\right)_X \tag{4.27}$$

By comparing Eqs. 4.26 and 4.27 we obtain the following expression.

$$\left(\frac{\partial M}{\partial Y}\right)_X = \left(\frac{\partial N}{\partial X}\right)_Y \tag{4.28}$$

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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. 4.23, with values of M and N given in Eq. 4.24. Use of Eq. 4.28 in each of these four cases gives the following relationships between the appropriate partial derivatives:

4.5.1 Internal Energy

$$dU = TdS - PdV \rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{4.29}$$

4.5.2 Enthalpy

$$dH = TdS + VdP \to \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{4.30}$$

4.5.3 Helmholtz Free Energy

$$dF = -SdT - PdV \rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{4.31}$$

4.5.4 Gibbs Free Energy

$$dG = -SdT + VdP \to -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \tag{4.32}$$

4.6 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.

4.6.1 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:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \tag{4.33}$$

We can use Eq. 4.32 to replace $\left(\frac{\partial S}{\partial P}\right)_T$ with $-\left(\frac{\partial V}{\partial T}\right)_P$:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT - \left(\frac{\partial V}{\partial T}\right)_P dP \tag{4.34}$$

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Now we can use the definition of the thermal expansion coefficient, α , (Eq. 4.14) to replace $\left(\frac{\partial V}{\partial T}\right)_P$ with $V\alpha$:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT - V\alpha dP \tag{4.35}$$

Finally, we use the definition of the constant pressure heat capacity, C_p , (Eq. 4.18) to replace $\left(\frac{\partial S}{\partial T}\right)_P$ with $\frac{C_P}{T}$, which yields the following relationship expressiong dS in terms of dT and dP, and which involves the two material properties, α and C_P :

$$dS = \frac{C_P}{T}dT - V\alpha dP$$
(4.36)

4.6.2 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:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \tag{4.37}$$

The two partial derivatives in this expression appear in the definitions of the volume thermal expansion coefficient, α , and the isothermal compressibility, β , which are 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. 4.37 in the following way:

$$dV = \alpha V dT - \beta V dP \tag{4.38}$$

4.6.3 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. 4.38 to get an expression for dP:

$$dP = \frac{\alpha}{\beta} dT - \frac{dV}{\beta V} \tag{4.39}$$

This expression for dP can be substituted into Eq. 4.36 for dS to give:

$$dS = \left(\frac{C_P}{T} - \frac{V\alpha^2}{\beta}\right)dT + \frac{\alpha}{\beta}dV \tag{4.40}$$

From this we see that $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_P}{T} - \frac{V\alpha^2}{\beta}$. We get the constant-volume heat capacity, C_V , from it's definition in Eq. 4.21:

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$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V = C_P - \frac{TV\alpha^2}{\beta}$$
(4.41)

Note that $C_V < C_P$, as mentioned earlier.

5 The Ideal Gas

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

$$PV = nRT \tag{5.1}$$

Here n is the number of moles and R is the **gas constant**:

$$R = 8.314 (J/mol \cdot K) = 1.987 (cal/mol \cdot K) = 0.08206 (l - atm/mol \cdot K)$$
(5.2)

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

5.1 Thermal Expansion Coefficient of an Ideal Gas

We get the volume thermal expansion coefficient, α , by substituting the ideal gas constitutive law into Eq. 4.14:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{P}{nRT} \frac{\partial}{\partial T} \left(\frac{nRT}{P} \right)_P = \frac{P}{nRT} \cdot \frac{nR}{P} = \frac{1}{T}, \tag{5.3}$$

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

5.2 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. 4.15:

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = -\frac{P}{nRT} \frac{\partial}{\partial P} \left(\frac{nRT}{P}\right)_T = -\frac{P}{nRT} \left(\frac{-nRT}{P^2}\right) = \frac{1}{P}$$
(5.4)

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

5.3 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. 3.15):

$$dU = TdS - PdV \tag{5.5}$$

Using Eq. 4.36 for dS and Eq. 4.38 for dV gives:

$$dU = (C_p - PV\alpha)dT + V(P\beta - T\alpha)dP$$
(5.6)

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:

$$dU = \left(C_p - \frac{PV}{T}\right)dT \tag{5.7}$$

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

$$dU = (C_p - nR) dT \tag{5.8}$$

We see from this result that the internal energy of an ideal gas is independent of the pressure and depends only on the temperature. From Eq.4.41 we see that $C_V = C_P - \frac{TV\alpha^2}{\beta}$, which for an ideal gas gives:

$$C_V = C_P - \frac{PV}{T} = C_p - nR \tag{5.9}$$

Comparison of Eqs. 5.9 and

$$\therefore dU = C_V dT$$
, and $C_V = \frac{3}{2}R$

One can then integrate from T_1 to T_2 to get the total change in internal energy at a fixed volume:

$$\Delta U = \frac{3}{2}R(T_2 - T_1) \tag{5.10}$$

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

5.4 Specific Heat of Ideal Gas

$$C_V = C_P - \frac{T \left(V\alpha\right)^2}{\beta} = C_P - R \tag{5.11}$$

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

Example:

Calculate the change in T when 1 mole of gas is compressed reversibly 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 $dT_S = \frac{-T}{C_V}\frac{P}{T}dV_S = -\frac{P}{C_V}dV_S$. But $P = \frac{RT}{V}$

 $\Rightarrow dT_S = \frac{-RT}{C_V} \frac{dV_S}{V}$. Evaluate by integrating.

$$\int_{T_1}^{T_2} \frac{dT_S}{T} = \frac{-R}{C_V} \int_{V_1}^{V_2} \frac{dV_S}{V} \to \ln\left(\frac{T_2}{T_1}\right) = \frac{-R}{C_V} \ln\left(\frac{V_2}{V_1}\right)$$
$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left[\left(\frac{V_2}{V_1}\right)^{-R/C_V}\right] \Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$
$$C_V = \frac{3}{2}R$$

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

 $\left(\frac{V_1}{V_2}\right) > 1$ 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).

5.5 Some Examples of Ideal Gas Behavior

5.5.1 Free expansion of an ideal gas



Figure 5.1: Free expansion of an ideal gas - the value is opened at t_2 and fills both chambers

Walls are <u>rigid</u>: $\delta W = 0$ Walls are <u>insulating</u>: $\delta Q = 0$ System is <u>closed</u>. $\Rightarrow \Delta S_t = 0, \Delta U = 0 \Rightarrow \Delta T = 0$ (ideal gas) The gas expands irreversibly.

Entropy is produced, but ΔS is <u>not</u> process dependent because S is a state function. What is ΔS when 1 mole of gas expands freely to twice its volume? (recall $\Delta T = 0$).

$$dS = \frac{C_V}{T} dT + \frac{\alpha}{\beta} dV, \ dT = 0$$
$$PV = RT$$
$$\frac{P}{T} = \frac{R}{V}$$
$$dS = \frac{\alpha}{\beta} dV_T = \frac{P}{T} dV_T = \frac{R}{V} dV_T$$
$$\Delta S_T = \int_{V_1}^{V_2} \frac{R}{V} dV = R \ln\left(\frac{V_2}{V_1}\right) = R \ln\left(\frac{2V_1}{V_1}\right) = R \ln 2$$
$$\therefore \Delta S_T = 5.76 \text{J/mol-K}$$

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.

5.5.2 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: $\delta Q_{rev,T} = T dS_T$

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

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

$$dS_T = \frac{-R\mathcal{I}}{P} \frac{1}{\mathcal{I}} dP = -R \frac{dP}{P}$$
$$\Delta S_T = -R \int_{P_i}^{P_f} \frac{dP}{P} = -R \ln\left(\frac{P_f}{P_i}\right)$$

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

5.5.3 Reversibility requires work/heat

The piston in Figure 5.2 below may be withdrawn very slowly to maintain equilibrium.

$$\Delta U = 0 \to \Delta T = 0$$

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



Figure 5.2: Piston-cylinder device

But no entropy can be <u>produced</u>, 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 5.3: Irreversible Process (top) and reversible process (bottom)

Irreversible process	Reversible process
$\Delta Q = 0$	$\Delta Q \neq 0$
W=0	$W \neq 0$
$\Delta U = 0$	$\Delta U = 0$
$\Delta T = 0$	$\Delta T = 0$

Table 1: Irreversible vs reversible process characteristics

$$\Delta U = 0 \rightarrow W = -\Delta Q \tag{5.12}$$
$$W < 0, \Delta Q > 0$$
$$\rightarrow \Delta S_t > 0$$

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

$$\delta Q_{rev,P} = TdS_p \equiv C_P dT_P$$

$$C_P = \frac{5}{2}R$$

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

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

5.5.4 Some useful relations for heat flow

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

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

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

Example 4.3: Relate S(P,V)

$$dS = MdP + NdV$$

$$dS = MdP + N(V^{\alpha}dT - V\beta dP) = (M - NV_{\beta})dP + NV^{\alpha}dT$$

$$dS = -V^{\alpha}dP + \frac{C_{P}}{T}dT \rightarrow N = \frac{C_{P}}{V^{\alpha}T} = \left(\frac{\partial S}{\partial V}\right)_{P}$$

$$M - NV\beta = -V^{\alpha}$$

$$M = -V^{\alpha} + \frac{C_{P}}{\mathcal{V}_{\alpha}T}\mathcal{V}\beta$$

$$M = \frac{C_{P}\beta}{\alpha T} - V^{\alpha} = \left(\frac{\partial S}{\partial P}\right)_{V}$$

$$dS = \left(\frac{C_{P}\beta}{\alpha T} - V^{\alpha}\right)dP + \frac{C_{P}}{V^{\alpha}T}dV$$

Luijten examples

1. Q for ΔP at constant T

Reversible, $\rightarrow \delta Q_{rev,T} = TdS$ Use S(T, P) like 4.10(a)

- 2. Find ΔT given ΔP at constant S Use S(T, V), also ideal gas law (~4.8)
- 3. Free expansion of ideal gas, find ΔS for ΔV 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 PG(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:

$$dS = MdT + NdP = 0$$

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

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

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

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

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

Use PV = RT to get to two variables

$$P = \frac{RT}{V}, C_V = \frac{3}{2}R$$
$$dT = \frac{-RT}{C_V V} dV =$$
$$\frac{dT}{T} = \frac{-R}{3/2R} \frac{dV}{V} = \frac{-2}{3} \frac{dV}{V}$$
$$\int_{T_1}^{T_2} \frac{dT}{T} = -\frac{2}{3} \int_{V_1}^{V_2} \frac{dV}{V} \to \ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_1}{V_2}\right)^{2/3}$$
$$\frac{V_1}{V_2} = \frac{1}{2}, T_2 = T_1 \left(\frac{1}{2}\right)^{2/3} = 189K$$
Note $P_1 = \frac{300 \cdot R}{10^{-3}m^3} = 3 \times 10^5 R$
$$P_2 = \frac{189R}{2 \times 10^{-3}m^3} = 0.95 \times 10^5 R$$

Pressure drops by threefold

 $\downarrow PV \uparrow = RT \downarrow$

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

$$dS = \frac{C_p}{T}dT - V^{\alpha}dP$$

 $\frac{dT}{T} = \frac{V^{\alpha}}{C_P} dP \text{ need exponential values}$ Does C_P vary with T? If $\frac{dC_P}{dT} \approx 0$, then

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

$$\alpha = 36 \times 10^{-6} \,\mathrm{K}^{-1}$$

$$C_P \approx 45.3 \,\mathrm{J/mol} - \mathrm{K}$$

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

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

$$T_2 = T_1 \times 1.006 = 300K$$

6 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 ΔG 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.

$$dS = \frac{C_P}{T} dT - V^{\alpha} dP = \frac{C_P}{T} dT$$
$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$
$$S = S_o + \int \frac{C_P(T)}{T} dT$$
$$C_P = a + bT, S_o = 26.8J/mol - K$$

$$S = S_o + \int_{T_1}^{T_2} dT \left(\frac{a}{T} + b\right)$$

6 SOLIDS AND LIQUIDS

Evaluate expression, substitute data at the end

$$S = S_o + \int \frac{C_P(T)}{T} dT = S_o + \int_{T_1}^{T_2} dT \left(\frac{a}{T} + b\right)$$

$$S = S_o + a \ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1)$$

$$T_1 = 300K, T_2 = T$$

$$S(T) = S(300K) + a \ln\left(\frac{T}{300}\right) + b(T - 300)$$

$$\equiv a \ln T + bT + \underbrace{\left[S_o - a \ln 300 - 300b\right]}_{\text{constant}}$$

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

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

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

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

 \uparrow Check this, see also sec 7.3 p. 180

$$a = 48.99 \frac{J}{mol - K}, \ b = 3.43 \times 10^{-3} \frac{J}{mol K^2}$$

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

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.

6 SOLIDS AND LIQUIDS

For an isobaric, reversible process: $dH = TdS = \delta Q_{rev}$ Consider the change in enthalpy for each half-reaction:

$$2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3 \quad \Delta H_1 = -1675.7 \frac{kJ}{mol}$$

$$Fe_2O_3 \rightarrow 2Fe + \frac{3}{2}O_2 \quad \Delta H_2 = 823 \frac{kJ}{mol}$$

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

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

The minus sign implies that the reaction is <u>exothermic</u>. 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 Al_2O_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. <u>Step 1</u>: Heat *Fe* and Al_2O_3 to the melting point of *Fe*.

$$\Delta H_{Al_2O_3,1} = \int_{289}^{1809} C_P(T)dT = 183,649 \text{ J}$$

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

$$\uparrow \alpha \to \gamma : 2 \int_{289}^{1187} C_{P,\alpha} dT + \Delta H_{\alpha \to \gamma}$$

$$\uparrow \gamma \to \delta : 2 \int_{1187}^{1164} C_{P,\gamma} dT + \Delta H_{\gamma \to \delta}$$

$$\uparrow \delta \to l : 2 \int_{1664}^{1809} C_{P,\delta} dT + \Delta H_{melt}$$

$$C_{P,\delta} = C_{P,\alpha}$$

Considering the three integrals of T and three latent heats,

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

So through step 1, we have $\Delta H_{Fe,1} + \Delta H_{Al_2O_3,1} = 341.390 \text{ J}$ Step 2: Heat Fe and Al_2O_3 to melting point of Al_2O_3 .

$$\Delta H_{Al_2O_3,2} = \int_{1809}^{2325} C_{P,Al} dT + \Delta H_{Al_2O_3}(S \to l) = (71, 240 + 107, 000) \text{ J}$$

$$\Delta H_{Fe,2} = 2 \int_{1809}^{2325} C_{P,Fe(l)} dT = 43,178 \text{ J}$$

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?

272,600 J
$$\begin{cases} \Delta H_{Fe,3} = 2 \int_{2325}^{3343} C_{P,Fe}(l) dT \\ \Delta H_{Al_2O_3,3} = \int_{2325}^{3343} C_{P,Al_2O_3}(l) dT \end{cases}$$
 leaving 16.892 J

How much Fe evaporates?

$$\frac{Q}{\Delta H_{Fe}(l \to g)} = \frac{16,892J}{340,159J} = 0.05 \text{moles or } 5\%$$
$$\Delta H(T) = \Delta aT + \frac{\Delta b}{2}T^2 - \Delta C\frac{1}{T} + \frac{\Delta d}{3}T^3 - \Delta D$$
$$\Delta D = \Delta H(T_o) - [\Delta aT_o + \frac{\Delta b}{2}T_o^2 - \Delta C\frac{1}{T_o} + \frac{\Delta d}{3}T_o^3]$$
$$2Al + Fe_2O_3 \to 2Fe + Al_2O_3 \text{ Exothermic}$$

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

$$dT, Q = 0, dP = 0$$

Need initial S, C_P



Figure 6.1: Thermite reaction

Exothermic implies ΔT from heat released.

$$dS = MdT + Nd\mathscr{P}$$
$$dH = TdS + VdP + \delta W'$$
$$2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3 : \Delta H_1 = -1875 \text{kJ/mol}$$
$$2Fe + \frac{3}{2}O_2 \rightarrow Fe_2O_3: \Delta H_2 = -823.4 \text{kJ/mol}$$
$$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$$
$$2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3 ; \Delta H_1$$
$$\underline{Fe_2O_3 \rightarrow 2Fe + \frac{3}{2}O_2; -\Delta H_2}$$
$$2Al + Fe_2O_3 + \frac{3}{2}\mathscr{O}_2 \rightarrow Al_2O_3 + 2Fe + \frac{3}{2}\mathscr{O}_2$$
$$\Delta H_1 - \Delta H_2 = -852.3 \text{kJ/mol}$$
$$\delta Q_{rev,P} = -TdS = dH$$

Heat is reversibly absorbed by the system.

 $\Delta H_{Fe,1} = \int dH = \int_{298}^{1809} C_P dT = 157,741 \text{J for 2 mol}$ Include ΔH due to increasing T as well as due to phase transitions. For Al_2O_3 , just $\int C_P dT$

6 SOLIDS AND LIQUIDS

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

For a total change of 341,390 J

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

$$\int C_P dT + \Delta H_{melt}$$

Step 2 takes: 221,418 J

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



Figure 6.2: Changes in enthalpy in Fe and Al_2O_3

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

Good for constant V: relate ΔS to T change.

For constant T: relate ΔS to volume change.

For constant S, dS=0

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

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{5/3}$$
$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}$$
$$T_1^{\frac{\gamma}{1 - \gamma}} P_1 = T_2^{\frac{\gamma}{1 - \gamma}} P_2$$
$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$
$$\gamma = \frac{C_p}{C_V} = \frac{5/2}{3/2} = 5/3$$
$$\frac{5/3}{1 - 5/3} = \frac{5/3}{2/3} = 5/2$$
$$\gamma - 1 = 2/3$$

 $dU = (C_P - PV^{\alpha})dT + V(\rho\beta - T_{\alpha})dP$

$$dU = (\frac{5}{2}R - R)dT + V(1 - 1)dP = \frac{3}{2}RT$$
$$dS = \frac{C_P}{T}dT - V^{\alpha}dP = \frac{5}{2}\frac{R}{T}dT - \frac{V}{T}dP$$
$$dS = \frac{5}{2}\frac{R}{T}dT - \frac{R}{P}dP$$

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

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

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

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

7 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 ($\delta Q = 0, \delta W = 0$, 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 7.1. 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 7.1: 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 funciton of several variables when relationships (constraints) exist between those variables.

Approach: Lagrange Multipliers



Figure 7.2

 $\begin{array}{c} \underline{\text{Minimize: (will be S)}}{f(x_1, x_2, \dots x_n)} & \underline{\text{Given these constraints (other state functions, vars)}}{\Phi_1(x_1, x_2, \dots x_n) = 0} \\ \\ \underline{\text{function of n variables}} & \Phi_2(x_1, x_2, \dots) = 0 \\ \\ \\ \underline{\text{degrees of freedom=n-m}} & \vdots \\ \\ \Phi_m(x_1, x_2, \dots) = 0 \end{array}$

m constraints.

Define: $df + \lambda_1 d\Phi_1 + \lambda_2 d\Phi_2 + ... + \lambda_m d\Phi_m = 0$ λ_m : Lagrange multiplier $dF = \frac{\partial F}{\partial x_1} dx_1 + \frac{\partial F}{\partial x_2} dx_2 + ... + \frac{\partial F}{\partial x_n} dx_n$ In general, $dF = \frac{\partial F}{\partial x_1} dx_1 + \frac{\partial F}{\partial x_2} dx_2 + ... + \frac{\partial F}{\partial x_n} dx_n$. To guarantee that dF=0 for all $x_1, x_2...x_n$, 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<u>Constraints</u> $\diamond u = x + y + 12 \rightarrow \Phi_1 = x + y + 12 - u = 0$ $\diamond v = x - y - 8 \rightarrow \Phi_2 = x - y - 8 - v = 0$ u, v: dependent x, y: independent

 $dz + \lambda_1 d\Phi_2 + \lambda_2 d\Phi_2 = 0$ Minimize z subject to constraints

 $= xdu + udx + ydv + vdy + \lambda_1(dx + dy - du) + \lambda_2(dx - dy - dv) = 0$

$$= (x - \lambda_1)du + (y - \lambda_2)dv + (u + \lambda_1 + \lambda_2)dx + (v + \lambda_1 - \lambda_2)dy = 0$$

$$\begin{cases} x - \lambda_1 = 0\\ y - \lambda_2 = 0 \end{cases} \Rightarrow \begin{array}{l} \lambda_1 = x\\ \lambda_2 = y \end{cases}$$

$$\begin{array}{l} u + \lambda_1 + \lambda_2 = 0\\ v + \lambda_1 - \lambda_2 = 0 \end{array} \Rightarrow \begin{array}{l} u = -\lambda_1 - \lambda_2\\ v = -\lambda_1 + \lambda_2 \end{array} \Rightarrow$$

$$u = -x - y$$

$$v = -x + y$$

$$x + y + 12 - u = 0$$

$$\frac{x - y - 8 - v = 0}{2x + 4 - (-x - y) - (-x + y)} = 0 \quad -1 - y - 8 - (-(-1) + y) = 0$$

$$4x + 4 = 0 \Rightarrow x = -1 \quad -10 - 2y = 0 \Rightarrow y = -5$$

7.1 Finding equilibrium conditions

A unary 2-phase system is in equilibrium when the T, P and μ for both phases are equal. Consider 2 phases α and β 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_{α} is the number of moles of α phase.

Then $dV^{\alpha} = T_{\alpha}dS^{\alpha} - P_{\alpha}dV^{\alpha} + \mu_{\alpha}dn_{\alpha}$, where $\mu \equiv \left(\frac{\partial V^{\alpha}}{\partial n_{\alpha}}\right)_{V_{\alpha},S^{\alpha}}$

 μ_{α} is the <u>chemical potential</u> of the α phase. To find the equilibrium condition, maximize S.

$$dS^{\alpha} = \frac{dU\alpha}{T_{\alpha}} + \frac{P_{\alpha}}{T_{\alpha}}dV^{\alpha} - \frac{\mu_{\alpha}}{T_{\alpha}}dn_{\alpha}, dS^{\beta} = \frac{dV_{\beta}}{T_{\beta}} + \frac{P_{\beta}}{T_{\beta}}dV_{\beta} - \frac{\mu_{\beta}}{T_{\beta}}dn_{\beta}$$
$$dS = dS^{\alpha} + dS^{\beta} = \frac{dU\alpha}{T_{\alpha}} + \frac{P_{\alpha}}{T_{\alpha}}dV^{\alpha} - \frac{\mu_{\alpha}}{T_{\alpha}}dn_{\alpha} + \frac{dV_{\beta}}{T_{\beta}} + \frac{P_{\beta}}{T_{\beta}}dV_{\beta} - \frac{\mu_{\beta}}{T_{\beta}}dn_{\beta}$$

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

$$dU = dU^{\alpha} + dV_{\beta} = 0 \rightarrow dU^{\alpha} = -dU^{\beta} \text{ (no heat is exchanged)}$$
$$dV = dV^{\alpha} + dV_{\beta} = 0 \rightarrow dV^{\alpha} = -dV_{\beta} \text{ (no work is done)}$$
$$dn_{\alpha} = -dn_{\beta} \text{ (particle number is conserved)}$$

Then $dS = \left(\frac{1}{T_{\alpha}} - \frac{1}{T_{\beta}}\right) dU^{\alpha} + \left(\frac{P_{\alpha}}{T_{\alpha}} - \frac{P_{\beta}}{T_{\beta}}\right) dV_{\beta} - \left(\frac{\mu_{\alpha}}{T_{\alpha}} - \frac{\mu_{\beta}}{T_{\beta}}\right) dn_{\alpha} = 0$

To guarantee dS=0, these coefficients must be zero independently.

Hence,

$$T_{\alpha} = T_{\beta}, P_{\alpha} = P_{\beta}, \mu_A = \mu_B$$
 Conditions for Equilibrium
7.2 Energy Minima

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

$$\begin{split} dU &= TdS + PdV + \sum_i^m \mu_i dn_i \text{ where } i: \text{index of components} \\ dU &= \delta Q + \delta W + \delta W' \end{split}$$

Consider a reversible process in an isolated system

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

Claim: For a system of constant S, V, n_{λ} , 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 $S_{v,n}$).

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

$$\begin{split} dS &= 0 \rightarrow dS^{\alpha} = -dS^{\beta} \\ dV &= 0 \rightarrow dV^{\alpha} = -dV_{\beta} \\ dn &= 0 \rightarrow dn_{\alpha} = -dn_{\beta} \\ dU^{\alpha} &= T_{\alpha}dS^{\alpha} - P_{\alpha}dV^{\alpha} + \mu_{\alpha}dn_{\alpha} \\ \frac{dU^{\beta} &= T_{\beta}dS^{\beta} - P_{\beta}dV_{\beta} + \mu_{\beta}dn_{\alpha}}{dU &= (T_{\alpha} - T_{\beta})dS^{\alpha} - (P_{\alpha} - P_{\beta})dV^{\alpha} + (\mu_{\alpha} - \mu_{\beta})dn_{\alpha} = 0 \\ \Rightarrow T_{\alpha} &= T_{\beta} , P_{\alpha} = P_{\beta}, \mu_{\alpha} = \mu_{\beta} \text{ (Additional condition: second derivative)} \\ \Rightarrow \text{Thermal, mechanical, and chemical equilibrium} \end{split}$$

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

Variables Held Constant	Equilibrium Condition
S, P	dH = 0
T, V	dF = 0
T, P	dG = 0
S, V	dU = 0

 Table 2: 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:
$$\Delta G = [Q + W + W'] - W_{rev} - Q_{rev}$$
$$\Delta G = \underbrace{(Q - Q_{rev})}_{<0} + \underbrace{(W - W_{rev})}_{<0} + \underbrace{W'}_{<0}$$

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

Example for two component system Two isolated systems are defined - each in equilibrium with separate environments.

 $\begin{array}{l} P_1V_1 = n_1RT_1\\ P_2V_2 = n_2RT_2 \end{array} \right\} \mbox{Let them come to equilibrium in isolation} \\ \Delta U_1 + \Delta U_2 = 0\\ \\ \frac{3}{2}n_1R(T_f - T_i) + \frac{3}{2}n_2R(T_f - T_i) = 0\\ \\ \Rightarrow n_1T_f - n_1T_1 = -n_2T_f + n_2T_2 \Rightarrow T_f = \frac{n_1T_1 + n_2T_2}{n_1 + n_2} \end{array}$

We can also solve for P_f, V_i

$$\begin{split} P_{f} &= \frac{(n_{1}+n_{2})RT_{f}}{V_{1}+V_{2}} = \frac{R(n_{1}T_{1}+n_{2}T_{2})}{V_{1}+V_{2}} \text{ and } V_{1} = \frac{n_{1}RT_{f}}{P_{f}} , \, V_{2} &= \frac{n_{2}RT_{f}}{P_{f}} \\ V_{1} + V_{2} &= \frac{n_{1}RT_{f}}{P_{f}} + \frac{n_{2}RT_{f}}{P_{f}} \\ \hline P_{f} \quad V \\ n_{1} + n_{2} \quad T_{f} \end{split} \text{Final}$$

7.3 Maxwell Relations

For free energies:

- \diamond coefficients in opposite corners
- $\diamond~$ derivatives in adjacent corners
- $\diamond\,$ minus signs apply to coefficients

For Maxwell Relations:

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

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

Useful relations between S,T,P,V for an ideal monatomic gas $dS = \frac{C_{P}}{T}dT - V^{\alpha}dP = \frac{5}{2}\frac{R}{T}dT - \frac{V}{T}dP = \frac{5}{2}\frac{R}{T}dT - \frac{R}{P}dP$ $dS = \frac{C_{V}}{T}dT + \frac{\alpha}{\beta}dV = \frac{3}{2}\frac{R}{T}dT + \frac{P}{T}dV = \frac{3}{2}\frac{R}{T}dT + \frac{R}{V}dV$ Constant P: { $\Delta S = \frac{5}{2}R \ln\left(\frac{T_{2}}{T_{2}}\right)$ Constant T: $\begin{cases} \Delta S = -R \ln\left(\frac{P_{2}}{P_{1}}\right) \\ \Delta S = -R \ln\left(\frac{V_{2}}{V_{1}}\right) \end{cases}$ Constant V: $\Delta S = \frac{3}{2}R \ln\left(\frac{T_{2}}{T_{1}}\right)$ Constant S: $\frac{P_{2}}{P_{1}} = \left(\frac{T_{2}}{T_{1}}\right)^{5/2} = \left(\frac{V_{1}}{V_{2}}\right)^{5/3}$ P Reversible (!)path T

Figure 7.3

$$dS = \frac{C_v}{T}dT + \frac{\alpha}{\beta}dV = \frac{3}{2}\frac{R}{T}dT + \frac{P}{T}dV = \frac{3}{2}\frac{R}{T}dT + \frac{R}{V}dV$$
$$0 = \frac{3}{2}\frac{R}{T}dT + \frac{R}{V}dV \rightarrow \frac{3}{2}\ln\left(\frac{T_2}{T_1}\right) = -\ln\left(\frac{V_2}{V_1}\right)$$
$$\left(\frac{T_2}{T_1}\right)^{3/2} = \frac{V_1}{V_2}, \left(\frac{T_2}{T_1}\right)^{5/2} = \left(\frac{V_1}{V_2}\right)^{5/3} = \frac{P_2}{P_1}$$

One can show this using $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ and substituting.

8 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, $8.317 \times 10^{-5} eV/K$, $1.38 \times 10^{-23} J/K$ and Ω = 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.

8.1 Microstates and Macrostates

Microstate: Specification of the state (<u>e.g.</u> energy level) of <u>every</u> 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 8.1

# Microstates	Distribution
1	(4,0)
6	(2,2)
4	(1,3)

 Table 3: 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:



Figure 8.2: Macrostate (1,3)

- 1. The <u>distribution function</u> specifies the occupation of atomic states by identical particles, and thus the macrostate.
- 2. Number of macrostates \ll number of microstates
- 3. If all microstates are equally likely, then some macrostates are <u>much</u> more likely. (e.g. (2,2))

 \Rightarrow How do we see this?

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

$$\Omega = \frac{N_o!}{n_1! n_2! n_3! \dots n_r!} \qquad n! \equiv n(n-1)(n-2) \dots 3 \cdot 2 \cdot 1$$
$$= \frac{N!}{\prod_{i=1}^{n} n_i!}$$

Number of Microstates	Distribution	
1	(4,0)	$\Omega_{4,0} = \frac{4!}{4!0!} = 1$
6	(2,2)	$\Omega_{2,2} = \frac{4!}{2!2!} = \frac{4 \cdot 3 \cdot 2 \cdot 1}{2 \cdot 1 \cdot 2 \cdot 1} = 6$
4	(1,3)	$\Omega_{1,3} = \frac{4!}{1!3!} = \frac{4 \cdot 3 \cdot 2 \cdot 1}{1 \cdot 3 \cdot 2 \cdot 1} = 4$

Table 4: Microstates corresponding to given macrostates

Total number of possibilities is r^{N_o} , 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.
- \diamond Compartments are so small that M \gg 4 and occupation is 0 or 1.

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

Case I: Ω_I



Figure 8.3

$$\begin{pmatrix} 2M\\4 \end{pmatrix} = \frac{(2M)!}{4!(2M-4)!} = \frac{2M \cdot (2M-1)(2M-2)(2M-3)}{4!} \approx \frac{(2M)^4}{4!}$$

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

$$\Omega_{II} = \begin{pmatrix} M \\ 4 \end{pmatrix} \approx \frac{M^4}{4!}$$

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

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 - 4×10^{-5} 10000 - 2×10^{-44}

8.1.1 Postulate of Equal Likelihood

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

 $P_j = \frac{\Omega_j}{r^{N_o}}$ is the probability of finding the system in macrostate j. The most probable macrostate is the one that represents the most microstates in Ω .

8.1.2 The Boltzmann Hypothesis (to be derived)

 $S = k_B \ln \Omega$

 $k_B = 1.38 \times 10^{-23} J/K$

Maximum in Ω corresponds to a maximum in S.

How do we determine the most probable macrostate?

What are the conditions of equilibrium?



Figure 8.4

8.2 Conditions for equilibrium

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

$$S = k_B \underbrace{\left(\frac{N_o!}{\prod_{i=1}^r n_i!}\right)}_{\Omega}$$

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: $\ln x! \cong x \ln x - x$

This is very accurate for large x. How large?

1. Express Ω as a sum over logarithms of occupation numbers.

$$\Omega = \frac{N!}{\prod_{i=1}^{r} n_i!} \to \ln \Omega = \ln N! - \ln \left(\prod_{i=1}^{r} n_i! \right)$$

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

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

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

2. Differentiate

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

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

3. Impose constraints

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

$$N = n_1 + n_2 + \dots n_r = \sum_{i=1}^r n_i, \, dN = 0$$
$$U = n_1 \Sigma_1 + n_2 \Sigma_2 + \dots + n_r \Sigma_r = \sum_{i=1}^r n_i \Sigma_i, \, dU = 0$$

To impose constraints, we use Lagrange Multipliers.

$$d \ln \Omega + \lambda_1 dN + \lambda_2 dU = 0$$

- $\sum_{i=1}^r \ln \left(\frac{n_i}{N}\right) dn_i + \lambda_1 \sum_{i=1}^r dn_i + \lambda_2 \sum_{i=1}^r \Sigma_i dn_i = 0$
- $\sum_{i=1}^r \left[\ln \left(\frac{n_i}{N}\right) dn_i + \lambda_1 - \lambda_2 \Sigma_i\right] dn_i = 0 \Rightarrow \text{Gives r equations, e.g.}$
 $\ln \left(\frac{n_i}{N}\right) - \lambda_1 - \lambda_2 \Sigma_i = 0 \Rightarrow \frac{n_i}{N} = e^{\lambda_1} e^{\lambda_2 \Sigma_i}, i = 1, 2, ..., r$

4. Use constraints to eliminate λ_1, λ_2

$$\frac{n_i}{N} = e^{\lambda_1} e^{\lambda_2 \Sigma_i}$$

$$\sum_{i=1}^r \frac{n_i}{N} = 1 \rightarrow \sum_{i=1}^r e^{\lambda_1} e^{\lambda_2 \Sigma_i} = 1$$

$$e^{\lambda_1} = \frac{1}{\sum_{i=1}^r e^{\lambda_2 \Sigma_i}} \rightarrow \frac{n_i}{N} = \frac{e^{\lambda_2 \Sigma_i}}{\sum_{j=1}^r e^{\lambda_2 \Sigma_j}} \equiv \frac{1}{Z} e^{\lambda_2 \Sigma_i}$$

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

 \mathbf{So}

$$\ln \Omega_i = -\sum_{i=1}^r n_i \left(\frac{n_i}{N}\right) = -\sum_{i=1}^r n_i \ln \left(\frac{e^{\lambda_2 \Sigma_i}}{Z}\right)$$
$$= -\sum_{i=1}^r n_i (\lambda_2 \Sigma_i - \ln Z)$$
$$\ln \Omega = -\lambda_2 \sum_{i=1}^r n_i \Sigma_i + \ln Z \sum_{i=1}^r n_i = -\lambda_2 U + N \ln Z$$

What is λ_2 ?

Consider response of system to the reversible absorption of an infinitesimal amount of heat δQ .

$$d \ln \Omega = -\lambda_2 dU + d(\underline{N \ln Z})$$
$$dU = \delta Q_{rev} = T dS$$
$$d \ln \Omega = -\lambda_2 T dS$$
So

$$S \propto \ln \Omega$$

$$S = \underbrace{-\frac{1}{\lambda_2 T}}_{k_B} \ln \Omega = k_B \ln \Omega \to \lambda_2 = -\frac{1}{k_B T}$$
$$\frac{n_i}{N} = \frac{e^{-\Sigma_i/kT}}{\sum_{i=1}^r e^{-\Sigma_i/kT}} \equiv \frac{1}{Z} \underbrace{e^{-\Sigma_i/kT}}_{\text{Boltzmann factor}}$$
Partition function

We can calculate macroscopic properties from the partition function.

Recall $\ln \Omega = -\lambda_2 U + N \ln Z$, $S = k \ln \Omega$ $(k \ln \Omega =) S = -\frac{U}{T} + k_B N \ln Z$ $-kT \ln Z = U - TS \equiv F$ 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 .

9 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:

$$\sum \frac{1}{2}mv^2 = \sum \frac{m}{2}\left(v_x^2 + v_y^2 + v_z^2\right) \tag{9.1}$$

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9 NONINTERACTING (IDEAL) GAS

♦ The energy distribution of free particles is continuous.

$$\sum \rightarrow \int$$

 $\diamond\,$ For convenience, assume box of dimensions $L\times L\times L=V$

$$Z = \underbrace{\int_{0}^{L} \int_{0}^{L} \int_{0}^{L}}_{V} dx dy dz \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{1}{2kT}(v_{x}^{2} + v_{y}^{2} + v_{z}^{2})} dv_{x} dv_{y} dv_{z}$$

$$= V \int_{-\infty}^{\infty} e^{-\frac{1}{2kT}mv_{x}^{2}} dv_{x} \int_{-\infty}^{\infty} e^{-\frac{1}{2kT}mv_{y}^{2}} dv_{y} \int_{-\infty}^{\infty} e^{-\frac{1}{2kT}mv_{z}^{2}} dv_{z}$$
$$\int_{-\infty}^{\infty} e^{-\alpha x^{2}} dx = \sqrt{\frac{\pi}{\alpha}} \text{ (for } \alpha > 0 \text{)}$$
$$\underbrace{-\frac{\alpha}{e^{-\frac{1}{2kT}mv_{x}^{2}}}}_{e^{-\frac{1}{2kT}mv_{x}^{2}}}$$

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

Now we can easily derive many functions.

,

$$\ln Z = \ln V + \frac{3}{2} \ln \left(\frac{2\pi k}{m}\right) + \frac{3}{2} \ln T$$
$$\frac{\partial \ln Z}{\partial T} = \frac{3}{2} \frac{1}{T}$$
$$\Rightarrow F = -NkT \ln Z = -NkT \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi kT}{m}\right)\right]$$
$$U = NkT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V = NkT^2 \left(\frac{3}{2} \frac{1}{T}\right) = \frac{3}{2}NkT$$
$$\boxed{\frac{U}{N} = \frac{3}{2}kT} \qquad \text{Energy per particle}$$
$$\sum_{V=1}^{N} \sum_{V=1}^{N} K = \frac{3}{2} \left(\frac{N}{N}\right) kN_A = \frac{3}{2}nR$$

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

$$\frac{C_V}{n} = \frac{3}{2}$$
R n: moles

9.1 Ideal gas Law

$$dF = -SdT - PdV + \delta W'$$

$$-P = \left(\frac{\partial F}{\partial V}\right)_T$$
$$P = -NkT \left(\frac{\partial \ln Z}{\partial V}\right)_T = NkT \left[\frac{\partial}{\partial V} \left(\ln V + \frac{3}{2}\ln\left(\frac{2\pi k}{m}\right) + \frac{3}{2}\ln T\right)\right]_T$$
$$\boxed{P = NkT \cdot \frac{1}{V} = \frac{nRT}{V}}$$

◊ Note that we have ignored interactions between particles/atoms. Attractive interactions lead to, e.g. condensation.

◊ We have also ignored <u>repulsive</u> interactions, i.e. atoms occupy finite volumes. Including these leads to the van der Waals equation:

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

10 Diatomic Gases

Diatomic gases possess rotational and vibrational degrees of freedom.

The kinetic energy of a gas molecule with p degrees of freedom is

 $\Sigma = \sum_{j=1}^{P} b_j v_j^2 \text{, and } Z = V \prod_{j=1}^{P} \sqrt{\frac{\pi kT}{b_j}}$ (e.g. $b = \frac{m}{2}$ for translations) For rotations $v \to \omega$, $M \to I$ Surprisingly, U and C_V do not depend on b_j :

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

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.

- \diamond Monatomic: 3 translational
- \diamond Heteronuclear Diatomic: 3 translational + 2 rotational + 2 vibrational



Figure 10.1: Diatomic gas

11 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

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



Figure 11.1: Vibration of atoms in harmonic potential

 \diamond 3 bonds/atom, 3N bonds in crystal

Figure 11.2: Binding to six nearest neighbors

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

$$\sum_i=(i+\frac{1}{2})\hbar\omega=(i+\frac{1}{2})hv~i=0,1,2...$$

h: Planck's constant , v : frequency , $\hbar : \frac{h}{2\pi}$

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

$$Z = \sum_{i=0}^{n} e^{-\sum_{i}/kT} = \sum_{i=0}^{n} e^{-(i+\frac{1}{2})hv/kT} = e^{-\frac{1}{2}\frac{hv}{kT}} \sum_{i=0}^{n} e^{-ihv/kT}$$

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

 $\therefore \sum_{i=0}^{\infty} e^{-ihv/kT} = \frac{1}{1 - e^{-hv/kT}}, \ Z = \frac{e^{-1/2}\frac{hv}{kT}}{1 - e^{-hv/kT}}$

11.1 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!
$$U = -\frac{\partial}{\partial\beta}\ln Z = kT^2\frac{\partial\ln Z}{\partial T} \ (\beta = kT) \ (\text{per particle?})$$
$$U = 3NkT^2\frac{\partial\ln 2}{\partial T} = 2NkT^2\frac{\partial}{\partial T} \left[-\frac{1}{2}\frac{hv}{kT} - \ln(1 - e^{-hv/kT})\right]$$

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

How does this change with temperature?

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



Figure 11.3: Heat capacity in an atom as a function of temperature

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

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.

12 Unary Heterogeneous Systems

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 ΔH given the $C_P(T)$, assuming a negligible contribution from thermal expansion.
- 7. Calculate $\Delta V^{\alpha \to \beta}$ assuming ideal gas behavior.
- 8. Integrate $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$ with the assumption that ΔS and ΔV 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 $\Delta V^{\alpha \to \beta}$.
- 11. State Trouton's rule and justify its validity qualitatively.
- 12. Sketch the P-T diagram for a one-component system.

12.1 Phase Diagrams

Figure 12.1 shows the unary (one component) phase diagram for copper. The phases in this case are solid (S), liquid (L) and gas (S). In some cases, multiple solid phases are observed, as with



Figure 12.1: Phase Diagram for copper.

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. $s \to \ell, \ell \to v, s \to v$.



Figure 12.2: Phase for carbon.



Figure 12.3: Phase diagram for water (H_2O) .

12.2 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 α , solid β , liquid, etc.)



Figure 12.4: Solid α and liquid L

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

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

AB: solid + liquid



Figure 12.5: Intersection of $\mu^L(T, P)$ and $\mu^S(T, P)$



Figure 12.6: Superposition of Solid, Liquid, and Gas phase μ

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: Extensive $dU' = TdS' - PdV' + \mu dn_1$, $\mu = \left(\frac{\partial u'}{\partial n}\right)_{S',V'}$ G' = U' + PV' - TS'dG' = dU' + PdV' + V'dP - TdS' - S'dTSusbstitute dU'

$$\begin{split} dG' &= \mathcal{F}dS' - \mathcal{F}dV'' + \mu dn + \mathcal{F}dV'' + V'dP - \mathcal{F}dS' - S'dT \\ dG' &= -S'dT + V'dP + \mu dn \\ \mu &= \left(\frac{\partial G'}{\partial n}\right)_{T,P} \\ \mu &= \left(\frac{\partial G'}{\partial n}\right)_{T,P} = \left(\frac{\partial}{\partial n}(nG)\right)_{T,P} = G\left(\frac{\partial}{\partial n}\right)_{T,P} = G \end{split}$$

12.3 $\mu(T, P)$ Surfaces

 $d\mu^{\alpha} = dG^{\alpha} = -S^{\alpha}dT + V^{\alpha}dP$

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

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

To compare μ^{α} with μ^{L} , we need to calculate μ^{L} from the same reference point. Conneciting μ^{α} with μ^{L} at the melting point T_{m} :

$$\mu^{L}(T) - \mu^{\alpha}(298) = \underbrace{\left[\mu^{L}(T) - \mu^{L}(T_{m})\right]}_{\text{integral of } -S^{L} \text{from Tj} \# ST} \underbrace{\left[\mu^{\alpha}(T_{m}) - \mu^{\alpha}(298)\right]}_{\text{Talculated this integral}}$$

$$\mu^{L} = \mu^{L}(T_{m}) - \int_{T_{Mm}}^{T} \left[S^{L}(T_{m})^{*} + \int_{T_{m}}^{T^{"}} \frac{C_{P}^{L}(T')}{T'} dT' \right] dT^{"}$$

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

* Note the entropy changes with the phase change

 $S^{L}(T_{m}) = S^{\alpha}(T_{m}) + \Delta S^{\alpha \to L}(T_{m})$

 ΔS : latent heat

$$S^{L}(T_m) = \underbrace{S^{\alpha}(T_m)}_{S^{\alpha}_{298} + \int_{298}^{T_m} \frac{C^{\alpha}_{p}(T)dT}{T}} + \underbrace{\Delta S^{\alpha \to L}(T_m)}_{\text{latent heat}}$$
$$G^{L}(T) - G^{\alpha}(298) = G^{L}(T) - G^{L}(T_m) + G^{\alpha}(T_m) - G^{\alpha}(298) =$$

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$$= \int_{T_m}^{T} - \left\{ \underbrace{\left[\underbrace{S^{\alpha}(298 + \int_{298}^{T_m} \frac{C_{P}^{\alpha}(T')}{T'} dT' + \Delta S^{\alpha \to L}(T_m)}_{S^{L}(T_m)} \right]}_{+ \int_{T_m}^{T^*} \frac{C_{P}^{L}(T')}{T'} dT' \right\} \\ + (-) \int_{298}^{T_m} \left[S^{\alpha}(298) + \int_{298}^{T^*} \frac{C_{P}^{\alpha}(T)}{T'} dT' \right] dT''$$

Figure 12.7: Determining the equilibrium state (at fixed P)

12.4 Clausius-Clapeyron Equation

The Clausius-Clapeyron Equation describes the pressure dependence of the temperature at which two phases are in equilibrium with one another. For a single component system it allows us to determine the complete phase diagram in P-T (pressure - temperature) space. We begin by considering the thermodynamic requirement to have two phases, α and β in equilibrium with one another:

$$T^{\alpha} = T^{\beta} = T$$

$$P^{\alpha} = P^{\beta} = T$$

$$\mu^{\alpha} = \mu^{\beta}$$
(12.1)

We can use Eq. xx to write differential changes in μ^{α} and μ^{β} to differential changes in T and P:

$$d\mu^{\alpha} = -S^{\alpha}dT^{\alpha} + V^{\alpha}dP^{\alpha}$$
$$d\mu^{\beta} = -S^{\beta}dT^{\beta} + V^{\beta}dP^{\beta}$$

But we require equilibrium:

$$dT^{\alpha} = dT^{\beta} \quad dP^{\alpha} = dT^{\beta} \quad d\mu^{\alpha} = d\mu^{\beta}$$

$$-S^{\alpha}dT + V^{\alpha}dP = -S^{\beta}dT + V^{\beta}dP$$

 $(S^{\beta} - S^{\alpha})dT = (V^{\beta} - V^{\alpha})dP$

$$\Delta S^{\alpha \to \beta} dT = \Delta V^{\beta \to \alpha} dP$$

 $\Delta S^{\alpha \to \beta}$: difference in molar entropy

 $\Delta V^{\alpha \rightarrow \beta} :$ difference in molar volume

$$\boxed{\frac{dP}{dT} = \frac{\Delta S^{\alpha \to \beta}}{\Delta V^{\alpha \to \beta}}}$$
Classius-Claperyon Equation

$$Slope = \frac{Entropy Change}{Volume Change}$$

But how do we measure entropy change?

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

So, $Q^{\alpha \to \beta} = \Delta H^{\alpha \to \beta}$

In equilibrium,

$$G^{\alpha} = G^{\beta} \quad H^{\alpha} - TS^{\alpha} = H^{\beta} - TS^{\beta} \quad (T^{\alpha} = T^{\beta})$$

So $\Delta S^{\alpha \to \beta} = \frac{\Delta H^{\alpha \to \beta}}{T}$, and

$$\frac{dP}{dT} = \frac{\Delta H^{\alpha \to \beta}}{T \Delta V^{\alpha \to \beta}}$$

Can be integrated to get P(T) for 2-phase coexistence. We need $\Delta H(P,T)$, $\Delta V(P,T)$ from Chapter 4.

12.4.1 Step 1: Find $\Delta H(T, P)$ $d(\Delta H^{\alpha \to \beta}) = d(H^{\beta} - H^{\alpha}) = dH^{\beta} - dH^{\alpha}$

$$dH = C_P dT + V(1 - T_\alpha) dP$$

$$d\Delta H^{\alpha \to \beta} = \Delta C_P dT + \underbrace{\Delta [V(1 - T_\alpha)dP]}_{\text{negligible for pressures up to}} \sim 10^{-5} \text{bar}$$

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

 $C_P = a + bT + \frac{c}{T^2} + dT^2$ (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 ΔH .

12.4.2 Step 2: Find $\Delta V^{\alpha \to \beta}(T, P) \equiv V^{\beta}(P, T) - V^{\alpha}(P, T)$

First consider the case of β as a vapor phase, and α as liquid or solid.

 $\diamond ~V^\beta \gg V^\alpha$

♦ 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 β ,

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

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

For solid \rightarrow solid transformations, (β is the stable phase at high T)

positive (
$$\Delta H, \Delta S_i 0$$

$$\frac{dP}{dt} = \frac{\Delta C_P^{\alpha \to \beta}(T) dT}{\underline{T} \Delta V}$$
determines sign of else

determines sign of slope

 ΔV is usually positive but can be negative (e.g. H_2O)

 ΔV ~ 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, α, β , but suppose the variation with temperature is weak.

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

The slope $\frac{dP}{dT}$ is generally large since ΔV 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 $\frac{d}{dT}\Delta H = 0$,

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



Figure 12.8

 $\left|\frac{dP}{dT}\right|^{S \rightarrow L} > \left|\frac{dP}{dT}\right|^{S \rightarrow V}$

12.4.3 Justification for Approximations

Consider the enthalpy of transformation $d\Delta H^{\alpha \to \beta}(T) = \Delta C_p(T) dT$, and integrate

$$\Delta H(T) = \underbrace{\Delta H(T_o)}_{\text{Typically} ~~100 \text{kJ}} + \int_{T_o}^T \Delta C_P(T) dT$$

$$\underbrace{\text{Typically} ~~100 \text{kJ}}_{\text{Typically few kJ over few 100K}} + \underbrace{100 \text{kJ}}_{\text{Typically}} + \underbrace{100 \text{kJ}}_{$$

 $\Delta H(T_o)$: 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,

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

12.4.4 Trouton's Rule

 ΔS_{vap} is approximately the same for all materials. $\Delta S = \frac{\Delta H}{T} \rightarrow$ materials with high boiling points have larger ΔH_{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 12.9

13 Open Multicomponent Systems

Outcomes for this section:

- 1. Given sufficient information about the dependence of a total property B or ΔB 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 $\mu_k^0 \mu_k^0$ 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 γ 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.

13.1 Partial Molal Properties of Open Multicomponent Systems

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

C: # components $x_c:$ mole fraction $n_k: \#$ moles of component k

Then

$$dV' = \left(\frac{\partial V'}{\partial T}\right)_{P,n_m} dT + \left(\frac{\partial V'}{\partial P}\right)_{T,n_k} dP + \sum_{k=1}^c \left(\frac{\partial V'}{\partial n_k}\right)_{T,P,n_o \neq n_k} dn_k$$

We previously defined coefficients of dP, dT

For convenience, define $\bar{V}_K \equiv \left(\frac{\partial V'}{\partial n_k}\right)_{T,P,n_j \neq n_k}$ as partial molal volumes. We can do the same for any other extensive property B'(U', S', F', G', H')

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

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

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

$$V' = \sum_{k=1}^{C} \bar{V}_k dn_k = \sum_{k=1}^{C} \bar{V}_k \int_0^{n_k} dn_k = \sum_{k=1}^{C} \bar{V}_k n_k$$

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.

13.2 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:

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

$$dB' = \underbrace{MdT + NdP}_{0} + \sum_{k=1}^{C} \bar{B}_k dn_k$$

$$\to \sum_{k=1}^{C} n_k d\bar{B}_k = 0$$

Gibbs Duhem equation relates the different partial molal properties. To be shown: given one, the others can be computed. For two components: $n_1 d\bar{B}_1 + n_2 \bar{B}_2 = 0$

13.3 The Mixing Process: Calculating changes in energy



Figure 13.1: Mixing of three states into B_{soln}

Reference and Final States have the same T and P.

 $B_k^o: \mathrm{value} \ \mathrm{of} \ \mathrm{property} \ \mathrm{B} \ \mathrm{for} \ \mathrm{pure} \ \mathrm{component}, \ \mathrm{per} \ \mathrm{mole}.$

 $B'^o = \sum_{k=1}^C B_k^o n_k$: total value of B $\Delta B'_{mix} - B'_{so\ln} - B'^o$

$$\Delta B'_{mix} = \sum_{k=1}^{C} \bar{B}_k n_k - \sum_{k=1}^{C} B_k^o n_k = \sum_{C=1}^{k} \overbrace{(\bar{B}_k - \bar{B}_k)}^{\Delta B_k} n_k$$
$$\Delta B'_{mix} = \sum_{k=1}^{C} \Delta \bar{B}_k n_k$$

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?

$$\Delta B'_{mix} = \sum_{k=1}^{C} \Delta \bar{B}_k n_k$$
$$d(\Delta B') = \sum_{k=1}^{C} (\bar{B}_k dn_k - B_n^o dn_k) = \sum_{k=1}^{C} \Delta \bar{B}_k dn_k$$

Alternatively, we could have written

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

We can also express these per mole:

$$d\Delta B_{mix} = \sum_{k=1}^{C} \Delta \bar{B}_k dX_k$$
$$\sum_{k=1}^{C} X_k d\Delta \bar{B}_k = 0$$

How do we find molal properties?

- 1. Measurement of total property B or ΔB versus composition.
- 2. Measurements of PMP \bar{B}_k versus composition.

We will first apply to two component systems.

$$B = \bar{B}_1 x_1 + \bar{B}_2 x_2, dB = \bar{B}_1 dx_1 + \bar{B}_2 x_2$$
$$dx_1 = -dx_2$$
$$x_1 + x_2 = 1, x_2 = 1 - x_1$$
$$dB = (\bar{B}_1 - \bar{B}_2) dX_1$$
$$\frac{dB}{dX_1} = \bar{B}_1 - \bar{B}_2$$
$$B = \bar{B}_1 x_1 + \left(\bar{B}_1 - \frac{dB}{dX_1}\right) (1 - X_1) = \bar{B}_1 - \frac{dB}{dX_1} + \frac{dB}{dX_1} X_1$$

Solve for \bar{B}_1

$$\bar{B}_1 = B + (1 - X_1) \frac{dB}{dX_1}$$
 and $\bar{B}_2 = B + (1 - X_2) \frac{dB}{dX_2}$

Note also that

$$\Delta B_1 = \Delta B + (1 - X_1) \frac{d\Delta B}{dX_1}; \ \Delta B_2 = \Delta B + (1 - X_2) \frac{d\Delta B}{dX_2} \text{ from Daltoff 8.2.1}$$

Problem 8.3: Given behavior of volume change upon mixing $\Delta V_{mix} = 2.7X_1X_2^2$ (L??/mol), derive expressions for partial molal volumes of each component as a function of composition.

$$\Delta V_{mix} = 2.7X_1 X_2^2 = a X_1 X_2^2 \ a = 2.7$$

To take derivative, express in terms of X_2 :

$$\Delta V_{mix} = a(1 - X_2)X_2^2$$
$$\frac{d\Delta V_{mix}}{dX_2} = 2aX_2 - 3aX_2^2 = -\frac{d\Delta V_{mix}}{dX_1}$$

Now use relations derived in lecture:

$$\Delta \bar{B}_1 = \Delta B_{mix} + (1 - X_1) \frac{d\Delta B_{mix}}{dX_1} \ (B \to V)$$

13.4 Graphical Determination of Partial Molal Properties $\Delta \bar{B}_2 = \Delta B_{mix} + (1 - X_2) \frac{d\Delta B_{mix}}{dX_2}$ $\Delta \bar{B}_2 = AB + PB \cdot \frac{BC}{PB} = AB + BC = AC$



Figure 13.2

Evaluations of PMPs: given $\bar{B}_1(X) \rightarrow \bar{B}_2(X_1)$, BGibbs - Duhem: $X_1 d\bar{B}_1 + X_2 d\bar{B}_2 = 0$, $d\bar{B}_1 = -\frac{X_2}{X_1} d\bar{B}_2$ $\bar{B}_1 = \bar{B}_1(x=0) + \int_0^{X_2} d\bar{B}_1 = B_1^0 + \int_0^{X_2} \left(\frac{-X_2}{X_1} d\bar{B}_2\right)$ $d\bar{B}_2 = \frac{d\bar{B}}{dX_2} dX_2$ \therefore 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 $\Delta \overline{H}_2$, find $\Delta \overline{H}_1$ and ΔH .

 $\Delta \bar{H}_2 = a X_1^2$ Compute total derivative:

$$\frac{d\Delta H_2}{dX_2} = 2aX_1 \frac{dX_1}{dX_2} = -2aX_1$$
$$\underset{\longrightarrow}{X_1 + X_2} = 1dX_1 + dX_2 = 1$$
$$dX_1 = -dX_2$$

$$\Delta \bar{H}_1 = -\int_{X_2=0}^{X_2} \frac{X_2}{X_1} \frac{d\Delta \bar{H}_2}{dX_2} dX_2 = -\int_{X_2=0}^{X_2} \frac{X_2}{X_1} (-2aX_1) dX_2$$
$$\Delta \bar{H}_1 = 2a \int_0^{X_2} X_2 dX_2 = aX_2^2$$

 $\Delta H = X_1 \Delta \bar{H}_1 + X_2 \Delta \bar{H}_2 = X_1 (aX_2^2) + X_2 (aX_1^2) = aX_1 X_2 \underbrace{(X_1 + X_2)}_{=1}$

$$\Delta H = a X_1 X_2$$

13.5 Relationships between partial molal properties:

 $({\rm F}',\,{\rm G}',\,{\rm H}',\,{\rm S}',\,{\rm U}',\,{\rm their}$ 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.

13.6 Chemical Potential in Multicomponent Systems

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

The thermodynamic state is specified by C+2 variables:

$$dU' = TdS' - PdV' + \sum_{k=1}^{C} \mu_k dn_k$$
, so $\mu_k \equiv \left(\frac{\partial U'}{dn_K}\right)_{S,V,n_k}$

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 $\mu_k(T, P) = \overline{G}_k$, we can express all PMP's in terms of μ_k :

 $\bar{S}_k, \bar{V}_k, \bar{H}_k, \bar{U}_k, \bar{F}_k$

$$\bar{S}_{k} = -\left(\frac{\partial \bar{G}_{k}}{\partial T}\right)_{P,n_{k}} = -\left(\frac{\partial \mu_{k}}{\partial T}\right)_{P,n_{k}}$$
$$\bar{V}_{k}' = \left(\frac{\partial \bar{G}_{k}}{\partial P}\right)_{T,n_{k}} = \left(\frac{\partial \mu_{k}}{\partial P}\right)_{T,n_{k}}$$

 \mathbf{So}

$$\bar{H}_{k} = \bar{G}_{k} + T\bar{S}_{k} = \mu_{k} - T\left(\frac{\partial\mu_{k}}{\partial T}\right)_{P,n_{k}} - P\left(\frac{\partial\mu_{k}}{\partial P}\right)_{T,n_{k}}$$
$$\bar{F}_{k} = \bar{U}_{k} - T\bar{S}_{k} = \mu_{k} - P\left(\frac{\partial\mu_{k}}{\partial P}\right)_{T,n_{k}}$$

 μ_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 $\mu_k \to \Delta \mu_k = \mu_k - \mu_k^0$

13.7 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 $\mu_k - \mu_k^0 = \Delta \mu_k \equiv RT \ln a_k$, where a_k is the activity of component k. Further we define the activity coefficient γ_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.

13.8 Properties of ideal solutions (e.g. ideal gas mixtures)

Imagine removing the partitions in Figure 13.3 below and allowing the gases to mix while keeping T,P constant. The process is analogous to free expansion.



Figure 13.3: Mixture of ideal gases

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 $d\mu_K$:

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

For an ideal gas,

 $V' = n_T \frac{RT}{P} = \frac{RT}{P} = \frac{RT}{P} \sum_{k=1}^C n_k,$ for which we can find $\bar{V}_k = \left(\frac{\partial V'}{\partial n_k}\right)_{T,P,n_i} = \frac{RT}{P}$

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?

 $\Delta \bar{G}_k = RT \ln X_k$

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

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

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

$$\Delta \bar{U}_k = \Delta \bar{H}_k - P \Delta \bar{V}_k = 0$$

$$\Delta \bar{F}_k = \Delta \bar{U}_k - T \Delta \bar{S}_k = RT \ln X_k$$

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 13.4: Properties of an ideal solution including $\Delta G_{mix}, \Delta S_{mix}, \Delta H_{mix}, \Delta V_{mix}, \Delta U_{mix}$ and ΔF_{mix} . Maximum temperature shown is 1400 K.

13.9 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: $\lim_{X_2\to 0} a_2 = \gamma_2^0 X_2 : \gamma_2^0(T, P)$ is Henry's Law constant (in particular range), the solute activity coefficient for a dilute solution.

Consider Solute A in Solvent B

 $\gamma_2 = e^{a_o X_1^2/RT}$ for $X_1 \to 1$, $\gamma_1^0 = e^{\alpha_0/RT}$

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 ΔH and ΔS given

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



Figure 13.5

$$\Delta S_{m,Al_2O_3} = \Delta S_{m,Cr_2O_3}$$

Recall that under isobaric, reversible conditions, $\Delta S^{\alpha \to P} = \frac{\Delta H^{\alpha \to \beta}}{T}$

$$\frac{\Delta H_{m,1}}{T_{m,1}} = \frac{\Delta H_{m,2}}{T_{m,2}} \Rightarrow \Delta H_{m,Cr_2O_3} = \Delta H_{m,Al_2O_3} = \Delta H_{m,Al_2O_3} \times \frac{T_{m,Cr_2O_3}}{T_{m,Al_2O_3}}$$

$$\Delta H_{m,Cr_2O_3} = 107,500 \frac{J}{mol - K} \times \frac{2538K}{2324K} = 117,400J/mol - K$$

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

Note: if heating of Cr_2O_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 $X_{Cr_2O_3} \rightarrow \Delta \bar{H}_{Al_2O_3} = 0$ Focus on change in 1 mole of solid Cr_2O_3 .

$$\Delta S = \Delta S_m + \Delta S_{mix}$$

$$\Delta S_m = \frac{\Delta H_m}{T_m} = \frac{117500}{2538} = 46.26 J/K$$

$$\Delta S_{mix} = -R \ln X^F - (-R \ln X^t), \text{ where } X^i_{Cr_2O_3} = 1 \text{ (assume } \gamma^0 = 1)$$

$$\Delta S_{mix} = -R\ln(0.2)$$

$$\Delta S = 46.26 + 13.38 = 59.64 J/K$$

$Cr_2O_3 - Al_2O_3$ Phase Diagram



Figure 13.6: $Cr_2O_3 - Al_2O_3$ Phase Diagram

13.10 Excess Properties, relative to ideal

 $\Delta \mu_k = RT \ln(a_k) = RT \ln(Y_k X_k)$, so we can write

$$\Delta \bar{G}_k = \underbrace{RT \ln \gamma_k}_{\text{differenceideal behavior}} + \underbrace{RT \ln X_k}_{k} = \Delta \bar{G}_k^{XS} + \Delta \bar{G}_k^{id}$$

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 γ_k . (See table 8.5)

$$\Delta H_k = \Delta \bar{G}_k - T \Delta S_k = \Delta \mu_k - T \left(\frac{\partial \mu_k}{\partial T}\right)_{P,\mu_k} = -RT^2 \left(\frac{\partial \ln \gamma_k}{\partial T}\right)_{P,n_k}$$
$$\Delta \bar{V}_k = \left(\frac{\partial \Delta \bar{G}_n}{\partial P}\right)_{T,n_k} = \frac{\partial}{\partial P} \left[(RT \ln \gamma_k + RT \ln X_R) \right]_{T,n_k} = RT \left(\frac{\partial \ln \gamma_k}{\partial P}\right)_{T,n_k}$$

= 0 for an ideal gas.

13.11 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, $\Delta H_{mix} = 0$, For regular : $\Delta H_{mix} = \Delta H_{mix}^{XS}(X_2, X_3, ... X_c)$
For a regular solution, $\Delta S_{mix}^{reg} = \Delta S_{mix}^{id}$, so $\Delta S_{mix}^{XS} = 0$
 $\Delta G_{mix}^{XS} = \Delta H_{mix}^{XS} - T \Delta S_{mix}^{XS}$

So $\Delta \bar{G}_m^{XS} = \Delta \bar{H}_k = RT \ln \gamma_k$

We see that γ_k can be evaluated from the heat of mixing: $\gamma_k = exp\left(\frac{\Delta \bar{H}_k}{RT}\right)$ (check in eq 8.102)

Let's look at the simplest binary example:

Let $\Delta H_{mix} = a_o X_1 X_2 = \Delta G_{mix}^{XS}$, where a_o is constant. This corresponds to example 8.1. The change in Gibbs Free energy.

$$\Delta G_{mix} = \Delta G^{XS} + \Delta G^{id} = a_o X_1 X_2 + \underbrace{RTX_1 \ln X_1 + RTX_2 \ln X_2}_{\text{Table 8.3}}$$

 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

$$\Delta H_{mix} = X_1 X_2 \left[\alpha_o(T) X_1 + \alpha_1(T) X_2 \right] = \Delta G_{mix}^{XS}$$

Let's examine the impact of interactions on ΔH_{mix} , ΔS_{mix} , and ΔG_{mix} , starting with the simpler regular solution.



Figure 13.7: Properties of an ideal solution

$$\Delta \bar{S}_{k} = -R \ln \gamma_{k} - R \ln X_{k} - RT \left(\frac{\partial \ln \gamma_{k}}{\partial T}\right)_{P,n_{k}}$$
$$\Delta \bar{U}_{k} = RT^{2} \left(\frac{\partial \ln \gamma_{k}}{\partial T}\right)_{P,n_{k}} - PRT \left(\frac{\partial \ln \gamma_{k}}{\partial P}\right)_{T,n_{k}}$$
$$\Delta \bar{F}_{k} = RT \ln \gamma_{k} + RT \ln X_{k} - PRT \left(\frac{\partial \ln \gamma_{k}}{\partial P}\right)_{T,n_{k}}$$

For reference, not lecture Gibbs Duhem Equations

OGnix = OG + OG x5 OHAir = O E5. $\Delta H_{mix} = 4 \cdot X_1 X_2 = \Delta G_{mix}^{XS} = 12500 X_1 X_2 (\frac{J}{mole})$ 4000 2000 ΔG_{mix} ΔH_{mix} ASmix $\left(\frac{J}{mol}\right)$ $\left(\frac{J}{\text{mol }K}\right)$ $\left(\frac{J}{mol}\right)$ 0 0 -4000 0 n 0 X, X_2 Х,

FIGURE 8.5 Variation of thermodynamics mixing properties with composition and temperature for the simplest regular solution model for a positive departure from ideal behavior with $a_0 = 12,500$ J/mol. Maximum temperature shown is 1200 K.

Figure 13.8: Properties of a regular solution

 $X_1 d\Delta \mu_1 + X_2 d\Delta \mu_2 = 0$ $\Delta \mu_k = RT \ln(a_k)$ $X_1 d \ln \gamma_1 + X_2 d \ln \gamma_2 = 0$ $a_k = \gamma_k X_k$ $\Delta \mu = -\int_{0}^{X_2} \frac{X_2'}{X_1} \frac{d\Delta \mu_2}{dX_2'} dX_2'$ $\ln \gamma_1 = -\int_{-\infty}^{X_2} \frac{X_2'}{X_1} \frac{d\ln \gamma_2}{dX_2'} dX_2'$ $\ln a_1 = -\int_{0}^{X_2} \frac{X_2'}{X_1} \frac{d\ln a_2}{dX_2'} dX_2'$ $\Delta \bar{S}_k = -\left(\frac{\partial \Delta \mu_k}{\partial T}\right)_{B\,\mathrm{res}}$ $\Delta \bar{H}_k = \Delta \mu_k + T \left(\frac{\partial \Delta \mu_k}{\partial T}\right)_{Pm}$ $\Delta \bar{G}_k = \Delta \mu_k = \Delta \bar{H}_k - T \Delta \bar{S}_k$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

For an ideal solution, $\Delta H_{mix}=0$, for a regular solution $\Delta S^{reg}_{mix}=\Delta S^{id}_{mix}$

$$\Delta G_{mix}^{XS} = \Delta H_{mix}^{XS} - T \Delta S_{mix}^{XS}$$

$$\Delta S_{mix}^{XS} = 0$$

The entropy of mixing for a regular solution is the same as for an ideal solution (hence $\Delta S^{XS} = 0$)

The enthalpy of mixing for a regular solution deciates from that of an ideal solution $(\Delta H^{id} = 0, \Delta H^{XS} \neq 0).$

Example: HW 8.4 One mole of solid Cr_2O_3 at 2500 K is dissolved in a large colume of a liquid Raoultian solution (2300 K) of Al_2O_3 and $Cr_2O_3(20\%)$.

Calculate the resulting ΔH and ΔS given

$$T_{m,Cr_2O_3} = 2538K$$

 $\Delta H_{m,Al_2O_3} = 107,500 \text{J/mol-K} @T_m (= 2324 \text{ K})$
 $\Delta S_{m,Al_2O_3} = \Delta S_{m,Cr_2O_3}$

Recall that under isobaric, reversible conditions, $\Delta S^{\alpha \to \beta} = \frac{\Delta H^{\alpha \to \beta}}{T}$

$$\frac{\Delta H_{m,1}}{T_{m.1}} = \frac{\Delta H_{m,2}}{T_{m,2}} \Rightarrow \Delta H_{m,Cr_2O_3} = \Delta H_{m,Al_2O_3} \times \frac{T_{m,Cr_2O_3}}{T_{m,Al_2O_3}}$$
$$\Delta H_{m,Cr_2O_3} = 107,500 \frac{J}{mol-K} \times \frac{2538K}{2324K} = 117,400 \frac{J}{mol-K}$$

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 $X_{Cr_2O_3} \rightarrow \Delta \bar{H}_{Al_2O_3} = 0$

Focus on change in 1 mole of solid Cr_2O_3

$$\Delta S = \Delta S_m + \Delta S_{mix}$$

$$\Delta S = \frac{\Delta H_m}{T_m} = \frac{117400}{2538} = 46.26 J/K$$

$$\Delta S_{mix} = -R \ln X^F - (-R \ln X^i) \text{, where } X^i_{Cr_2O_3} = 1$$

$$\Delta S_{mix} = -R \ln(0.2)$$

$$\Delta S = 46.26 + 13.38 = 59.64 \text{ J/K}$$

13.11.1 Mixtures of Real Gases: Fugacity

Describe "real" gases in terms fo their deviation from ideal behavior, starting with molar volume \bar{V}_k

Define
$$\alpha_k = \bar{V}_k - \frac{RT}{P}$$
 (note that $\alpha_k = 0 \leftrightarrow ideal$)

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

$$\Delta \mu_k \equiv \operatorname{RTln}\left(\frac{f_k}{P}\right)$$

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 13.9: Calculated and observed microstructures

Schematic



Figure 13.10: Multicomponent heterogeneous (multi-phase) system

14 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: $dU' = TdS' - PdV' + \sum_{\substack{k=1 \ (\delta W)}}^{C} \mu_k dn_k$



Figure 14.1: Multicomponent heterogeneous and homogeneous systems

sum over phases sum over components Heterogeneous System: $dU'_{sys} = \sum_{\alpha=1}^{P} \begin{bmatrix} T^{\alpha}dS'^{\alpha} - P^{\alpha}dV' + \sum_{k=1}^{C} \mu_{k}^{\alpha}dn_{k}^{\alpha} \end{bmatrix}$ $dV' = TdS' - PdV' + \sum_{k=1}^{\tilde{\nu}} \mu_{k}dn_{k}$ $\overrightarrow{\alpha}$ $\overrightarrow{\beta}$ $\overrightarrow{\alpha}$ $\overrightarrow{\alpha}$

Figure 14.2: Multicomponent heterogeneous (multi-phase) system

14.1 Conditions for Equilibrium

$$T^{\alpha} = T^{\beta} \quad P^{\alpha} = P^{\beta} \quad \mu^{\alpha} = \mu^{\beta}$$

likewise for all pairs of phases $\beta/\gamma, \gamma, \dots P$, where P =number of phases $T^{I} = T^{II} = \dots = T^{P} P - 1$ independent equations $P^{I} = P^{II} = \dots = P^{P} P - 1$ independent equations

$$\begin{array}{c} \mu_{1}^{I} = \mu_{1}^{II} = \ldots = \mu_{1}^{P} \\ \mu_{2}^{I} = \mu_{2}^{II} = \ldots = \mu_{2}^{P} \\ \vdots \\ \mu_{C}^{I} = \mu_{C}^{II} = \ldots = \mu_{C}^{P} \end{array} \right\} \begin{array}{c} " \\ C = \# \text{ components} \\ " \\ \end{array}$$

Equilibrium conditions generate (C+2)(P-1) = n equations. These are constraints on the variables

14.2 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?

 $\left. \begin{array}{ccc} T^{I},P^{I},X_{2}^{I},X_{3}^{I}...X_{C}^{I} & 2+C-1=C+1 \\ T^{II},P^{II},X_{2}^{II},X_{3}^{II}...X_{C}^{II} & & \\ & \vdots & & \\ T^{P},P^{P},X_{2}^{P},X_{3}^{P}...X_{C}^{P} & & \\ \end{array} \right\} \mathbf{P} \text{ sets of C+1 variables}$

$$\therefore m = P(C+1)$$

$$m-n=P(C+1)-(C+2)(P-1)=\mathcal{PC}+P-\mathcal{PC}-2P+C+2$$



Gibbs Phase Rule

15 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 $\Delta G_k^{0, \alpha \to \beta}$.
- 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.

15.1 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)



Figure 15.1: Unary (C=1) phase diagram

- 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.

15.2 Alternative Representations

P-V, T-X, etc.

Not all useful variables (e.g. V,X) are thermodynamic potentials 2-phase coexistence lines \rightarrow areas



Figure 15.2: Alternate representations

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.

15.3 Binary Phase Diagrams

C = 2

There are 5 possible phases: $\alpha, \epsilon, \beta, L, V$

F = C - P + 2

For a single phase region, $f = 3 \rightarrow \text{Plot in P}$, T, a_2 space. 2-phase regions are planes, 3-phase regions are lines, and 4-phase regions are points.



Figure 15.3: Binary (c=2) phase diagram

15.4 Alternative Representations: T vs. X

In Figure 15.4 below, the 2-phase coexistence lines are areas.

15.5 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:



Figure 15.4: T vs X for binary phase diagram

State P with average composition X_2^o at temperature T. The phase Σ is in equilibrium with the liquid $(T^{\Sigma} \neq T^L)$.

$$n_T X_2^o = n^{\Sigma} X_2^{\Sigma} + n^L X_2^L \to X_2^o = \frac{n^{\Sigma}}{n^T} X_2^{\Sigma} + \frac{n^L}{n^T} X_2^L = f^{\Sigma} X_2^{\Sigma} + f^L X_2^L$$

where n = # of moles and f = fraction In terms of X_2 ,

$$X_2^o = f^{\Sigma} X_2^{\Sigma} + (1 - f^{\Sigma}) X_2^L = X_2^L + f^{\Sigma} (X_2^{\Sigma} - X_2^o)$$

$$\therefore f^{\Sigma} = \frac{X_2^o - X_2^L}{X_2^{\Sigma} - X_2^L}$$

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.

15.6 The Lever Rule



Figure 15.5: Tie lines on an X-T diagram

$$f^{L} = \frac{X_{2}^{o} - X_{2}^{\Sigma}}{X_{2}^{L} - X_{2}^{\Sigma}} = \frac{AP}{AB}$$

$$f^{\Sigma} = \frac{X_2^o - X_2^L}{X_2^{\Sigma} - X_2^L} = \frac{PB}{AB}$$
$$X_2^{\Sigma} - X_2^L = AB$$
$$X_2^{\Sigma} - X_2^o = AP$$
$$X_2^o - X_2^L = PB$$

X-T diagrams gives temperature, compositions, and amounts.

15.7 Applications of Phase Diagrams: Microstructure Evolution

Following an isotherm in the X-T diagram of Figure shows the following microstructures:

- $\diamond T_o$: homogeneous melt
- $\diamond T_1 : \alpha + L$ (nucleation)
- $\diamond T_2$: increase in α phase
- $\diamond T_3$: solidification $\alpha + \beta$



Figure 15.6: Microstructure Evolution

15.8 Review

$$\Delta G_{mix} = \Delta H_{mix} - TS_{mix}^{id}$$

$$\Delta G_{mix} = \Delta G_{mix}^{XS} + RT(X_1 \ln X_1 + X_2 \ln X_2)$$

$$\Delta G_{mix}^{ideal} = RT(X_1 \ln X_1 + X_2 \ln X_2)$$



Figure 15.7: 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.

15.9 Types of $\alpha - L$ phase diagrams

 $\Delta H_{mix} = a_o X_1 X_2$

Note the curvature of the phase boundary in Figure 15.8 below - the sign follows that of a_o^2 .

16 Thermodynamics of Phase Diagrams

Goal: Generate phase diagrams from ΔG 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 ΔG_{mix}^{α} and ΔG_{mix}^{L} to determine regions of phase stability.

Needed: comparison of solid and liquid reference states

16.1 Calculation of ΔG_{mix} from pure component reference states

We can plot ΔG_{mix} for a solid (α) or liquid (L) solution using solid or liquid reference states for components 1,2 (4 possibilities).



Figure 15.8: Patterns of phase diagrams can generated by only two phases, α and L, with the simplest regular solution model

One cannot directly compare the following:

Need to change reference states

$$\Delta G^{\alpha}_{mix} = X_1^{\alpha} \left(\bar{G}_1^{\alpha} - G_1^{o\alpha} \right) + X_2^{\alpha} \left(\bar{G}_2^{\alpha} - G_2^{o\alpha} \right) \\ \Delta G^L_{mix} = X_1^{\alpha} \left(\bar{G}_1^L - G_1^{oL} \right) + X_2^{\alpha} \left(\bar{G}_2^L - G_2^{oL} \right)$$

Indicate choice of reference states with brackets:

Reference states the same for α and L phases}

$$\Delta G_{mix}^{\alpha} = X_1^{\alpha} \left(\overline{G}_1^{\alpha} - \overline{G}_1^{o\alpha} \right) + X_2^{\alpha} \left(\overline{G}_2^{\alpha} - \overline{G}_2^{o\alpha} \right)$$
$$\Delta G_{mix}^L = X_1^L \left(\overline{G}_1^L - \overline{G}_1^{oL} \right) + X_2^{\alpha} \left(\overline{G}_2^L - \overline{G}_2^{oL} \right)$$

Rewrite:

$$\begin{split} \Delta G^{\alpha}_{mix} &= X_1^{\alpha} \left(\bar{G}_1^{\alpha} - G_1^{o\alpha} \right) + X_2^{\alpha} \left(\bar{G}_2^{\alpha} - G_2^{o\alpha} \right) - X_2^{\alpha} \left(\bar{G}_2^{oL} - G_2^{o\alpha} \right) \\ \Delta G^{\alpha}_{mix}(\alpha, L) &= X_1^{\alpha} \left(\bar{G}_1^{\alpha} - G_1^{o\alpha} \right) + X_2^{\alpha} + X_2 \left(G_2^{o\alpha} - G_2^{oL} \right) \\ \Delta G^{\alpha}_{mix}(\alpha, L) &= \Delta G^{\alpha}_{mix}(\alpha, \alpha) + X_2^{\alpha} \Delta G_2^{oL \to \alpha} \end{split}$$

Similarly,

$$\Delta G^L_{mix}(\alpha,L) = \Delta G^L_{mix}(L,L) + X^L_1 \Delta G^{o\alpha \to L}_2$$

What do these look like?



Figure 16.1

Next step: plot ΔG^{α} , ΔG^{L} together and find <u>common tangent</u> to determine regimes of phase stability.



Figure 16.2

16.2 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 16.3. At this T and P, a solid of composition X_2^{α} can be in equilibrium with a liquid of composition $X_2^L(T^{\alpha} = T^L, P^{\alpha} = P^L, \mu_1^{\alpha} = \mu_1^L, \mu_2^{\alpha} = \mu_2^L)$.



Figure 16.3: Common tangent construction

The intercepts reflect the conditions for chemical equilibrium.

A:
$$\Delta \mu_1^{\alpha} = \mu_1^{\alpha}(X_2^{\alpha}) - \mu_1^{\alpha} \\ \Delta \mu_1^L = \mu_2^L(X_2^L) - \mu_1^{\alpha} \\ \end{pmatrix} \mu_1^{\alpha}(X_2^{\alpha}) = \mu_1^L(X_2^L)$$

Chemical equilibrium of component 1 between α, L

B:
$$\Delta \mu_2^{\alpha} = \mu_2^{\alpha}(X_2^{\alpha}) - \mu_2^{\alpha} \\ \Delta \mu_2^L = \mu_2^L(X_2^L) - \mu_2^{\alpha}$$

$$\mu_2^{\alpha}(X_2^{\alpha}) = \mu_2^L(X_2^L)$$

Chemical equilibrium of component 2 between α, L .

When are two-phase regions $(\alpha + L, \alpha + \beta)$ stable at intermediate compositions?



Figure 16.4

 $\left. \begin{array}{l} X_2 < D: \alpha \\ X_2 > F: \beta \end{array} \right\} \text{homogeneous mixtures of 1 and 2} \end{array} \right.$

 $D < X_2 < F : \alpha + \beta$ has lower energy than homogeneous mixture of 1 and 2 $B : \Delta G$ for 1 & 2 in β phase $A : \Delta G$ for 1 & 2 in α phase $M : \Delta G$ for $\frac{EF}{DF}$ of α and $\frac{DE}{DF}$ of β $\Delta G_M < \Delta G_A < \Delta G_B$

Sequential transitions between multiple two-phase regions 3 solid phases, 1 liquid phase



Figure 16.5

How are the single and two phase regions represented on a phase diagram?



Figure 16.6: Representing single and two phase regions on a phase diagram We need $\Delta G(X)$ for many temperature. Examine $G^{\alpha}(T)$ and $G^{P}(T)$.

To generate ΔG_{mix} vs. X curves, we need G(T) of pure components to establish "hanging points" (the $\Delta G_i^{o\alpha \to \beta}$)



Figure 16.7: G(T) of pure components

Next, examine changes in ΔG_{mix}^{α} and ΔG_{mix}^{L} versus T to establish which phases are present.

16.3 A Monotonic Two-Phase Field



Figure 16.8

$$a_o^{\alpha} = 1000 J/mol \ a_o^L = -6000 J/mol$$
$$\Delta H_{mix} = a_o X_1 X_2$$

16.4 Non-monotonic Two-Phase Field

$$a_o^{lpha} = 6000 J/mol$$

 $a_o^L = -2000 J/mol$
 $\Delta H_{mix} = a_o X_1 X_2$



16.5 Properties of a regular solution

Recall: Regular - $\Delta G_{mix}^{id} + \Delta G_{mix}^{XS}$



Figure 16.10: Variation of mixing properties with composition and temperature for the simplest regular solution model. Maximum temperature is 1200 K, and $a_o = 12,500 J/mol$

16.6 Misciblity Gap: Appearance Upon Cooling

 $\Delta H_{mix}=13.7 X_1 X_2 k J/mol:$ below critical T, mixture is driven towards phase separation

 $a_o^\alpha = 13,700 J/mol$

16.7 Spinodal decomposition: concave down region in ΔG drives unmixing and "uphill" diffusion



Figure 16.11: Miscibility gap



Figure 16.12: Spinodal decomposition

17 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.

17.1 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.

17.2 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 α , β , 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.

17.3 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.

17.4 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.

17.5 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 ΔH given the $C_P(T)$, assuming a negligible contribution from thermal expansion.
- 7. Calculate $\Delta V^{\alpha \to \beta}$ assuming ideal gas behavior.
- 8. Integrate $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$ with the assumption that ΔS and ΔV 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 $\Delta V^{\alpha \to \beta}$.
- 11. State Trouton's rule and justify its validity qualitatively.
- 12. Sketch the P T diagram for a one-component system.

17.6 Chapter 8

- 1. Given sufficient information about the dependence of a total property B or ΔB 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.

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- 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 γ 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.

17.7 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.

17.8 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 $\Delta G_k^{0,\ \alpha\to\beta}.$
- 3. Given G versus X at different T, construct a phase diagram in terms of T and X.

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- 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.

18 314 Problems

Contents

18.1 Phases and Components

(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?

18.2 Intensive and Extensive Properties

(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.

18.3 Differential Quantities and State Functions

(2014) Consider the function $z = 6x^2y^3\cos^2 u$.

- 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).

 $\left(2014\right)$ Why are state functions so useful in calculating the changes in a thermodynamic system?

(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.

18.4 Entropy

(2015) Following Section 3.6, compute the change in entropy in the formation of one mole of SiO_2 from Si and O at room temperature.

(2015) Consider an isolated system consisting of three compartments A, B, and C. Each compartment has the same volume \underline{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?

18.5 Thermodynamic Data

(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.

Material Type	Specific Material	α	Source (include
			page or
			link inio)
Elemental Metal	e.g. Gold		
Semiconductor			
Insulator			
Polymer			

- 2. What is a common material with a negative α ?
- 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.)

(2014) The density of silicon carbide at 298 K and 1 atm is $^{3.2}$ g/cm³. 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.

(2015) The density of aluminum at 298 K and 1 atm (or "bar") is 2.7 g/cm3. 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.

(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.

(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:

$$C_p = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

(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_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 (O2) 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.

(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.

(2015) Consider one mole of a monatomic ideal gas that undergoes a reversible expansion one of two ways.

- 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?

(2015) In class we learned that the change in entropy of a material with temperature is given by:

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT$$
(18.1)

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:

$$\int_{T_1}^{T_2} f(x) \approx (T_2 - T_1) \left[\frac{f(T_1 + f(T_2))}{2} \right]$$
(18.2)

where the function f(T) in our case is the right hand side of Equation , is simply the right hand side of Equation 18.1. 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:

(a)

$$C_p = 22.83 + 3.826x10^{-3}T - \frac{3.533x10^5}{T^2} + 2.131x10^{-8}T^2$$
(18.3)

(b) Use Equation 18.1 to analytically solve for the change in entropy using Equation 18.3. Which method do you think is more accurate? Explain your reasoning.

18.6 Temperature Equilibration

(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?

(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 600K. 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.

18.7 Statistical Thermodynamics

(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.

(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 (<u>e.g.</u> (3,5,1)) and repeat your calculation of the entropy. Which macrostate is more likely?

(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}.

18.8 Single Component Thermodynamics

(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.

(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.



(2015) DeHoff 7.6 See Lecture 17, last page.

(2015) DeHoff 7.7 variant: At what pressure will ice melt at -2°C?

(2015) DeHoff 7.8: At 1 atm pressure and below 1155 K, the ε form of titanium is stable; above 1155 K, the β form is the stable phase (ε becomes metastable). Given the following data:

- ♦ $\Delta S^{\epsilon \to \beta} = 3.43 \,\text{J/mol} \cdot \text{K}$ (This is the difference in molar entropy 3 between the phases).
- $\diamond~$ The change in molar entropy upon melting is 9.02 J/mol $\cdot\,{\rm K}.$
- $\diamond~T_m^\beta{=}1940$ K.

- 1. Sketch G^{ε} , G^{β} and G^{ℓ} in the temperature range of interest.
- 2. What is T_m^{ε} ?
- 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
 - (a) Find the ε phase of titanium (labeled as GHSERTI), the β 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 "^".

18.9 Mulitcomponent Thermodynamics

(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.

(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.

(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.

(2015) One mole of solid Cr_2O_3 at 2500 K is dissolved in a large volume of a liquid Raoultian solution (also at 2500 K) of Al_2O_3 and Cr_2O_3 with $X_{Cr_2O_3} = 0.2$. Calculate the resulting changes in the total enthalpy and entropy given the following:

$$\begin{split} T_{m,{\rm Cr}_2{\rm O}_3} = 2538\,{\rm K};\, \Delta H_{m,{\rm Al}_2{\rm O}_3} = 107,500\,{\rm J/mol\,at}\,T_{m,{\rm Al}_2{\rm O}_3} = 2324\,{\rm K};\\ \Delta S_{m,{\rm Al}_2{\rm O}_3} = \Delta S_{m,{\rm Cr}_2{\rm O}_3} \end{split}$$

18.10 Computational Exercises

(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:

$$\begin{split} C_p^{Pb} &= 0.1169 + 4.2 x 10^{-5} T \; \frac{\mathrm{kg}}{\mathrm{kg}\cdot\mathrm{K}} \\ C_p^{H_2O} &= 4.2 \; \frac{\mathrm{kJ}}{\mathrm{kg}\cdot\mathrm{K}} \\ \Delta H_{fus}^{H_2O} &= 344 \; \frac{\mathrm{kJ}}{\mathrm{kg}} \\ \frac{dH}{dt} &= a \Delta T \end{split}$$

Here a is a coefficient that controls the heat transfer in conduction, which we will assume to be $3.33 \times 10^{-3} \text{ kJ/K} \cdot \text{s}$, and ΔT is the temperature difference between the two materials.

Use the equations derived in class to plot the change in temperature for H2O and Pb. Assume dt=1 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 H2O. How can you tell when equilibrium is reached from this plot?

(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:

$$G_s - X_s \frac{dG_s}{dX_s} = G_\ell - X_\ell \frac{dG_\ell}{dX_\ell}$$
(18.4)

$$\frac{dG_s}{dX_s} = \frac{dG_\ell}{dX_\ell} \tag{18.5}$$

where G_s and G_ℓ are given by the following expressions:

$$G_{s}(X_{s}) = \Omega_{s}X_{s}(1 - X_{s}) + RT [X_{s} \ln X_{s} + (1 - X_{s}) \ln (1 - X_{s}) + 200X_{s} - 400 (1 - X_{s})].$$

$$G_{\ell}(X_{\ell}) = \Omega_{\ell} X_{\ell} (1 - X_{\ell}) + RT \left[X_{\ell} \ln X_{\ell} + (1 - X_{\ell}) \ln (1 - X_{\ell}) \right].$$

Here G_s is the Gibbs energy of the solid phase, G_ℓ the Gibbs free energy of the liquid phase, R the gas constant (8.314 J/K), T the absolute temperature, X_s and X_ℓ are the compositions of the solid and liquid phase respectively, and Ω_s , Ω_ℓ are parameters to be defined later. We can rewrite Eqs. 18.4 and 18.5 as follows:

$$G_s - X_s \frac{dG_s}{dX_s} - G_\ell + X_\ell \frac{dG_\ell}{dX_\ell} = 0$$
(18.6)

$$\frac{dG_s}{dX_s} - \frac{dG_\ell}{dX_\ell} = 0 \tag{18.7}$$

Create a MATLAB function that takes X_s , X_ℓ , T, Ω_s and Ω_ℓ as inputs and then create a script that uses the MATLAB command follow to calculate X_s and X_ℓ for T=700K, $\Omega_\ell = 1500$ cal/mol and $\Omega_s = 3000$ cal/mol.

(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:

$$\begin{split} T^{\alpha}_{m} &= 900 \, \mathrm{K} \\ T^{\beta}_{m} &= 600 \, \mathrm{K} \\ \Delta H^{\alpha}_{f} &= 2000 \, \frac{\mathrm{cal}}{\mathrm{mol}} \\ \Delta H^{\beta}_{f} &= 1300 \, \frac{\mathrm{cal}}{\mathrm{mol}} \end{split}$$

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 $R = 1.987 \text{ cal/mol} \cdot \text{K}$

$$\begin{aligned} G_s\left(X_s\right) &= \Omega_s X_s \left(1 - X_s\right) + RT + \\ \left[X_s \ln X_s + (1 - X_s) \ln \left(1 - X_s\right) + X_s \Delta G_{\beta}^{\ell \to s} + (1 - X_s) \Delta G_{\alpha}^{\ell \to s}\right]. \end{aligned}$$

$$G_{\ell}(X_{\ell}) = \Omega_{\ell} X_{\ell} (1 - X_{\ell}) + RT \left[X_{\ell} \ln X_{\ell} + (1 - X_{\ell}) \ln (1 - X_{\ell}) \right].$$

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:

$$\Delta G^{s \to \ell} = \Delta H^{s \to \ell} - T \Delta S^{s \to \ell}$$

(2015) 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:

$$RT \ln \left(\frac{X_s}{1 - X_s}\right) - \Omega_s \left(2X_s - 1\right)$$

Again, assume that $\Omega_s = 3000$ 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. $\Omega_s = 3000 \operatorname{cal/mol} : \Omega_\ell = 0$
- 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.