
MATERIALS AT EQUILIBRIUM

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1 Preliminaries, Vocab, Energy, and Forces

Welcome to 3.20, Materials at Equilibrium. This course is designed to provide all incoming students with a grounding in equilibrium thermodynamics, energy scales in materials processes, phase stability, and phase diagrams. The material in this course is broadly applicable to all fields of materials science and engineering and will serve you well throughout your research as a graduate student. For information related to the course, including lecture content, problem sets, exams, staff policies, and grading please refer to your course syllabus found on Stellar, or contact the professor directly at allanore@mit.edu.

1.1 Definitions

To begin our journey, we will define some frequently used terms for convenience.

1. System: Any collection of matter that can be uniquely identified and on which you can define macroscopic averages (a system is not necessarily homogeneous)
2. Environment: The complement of a system. Together, the system being studied and its environment make up the universe.

$$[\text{environment}] = [\text{universe}] - [\text{system}] \quad (1)$$

3. Extensive Variables: Variables that scale with the system size (i.e. volume, mass, number of particles, n_{e-} , etc.). If we bring two containers together, the volume is a sum of the individual volumes:

$$V = V_1 + V_2 \quad (2)$$

4. Intensive Variables: Variables that are independent of the system size. Intensive variables do *not* scale with system size (i.e. pressure, temperature, electric field, etc.). For example, the sum of two system's pressures is not equal to the pressure of the sum of both systems:

$$P \neq P_1 + P_2 \quad (3)$$

5. State Variables: The variables required to fully characterize a system (T , P , n , ...). These are *not* equal to the **state** of a system. However, at equilibrium, there is a one-to-one mapping between the macroscopic state of the system and the full set of state variables; the state variables fully define the macroscopic equilibrium state.¹
6. Boundaries: Conditions that are defined for the flow of extensive variables into or out of a system. These strongly depend on the system of interest. Boundaries can have

¹Some people say the macroscopic state is a *function* of the state variables. A function is actually not the proper word here: A function can map many inputs onto a single output (e.g. $x^2 = 1$ at $x = 1$ and $x = -1$). The mapping from macroscopic states to the state variables is what one would call a bijective function; it has the special property of being a one-to-one mapping.

properties such as: permeable (open to mass flow, dn), impermeable (closed to mass flow), adiabatic (closed to heat flow), diathermal (open to heat flow), rigid (constant volume), deformable, etc. The nature of the boundary defines how the system's state variables can change as it is subjected to different processes. For example, while a system with a rigid boundary is subject to possessing a constant volume during arbitrary processes, a system with a deformable boundary will, for sufficiently slow processes, have the same pressure as its surroundings.

In the first third of the course (classical thermodynamics), we will look at the transfer of energy and other extensive variables through the borders of systems as they undergo processes. Note that this approach treats the system as a black box; we have no idea what is going on microscopically inside the system. We will derive laws regarding the conservation and creation of the extensive variables. Using these laws of conservation, we will be able to define exactly how the macroscopic state of the system changes by only keeping track of what goes on at the boundaries of the system. We will then develop constitutive equations which relate changes in the thermodynamic state variables to one another during arbitrary processes. Integration of these constitutive equations is a powerful and general way to calculate changes in a systems during arbitrary processes. Last, we will use these constitutive relationships to look at a special set of processes; phase transitions. We will derive laws for how the conditions under which phase transitions occur must change as the boundary conditions on the system change.

1.2 Energy and Forces

What “forms” of energy do we have?

- Potential energy: Gravitational, electrostatic, etc.
- Kinetic energy: Translation, rotations, etc.

This energy can be manifest inside and outside the system. Other examples of energies are thermal energy (from heat), electromagnetic energy, and chemical energy. For 3.20, we will assume that changes in the total energy E of our system are equal to changes in the internal energy U of the system.

$$\Delta E = \Delta U \tag{4}$$

This is tantamount to neglecting changes in the translational energy of the system as a whole. We assume that U exists and that U is a function of only the extensive thermodynamic variables.² We will also assume that all types of energy exchange that can be represented as work terms represent changes in U , except for exchange of heat. We will define *work* and *heat* next.

²Since U is a function of only the state variables, we call it a **state function**

2 Heat, Work, and Path Dependence

One commonly observed form of energy transfer is **work**. A differential amount of work is equal to a force dotted with a displacement:

$$dW = \vec{F} \cdot d\vec{r} \quad (5)$$

2.1 Two examples of work

Example 1: Deformation of a material:

The work resulting from a change in strain energy is

$$dW = V \bar{\sigma} \cdot d\bar{\epsilon} \quad (6)$$

where the double overbars indicate that σ, ϵ are tensors. To check the validity of this statement, we note that the stress σ has units of $[\text{Pa}] = [\text{N}/\text{m}^2]$, the strain ϵ is dimensionless, and the volume $[\text{m}^3]$ together produce a quantity of $[\text{N} \cdot \text{m}] = [\text{Joules}]$. We note that the shear stresses in this example are denoted by off-diagonals of σ ($\sigma_{12}, \sigma_{13}, \sigma_{23}$). If we consider only hydrostatic pressure, we will have $\sigma_{11} = \sigma_{22} = \sigma_{33} = -P$.

$$\begin{aligned} dW_{\text{pressure}} &= V \cdot (-P) d(\epsilon_{11} + \epsilon_{22} + \epsilon_{33}) \\ &= -PV(d\epsilon_{11} + d\epsilon_{22} + d\epsilon_{33}) \end{aligned} \quad (7)$$

We note that the strain is defined as $\epsilon_{11} \equiv \Delta l_1/l_1^{\text{initial}}$, and $l_1 l_2 l_3 = V$, so we can substitute $V(d\epsilon_{11} + d\epsilon_{22} + d\epsilon_{33}) = dV$:

$$dW_{\text{pressure}} = -P dV \quad (8)$$

To make Eq. 8 quantitative, we need an equation of state $P(V)$ or $\sigma(\epsilon)$. In mechanics, the equation of state for a crystal is the elastic compliance, c_{ijkl} :

$$\frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}} = c_{ijkl}. \quad (9)$$

If our material is isotropic, then we will see that $\frac{\partial V}{\partial P}|_T = V \cdot \beta_T$ where β_T is the isothermal compressibility – a property of the material that describes volume changes at constant temperature. Hence, using this constitutive relation, $\beta_T(P, T)$, we can quantify the work done upon the system during an isothermal process.

Example 2: Electrical work on an isotropic dielectric medium: The voltage between two sides of a dielectric is given by the internal electric field and the length as $V = \mathcal{E} \cdot l$. The energy stored in this capacitor is a product of the voltage and the charge. If the charge, q , changes, we can produce a work term:

$$dW = V dq \quad (10)$$

Also, $q = D \cdot A$ where D , the electric displacement, is equal to $\epsilon_0 \mathcal{E} + \frac{\mathcal{P}}{A \cdot l}$. \mathcal{P} is the total polarization and it is normalized by the volume, $A \cdot l$. We can do some algebra to arrive at a new expression for this work term:

$$\begin{aligned} dW &= \mathcal{E}l \cdot d(A(\epsilon_0 \mathcal{E} + \frac{\mathcal{P}}{lA})) \\ &= \mathcal{E}lA \cdot d(\epsilon_0 \mathcal{E} + \frac{\mathcal{P}}{lA}) \\ &= V\epsilon_0 \mathcal{E}d\mathcal{E} + \mathcal{E}d\mathcal{P} \end{aligned} \tag{11}$$

Note how the dW nicely separates into a response that is independent of the system and one that is determined by the material properties of the system. Some energy, $V\epsilon_0 \mathcal{E}d\mathcal{E}$, is stored even when an electric field is applied to a vacuum. We are not interested in this energy. $\mathcal{E}d\mathcal{P}$, on the other hand, is system-dependent. This is the work term appropriate to the application of an electric field to a system.

You will notice some commonalities between the mechanical work terms discussed previously and the electrical work term: both products result in units of energy, and both can be written as the product of a generalized force (an intensive thermodynamic variable, P, \mathcal{E}), and a generalized displacement (an extensive thermodynamic variable, $dV, d\mathcal{P}$). These traits are common to all work terms which cause changes in the internal energy. A differential amount of work done upon a system can thus be written as a sum over orthogonal work terms:

$$dW = \sum_i y_i dx_i \tag{12}$$

where each y_i represents a generalized force, and each x_i represents a generalized displacement.

You might have noticed that we were careful to define the compressibility of a system, β , over a specific path. Specifically, we defined a compressibility wherein the system was held at constant temperature, β_T . This is because the compressibility is a function of the boundary conditions under which the compression takes place.³ This concept can be generalized to all work terms: *the work done in changing an extensive variable is a function of the path along which the work takes place*. Put simply, the change in internal energy due to the work terms is path dependent. In thermodynamics, we make a distinction between path-dependent and path-independent intergrals via exact differentials and inexact differentials.

- exact differentials: The integral of an exact differential is path independent; it is only a function of the endpoints. We use a d for exact differentials.
- inexact differentials: The integral of an inexact differential is path dependent; the integral depends both on the endpoints and the path to get to these two endpoints. We use a d for inexact differentials.

This is illustrated below with two examples.

³For example, it takes more energy to compress a gas if you don't let heat flow out of the gas during the compression; the adiabatic compressibility is larger than the isothermal compressiblity.

2.2 Practice with Differentials

Case 1, Exact Differentials: Consider heights as a function of position, $h(x, y)$. We will travel from some height $h_1 \rightarrow h_2$. Anytime we move downwards, we will simply gain kinetic energy. Anytime we move up a hill, we will first use any kinetic energy we have and then use some stored energy (say, from a battery). Once we have reached h_2 , we will give all our kinetic energy to the environment (say from some thermal energy dissipation, like brakes). The change in potential energy between the two heights is ΔE_{field} and the energy of the environment, i.e. the work required to move us to this new spot, is ΔE_{system} . From conservation of energy,

$$\Delta E_{\text{system}} + \Delta E_{\text{field}} = 0 \quad (13)$$

Therefore, we can calculate the work required to move us to the new spot via integration of the differential of the gravitational energy with respect to the position (the gravitational force field):

$$\begin{aligned} \Delta E_{\text{field}} = dW &= \int \vec{F} \cdot d\vec{r} \\ &= - \int \nabla E_{\text{field}} \cdot dr \\ &= -mg(h_2 - h_1) \end{aligned} \quad (14)$$

Ultimately, the energy change (or work required to move us) from $h_1 \rightarrow h_2$ is independent of the path taken. Hence, \vec{F} is an exact differential. Mathematicians would say that gravitational force fields are conservative vector fields. This is an equivalence; exact differentials define conservative vector fields.

Case 2, Inexact Differentials: Consider now a system where the force \vec{F} is non-conservative. The work terms associated with moving through this kind of a vector field are then inexact differentials. Dissipative forces tend to make the force vector-field non-conservative, resulting in path dependence. For example, moving in a gravitational field with a constant friction term would result in:

$$\begin{aligned} \vec{F} &= -\vec{\nabla}E - f_{\text{friction}}|\vec{e}_v| \\ \int \vec{F} \delta \vec{r} &= -mg\Delta h - f L_{\text{path}} \end{aligned}$$

In thermodynamics, you can get an inexact differential for two reasons. As described above, dissipation leads to inexact differentials. A second, related way, is simply not taking into account all of the forces during your integration. Such an incomplete description will result in path-dependent integrals, even if the underlying vector field is conservative. For example, if we are moving in three dimensions and do not describe the force in the y -direction, F'_y , then we would (incorrectly) describe the work when moving in three dimensions as:

$$dW_{\text{incomplete}} = dW_x + dW_z = F_x dx + F_z dz$$

Consider two different paths in a conservative 3D vector field. The integrated amount of work done due to the x- and z- forces may be different between the two paths, even though

the total work is the same. This results in a path dependence in the energy acquired while moving. For path #1 we might have $\int dW_x + dW_z = \int F_x dx + F_z dz = 0$ whereas for path #2 we could very well have $W_x = \int F_x dx \neq 0$. This is analogous to describing the changes in internal energy of a system through only work terms; we are missing an entire component of the internal energy change, the change due to heat flow into a system.

2.3 Heat

Heat is energy transferred between two bodies not due to work or mass transfer.⁴ The variable we will use to denote heat is Q . A system surrounded by an adiabatic boundary does not transfer heat across its boundaries, and so we say the heat exchanged between the system and the surroundings is 0; $dQ = 0$. The **first postulate of thermodynamics** is that energy is conserved. This can be expressed by stating that the energy of a system can only change due to work done upon the system or heat transferred to the system. Since such changes must be accompanied by equal and opposite changes in the surroundings of the system, the energy of the universe is constant.⁵

$$dU_{\text{system}} = dW_{\text{system}} + dQ_{\text{system}} \quad (15)$$

where again, the work terms can be written as $dW = \sum_i y_i dx_i$. The value of U is path independent via the conservation of energy. As such, U is a function of solely the system's state. Appropriately, functions which are completely defined by the thermodynamic state of the system are called **state functions**; their differentials must thus be exact differentials. On the contrary, W and Q are path dependent; transfer of energy can be accomplished in a multitude of ways. This is why we write both changes in heat and work with the inexact differential symbol, d , but the sum of the two as dU . We illustrated this with an example:

Example: Consider a simple system⁶ with all variables fixed except for the volume, like a piston. It then evolves “slowly” through a series of equilibrium states.⁷

$$W = - \int P dV \quad (16)$$

Assuming we are dealing with an ideal gas, we have the following equation of state: $P = \frac{nRT}{V}$. Inserting this into the above (and assuming an isothermal compression), we have an

⁴Historically, people used to think heat was transferred between bodies via the flow of an invisible substance, *phlogiston*. Hot bodies contained more of this self-repelling fluid than cold bodies. However, Antoine Lavoisier showed that metals gained mass when they oxidized, even though they were supposed to lose phlogiston, so phlogiston would need to have negative mass. This lead to phlogiston theory being replaced by caloric theory, in which calor, another invisible liquid, flowed from hot to cold bodies. All caloric theories assumed that calor was conserved. Sir Benjamin Thompson (a.k.a. Lord Rumford) disproved this theory by showing that repeatedly boring a cannon could repeatedly produce heat, showing that heat was not a conserved quantity, but rather, could be generated. This lead to Rudolf Clausius proposing that it is not heat which is conserved, but rather energy. This was the birth of modern thermodynamics.

⁵As Clausius stated in 1865, *Die energie der welt ist konstant*

⁶In a simple system, work can only be done on the system via $P dV$ terms.

⁷We call such infinitely slow processes, wherein the system can be approximated as being in equilibrium the whole time quasistatic processes.

expression for work in terms of the initial and final volumes.

$$\begin{aligned} W &= -nRT \int \frac{dV}{V} \\ &= nRT \ln \left(\frac{V_f}{V_i} \right) \end{aligned} \tag{17}$$

It is often useful to think of these changes as paths in a pressure versus volume plot. Let's consider a path, ξ , where both the pressure and volume can change. We will compress the gas isothermally from a volume V_1 to a final volume $V_f = V_1/2$. Also, we are at room temperature, $T = 298K$.

$$\begin{aligned} W_\xi &= -nRT \int \frac{dV}{V} \\ &= -nRT \ln \left(\frac{V_f}{V_i} \right) \\ &= nRT \ln(2) \\ &= 1717 \frac{\text{J}}{\text{mol}} \end{aligned} \tag{18}$$

Let's now consider a separate path, η , that is first isobarically compressed ($dP = 0$), and then isochorically warmed ($dV = 0$), such that both the initial and final states are the same as those in ξ . For the constant volume pressure change, there will be no work done since $dV = 0$ and $W = -P dV$. Therefore all the work will come from the initial constant pressure process, or isobaric compression.

$$\begin{aligned} W_\eta &= -P_i \int dV \\ &= \frac{P_i V_i}{2} \\ &= \frac{nRT}{2} \\ &= 1239 \frac{\text{J}}{\text{mol}} \end{aligned}$$

Clearly, the amount of work done when changing between two states can be different, although the change in internal energy must be the same. Thus, there must have been different amounts of heat transferred along each path as well; both work and heat are path-dependent.

3 Heat Capacities, Enthalpy

Last time, we stated the first law of thermodynamics, namely that energy can only be transferred in and out of a system as work and heat: $dU = dQ + \sum y_i dx_i$. We now want to quantify the first term, or quantify heat exchange. We do this by defining the *heat capacity* for a system as:

$$C_{\text{path}}(T) = \frac{(dQ)_{\text{path}}}{dT}$$

$$c_{\text{path}}(T) = \frac{C_{\text{path}}}{N}$$

where C_{path} is the system heat capacity along a given path, and c_{path} is the specific heat capacity; the system heat capacity divided by the number of moles, N .⁸ If we consider a simple system with state variables (P, V) or (V, T) , we can define

$$c_p = \frac{1}{N} \frac{(dQ)_p}{dT}$$

$$c_v = \frac{1}{N} \frac{(dQ)_v}{dT}$$

as the heat capacities at constant temperature and volume, respectively. The two quantities are related; it is natural to wonder what this relationship is. The table below shows the molar heat capacity for a set of substances.

Substance	c_p (J/mol/K)	c_v (J/mol/K)
Air (room)	29.1	20.8
Argon	20.8	12.4717
Carbon dioxide	36.9	28.5
Liquid Water	75.3	74.5
Octane (Gasoline)	228	

You might notice a few things. First, the heat capacity increases with increasing molecular weight. Next, $c_p > c_v$ for all cases. Both of these phenomena are general. Last, you might see that $c_p \approx c_v$ for H_2O . This is also general for condensed phases. We will prove the generality of these statements. You can quickly estimate heat capacities for some substances using [equipartition theory](#), wherein each degree of freedom contributes $R/2$ to the molar heat capacity:

- (a) Gases: If we assume that an ideal, monatomic gas has a degree of freedom for every direction it can translate in, each gas molecules possesses three degrees of freedom, so:

$$c_v^{\text{monatomic gas}} = \frac{3}{2}R = 12.471 \text{ J/mol/K} \quad (19)$$

⁸This convention is used throughout: system quantities are uppercase, molar quantities are lowercase

Note how close this is to the value for argon, which exists as a monatomic gas.

A diatomic gas, can be modelled as two atoms attached by a spring, free to rotate about their center of mass. At low temperatures, this gives 2 rotational degrees of freedom in addition to the original translational degrees of freedom, so at low temperatures, the heat capacity of a diatomic gas is: $c_v^{\text{diatomic, low } T} = \frac{5}{2}R$. at higher temperatures, two more vibrational degrees of freedom are excited, giving: $c_v^{\text{diatomic, high } T} = \frac{7}{2}R$. This is borne out in the experimental data, as shown in Figure 1:

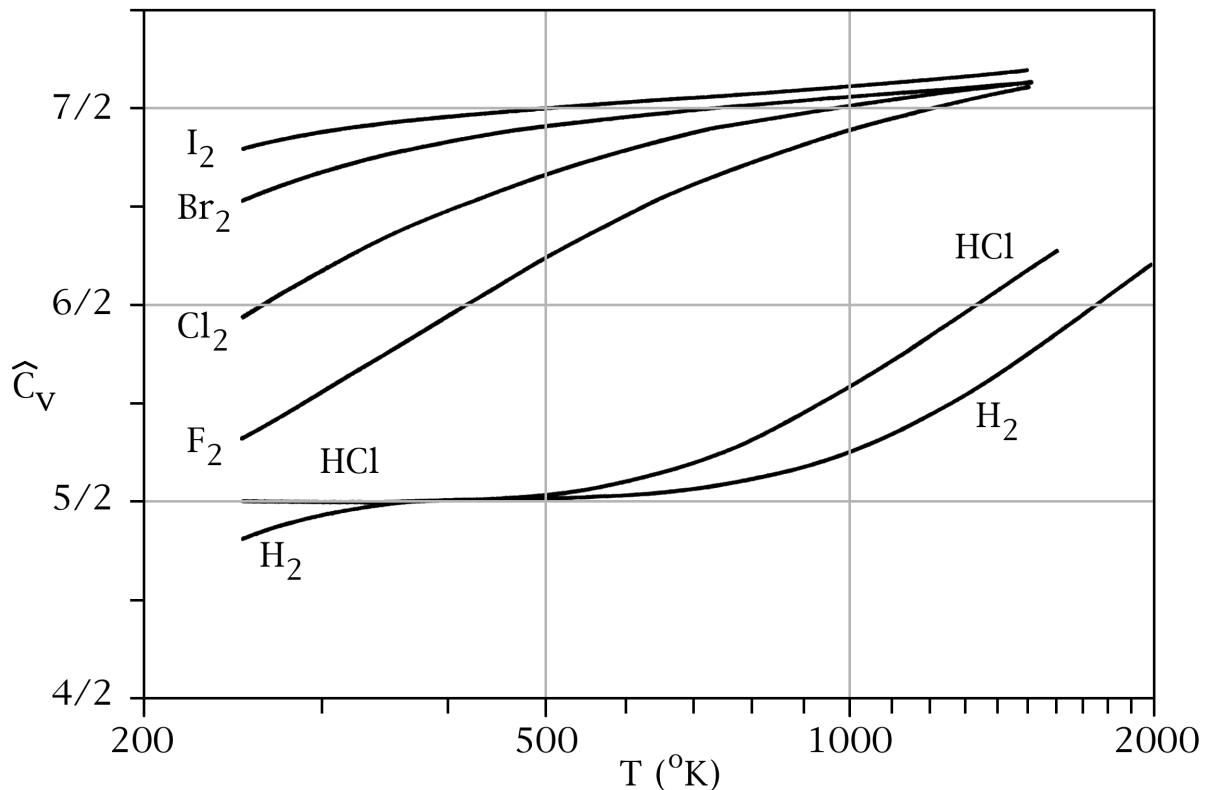


Figure 1: The specific heats of diatomic gases (normalized by R) as a function of temperature. The temperature at which the vibrational modes are excited is a function of the stiffness of the bond, with hydrogen exhibiting especially stiff bonds, and thus a late transition temperature.

(b) Solids: At room temperatures Dulong and Petit (1819) observed that all elemental solids seem to have a similar heat capacity:

$$C_v \approx 3R = 25\text{J/mol/K}$$

$$C_p \approx C_v$$

We will talk in detail about solid-state heat capacities during statistical mechanics, but for now it is enough to know that each atom has 6 degrees of freedom for its vibrations: 3

translational and 3 positional. So, by equipartition, c_v should be $6\frac{R}{2} = 3R$. For a non-metallic salt such as MgO, there are twice as many atoms per formula unit, so $c_p \approx 6R = 50\text{J/mol/K}$. If we examine some measured c_p , we see that at high T carbon reaches the $3R$ plateau. It takes a while to reach this because of the nature of carbon's strong covalent bonds (we will explain this in detail in statistical mechanics as well). There are discontinuities in Fe's diagram at 1550 °C because at this point it melts. Same with Hg, which becomes a gas at low T. For H₂O at RT we have $C_p = 75 \text{ J/mol/K}$.

3.1 We need another energy function

While c_v is naturally defined as the derivative of the internal energy with respect to temperature at constant volume: $c_v = \frac{1}{N} \left(\frac{\partial U}{\partial T} \right)_V$, the constant pressure heat capacity, c_p , is often what we measure in the lab. It would be convenient to have an energy function for which c_p is the derivative of the free energy with respect to temperature. The **enthalpy**, H , is this function.

$$\begin{aligned} H &= U + PV \\ dH &= dU + V dP + P dV \end{aligned}$$

and substitute $dU = dQ - P dV$

$$\begin{aligned} dH &= dQ + V dP \\ (dH)_p &= dQ \end{aligned}$$

Note how the enthalpy is naturally expressed with pressure held constant rather than volume held constant. Because H is defined in terms of state functions, the enthalpy is also a state function. In a somewhat too simplistic terms, H is the state function that describes heat exchange at constant pressure. It is thus the natural energy for discussing **calorimetry**, which is a major experimental technique. H is often called the “heat” content.

If we write down what $(dH)_p$ is, we get

$$\begin{aligned} (dH)_p &= C_p (dT)_p \\ \left(\frac{\partial H}{\partial T} \right)_p &= C_p \end{aligned}$$

If we heat a substance through a phase transition, the enthalpy change of the system can be broken into three parts:

$$H(T) = H(T_0) + \int_{T_0}^{T_f} C_p dT + \Delta H_{\phi T} \quad (20)$$

where the first term is the enthalpy of the system in its initial state, the second term is the contribution of the heat capacity as a function of temperature ignoring the phase transition,

and $\Delta H_{\phi T}$ is the enthalpy due to the phase transition, often called the *latent heat of the transition*⁹. Unlike T or P , there technically is no absolute zero for H or U ; only relative energies between states are physically measurable. As such, we often reference these state functions to their *standard states*. Under this convention, $H = 0$ for a pure element at atmospheric pressure ($P_0 = 101,325$ Pa) and room temperature ($T_0 = 298$ K). Note that because elements have zero enthalpy under standard conditions, compounds formed from reactions of several elements will generally have non-zero enthalpy relative to the standard state; heat is generally exchanged when a chemical reaction takes place.

The enthalpy as a function of temperature is plotted below for Fe over two temperature scales. The slope of these lines, $\frac{(dH)_p}{dT}$, is the heat capacity. Below 900°C, Fe is in the α (BCC) phase, from 900° < T < 1400° it is in the γ (FCC) phase, and from 1400→1535°C Fe is the δ (BCC2) phase. Above 1535°C , Fe melts. Fe evaporates near 2900°C. Each of these can be observed as discontinuities in the $H(T)$ curve.

The solid→solid phase transitions' discontinuities are barely visible on the left curve.

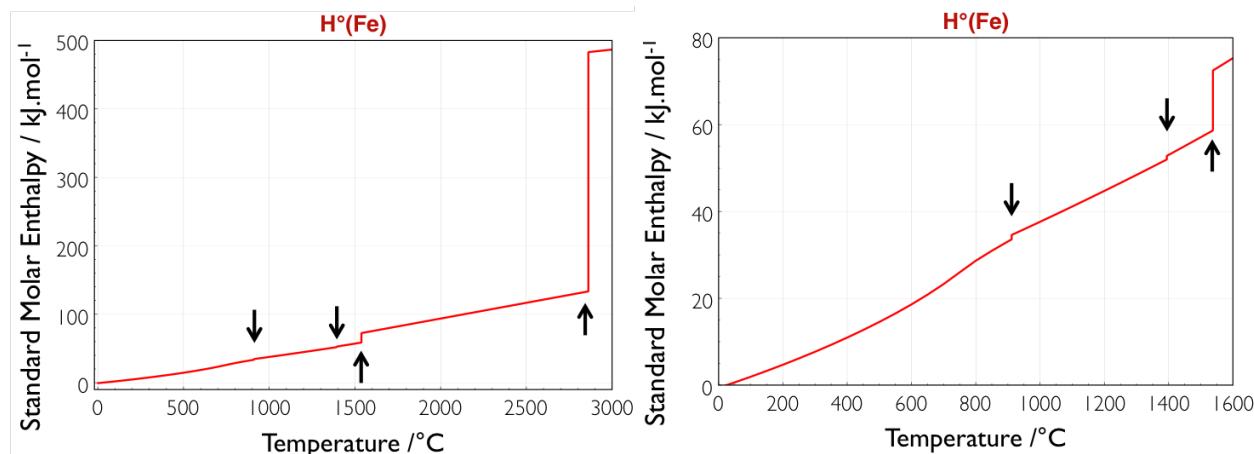


Figure 2: $H^\circ(T)$ for Fe over two temperature scales.

This is because the latent heats of the different phase transitions differ by several orders of magnitude: $\Delta H_{\text{Fe}}^{\alpha \rightarrow \gamma} \approx 1 \text{ kJ/mol}$ and $\Delta H_{\text{Fe}}^{\gamma \rightarrow \delta} \approx 1 \text{ kJ/mol}$. A “large” enthalpy for a solid→solid phase transition is observed for zirconia’s [martensitic phase transformation](#), where $\Delta H_{\text{ZrO}_2}^{\text{tetra} \rightarrow \text{non}} \approx 6 \text{ kJ/mol}$.

The enthalpy of fusion (equivalently, the enthalpy of melting) is generally much higher. Richard’s rule says that the enthalpy of fusion is proportional to the melting temperature of an element.

$$\Delta H_{\text{fusion}}[\text{J/mol}] \approx 9T_{\text{fusion}}[\text{K}] \quad (21)$$

In most metals ΔH_{fusion} is on the order of 10 kJ/mol. The elemental heat of vaporization follows a similar rule, Trouton’s rule, which states that the enthalpy of vaporization is

⁹For example, the solid→liquid phase transition has a *latent heat of melting*

proportional to the boiling temperature¹⁰..

$$\Delta H_{\text{vap}} \approx 90T_{\text{vap}} \quad (22)$$

In most metals, ΔH_{vap} is on the order of 100 kJ/mol. The binding energies of metals are also on the order of 100 kJ/mol; you can intuitively think of evaporation as putting in the energy to break the bonds between atoms. We will emphasize understanding the orders-of-magnitude of energy scales in materials science throughout, sticking to engineering units of kJ/mol¹¹.

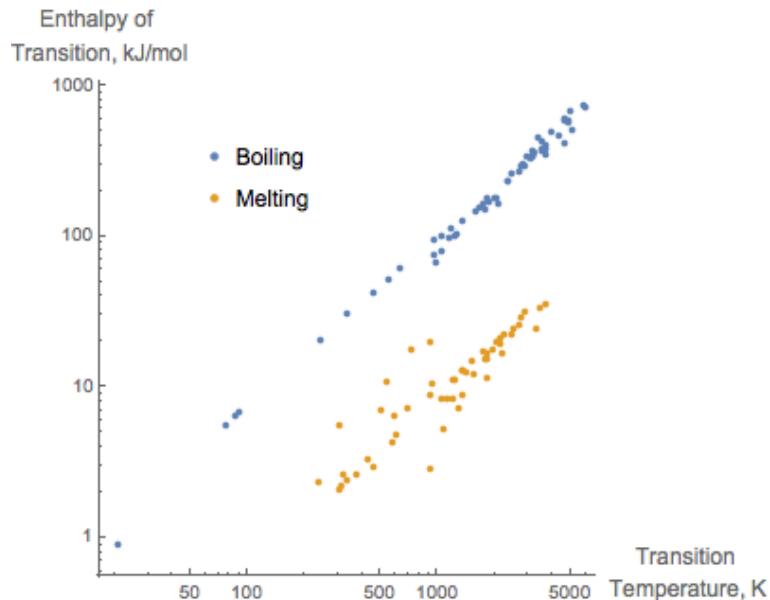


Figure 3: Elemental phase transition temperatures and enthalpies on a log-log scale. The slope of this correlation (on a linear scale) gives the entropy change of these phase transitions. The correlation is stronger for boiling as compared to melting because the liquid→gas transition's entropy change is dominated by the gain of translational degrees of freedom, whereas the gain in entropy upon melting can be appreciably changed by the local interactions in the solids and liquids of the elements. Positive deviations from Richard's rule occur for heavy semimetals: Sb, Bi, Sn, Te have larger entropies of melting than expected. Negative deviations occur for elements with unfilled f-orbitals: Pu, Ce, Nd have smaller entropies of melting than expected. Simple metals and transition metals are well-behaved.

Now, what is the relative contribution of the $P dV$ term to these phase transition enthalpies? We can estimate this by plugging in approximate numbers. We'll consider the case of two condensed phases, phase I → phase II. In a metal, $V_{\text{molar}} \approx 10 \text{ cm}^3 / \text{mol} = 10^{-5} \text{ m}^3 / \text{mol}$ and a good upper bound on the volume change is $\sim 10\%$ of the molar volume. At atmospheric

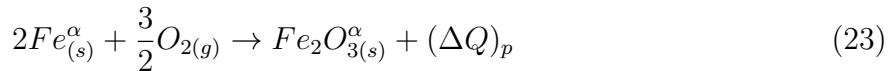
¹⁰As we will learn later, these rules imply that the entropies of melting and boiling are approximately equivalent for all of the elements: $\frac{\Delta H}{T} = \Delta S = \text{constant}$

¹¹Understanding in terms of atomic mechanisms is sometimes useful, wherein the natural units are eV/atom. 1 eV/atom = 96.354 kJ/mol ≈ 100 kJ/mol. An especially good article on energy scales in materials science is [Spaepen, Phil. Mag. 2005](#)

pressure, $P^\circ = 10^5 \text{ Pa}$, so $P\Delta V = 10^5 \cdot 10^{-6} = 0.1 \text{ J/mol}$. Note the use of J/mol instead of kJ/mol here. Remember, the enthalpies of solid-solid transitions are around 1 kJ/mol , so about 10^4 times bigger: *the energy scale associated with pressure-volume effects can only moderately perturb the energetics of condensed-matter phase transitions, except at very high pressures.*

Just as it is useful to understand the energy scales associated with P-V work, it is also useful for us to understand the energy scales associated with chemical reactions. In chemistry, this is characterized by the enthalpy of formation of molecules, in the solid state, the relevant quantity is the enthalpy of formation of compounds, e.g. Fe_2O_3 from Fe and O_2 ¹²:

At room temperature and pressure:



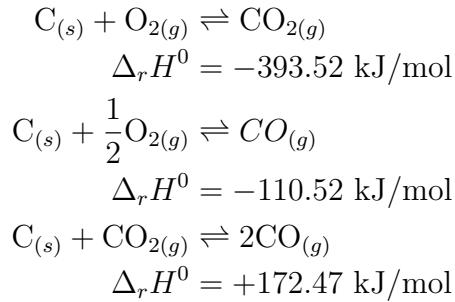
with $(\Delta Q)_p = -820.5 \text{ kJ/mol}$. The enthalpy of the reaction ΔH is sum of the enthalpies of the initial and final states:

$$\Delta_v H = \Delta H_{\text{Fe}_2\text{O}_3}^0 - \Delta H_{\text{Fe}}^0 - \frac{3}{2}\Delta H_{\text{O}_2}^0 \quad (24)$$

and, for reference, we have:

$$\begin{aligned} \Delta H_{\text{Fe}_2\text{O}_3}^0 &= -820.5 \text{ kJ/mol} \\ \Delta H_{\text{Fe}}^0 &= 0 \\ \Delta H_{\text{O}_2}^0 &= 0 \\ \Delta H_{\text{CO}}^0 &= -110.52 \text{ kJ/mol} \\ \Delta H_{\text{CO}_2}^0 &= -393.51 \cdot \text{kJ/mol} \end{aligned}$$

There are plenty of references to get these values, such as [Janaf tables](#). They provide H^0 , G^0 , $C_p(T)$, etc. One could similarly calculate the enthalpies of formation for various combinations of C and O:



¹² Most common minerals have names. Fe_2O_3 is known as *hematite*.

The ΔH only tells you how much heat is exchanged, it doesn't tell you which reaction is *spontaneous*. Exothermic reactions release heat, conceptually, this tells you that a given reaction is favorable in terms of its bonding. The first two reactions are exothermic; carbon and oxygen prefer to bond to one another. The last reaction is endothermic, meaning that the formation of $CO_{(g)}$ is not energetically favorable from $CO_{2(g)}$ and $C_{(s)}$. However, enthalpy is not the whole story in determining the spontaneity of reactions: energy conservation alone cannot tell you in which direction a reaction will occur.

4 Choice of Systems, The Second Law I

In previous lectures, we worked with the first law with both the heat and work terms. In continuation, we examine how different processes can be modeled within this framework, and the importance of the proper definitions of systems and boundary conditions in obtaining the correct results. We do so by considering different processes that an ideal gas can undergo.

An aside on the ideal gas: The ideal gas is a convenient system to examine thermodynamically because its internal energy can be defined in terms of just one state variable, the temperature: $U = U(T)$. Specifically, the internal energy of an ideal gas is¹³:

$$\begin{aligned} dU &= C_V dT = (C_P - nR) dT \\ \Delta U &= C_V \Delta T = (C_P - nR) \Delta T \end{aligned}$$

In addition, we also have a nice *equation of state* to relate changes in the thermodynamic state variables to one another, the ideal gas law, $PV = nRT$.

4.1 Throttling processes

Consider a bike tube initially at room temperature ($T = 298K$) with $P = 4.4\text{atm}$ (50 psi). Now, we release the pressure from the bike tire and let air out; the air exiting the tube undergoes what is called a *throttling process*. We are interested in how the thermodynamic state of the gas will change as it is released, in particular, what will be the temperature of the air right outside the nozzle?

First, we define our system as the gas which is released. It undergoes a sufficiently rapid expansion that the process can be approximated as adiabatic (not enough time for system to exchange heat with its environment). Then:

$$\begin{aligned} dU_{\text{gas}} &= dQ + dW = dW \\ &= -P dV \\ &= nC_V dT = -P dV \end{aligned}$$

Note that $V = nR\frac{T}{P}$, taking the total differential of V :

$$dV = \frac{nR}{P} dT - nRT \frac{dP}{P^2}$$

Plugging in this definition of dV above gives the final temperature in terms of the initial

¹³We'll prove this in statistical mechanics, but it is proven from the ideal gas law [here](#).

temperature and the ratio of the pressures:

$$\begin{aligned} nC_V dT &= -nR dT + RT \frac{dP}{P} \\ \left(\frac{T_2}{T_1}\right)^{C_P/R} &= \frac{P_2}{P_1} \\ T_2 &= T_1 \left(\frac{P_1}{P_2}\right)^{R/C_P} \end{aligned}$$

For the bike tube, this gives $T_2 = 206\text{K} = -67^\circ\text{C}$. Why didn't we actually reach this temperature? Well, the gas flowed through a nozzle instead of simply expanding in an unconstrained manner, and the pressure outside the gas was not equal to the pressure inside the gas during the expansion. Clearly, we need to examine this process from a different perspective. Often, in thermodynamics, this means you need to re-define your system. We do so below.

What is happening through the valve? We now define our system as the valve. In this case, the system is at constant volume, and the key process taking place is that gas is flowing through the system. These gas molecules have some well-defined internal energy, so there is an energy flux through the system due to the mass flux through the system:

$$dU_{\text{valve}} = U_{\text{in}}dn - U_{\text{out}}dn + dQ \quad (25)$$

The gas enters with P_{in} and a specific volume v_{in} then leaves with P_{out} and v_{out} . Even though the valve is a constant volume system, the mass flux implies that we will have a work term. The work done by the incoming gas is $P_{\text{in}}V_{\text{in}}$, the work done by the outgoing gas is $P_{\text{out}}V_{\text{out}}$. They have opposite signs due to the dn term. dQ is zero because the process is adiabatic, so:

$$dU_{\text{valve}} = dW = dn(P_{\text{in}}v_{\text{in}} - P_{\text{out}}v_{\text{out}}) \quad (26)$$

Equating these two definitions of dU_{valve} gives:

$$(U_{\text{in}} - U_{\text{out}}) = (P_{\text{in}}V_{\text{in}} - P_{\text{out}}V_{\text{out}})^{14}$$

Using the ideal gas equations:

$$nC_V\Delta T = nR(\Delta T)$$

This implies that either $C_V = R$, or $\boxed{\Delta T = 0}$. It turns out that an ideal gas undergoing this process should have $\Delta T = 0$.

Note how changing the way we interpret the process generally leads to a different answer. In this case, we needed to use an interpretation where the pressure on the gas during the expansion was not equal to its internal pressure. This means that the process is non-equilibrium and irreversible. This process is called a Joule-Thomson process. You can learn more about it on wikipedia, and/or refer to **Callen pg. 95**.

In general, we categorize processes in the following way:

¹⁴This is a statement that the enthalpy of the gas during the throttling process is constant: $U_{\text{in}} + P_{\text{in}}V_{\text{in}} = U_{\text{out}} + P_{\text{out}}V_{\text{out}}$, so $H_{\text{in}} = H_{\text{out}}$. Note that this doesn't need the ideal gas assumption, it's general.

- (I) Continuous and at equilibrium with environment (reversible). See Figure 2 in Callen.
- (II) Continuous but not necessarily at equilibrium with environment. This is considered quasi-static. Can be both reversible and irreversible. See Figure 3 in Callen.
- (III) Discontinuous and not in equilibrium. We can not do equilibrium thermodynamics for this (i.e. an explosion with $H_2 + O_2$ will proceed so fast we can not tell what is happening to get us to the final stage). See Figure 4 in Callen.

Second Law of Thermodynamics: In a closed system, there exists a state function, S , for which:

$$dS_{\text{system}} \geq \frac{dQ}{T}. \quad (27)$$

If a process is reversible (quasi-static), then we have $dS = \frac{dQ}{T}$. If it is irreversible, $dS > \frac{dQ}{T}$ (or $dS_{\text{irrev}} = dS_{\text{rev}} + \xi$ where $\xi > 0$). Note that this fixes the directions in which processes can occur, due to the inequality. Taking our system as the universe, a process will move forward if, for a given process $(1 \rightarrow 2)$ if $dS_{\text{universe}} > 0$ or backward $dS_{\text{universe}} < 0$. If $dS_{\text{universe}} = 0$ for a process, that process is stationary/reversible.

The first law said that U exists and

$$dU = dQ + \sum y_i dx_i \quad (28)$$

while the second law says S exists and for a closed system

$$dS \geq \frac{dQ}{T} \quad (29)$$

4.2 Quasistatic Piston

We now consider a piston slowly compressing a gas. See Callen Figure 5.

$$\sum_{i=1}^2 \frac{dQ_i}{T} = \text{constant} \quad (30)$$

Our path only depends on 1 (initial state) and 2 (final state). The above is also our state function.

Let's assume that $dS = \frac{dQ}{T}$.

Process 1: Let's take a reservoir that is adiabatically isolated with T_1 . Let's transfer dQ to the reservoir. The resulting temperature will then be T_2 .

Process 2: Now we have a propeller going into our reservoir with adiabatic walls and T_1 . Here, we have $dS_1 = dS_2 \neq \frac{dQ}{T}$.

If two compartments are connected (one at T_1 and the other at T_2), see Figure 6, we get

$$\begin{aligned} dQ_1 &= -dQ_2 \\ dS_{\text{system}} &= dS_1 + dS_2 \\ dS_{\text{system}} &= \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} \\ &= \frac{dQ_1}{T_1} - \frac{dQ_1}{T_2} \\ &= dQ_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \\ &= dQ_1\left(\frac{T_2 - T_1}{T_1 T_2}\right) \geq 0 \end{aligned}$$

If $T_2 > T_1$, $dQ_1 > 0$. Or if $T_2 < T_1$, then $dQ_1 < 0$. **The second law dictates that heat flows from hot to cold.**

5 Second Law II, The Third Law

As a reminder, the 1st law stated that U is a state function where

$$dU = dQ + \sum y_i dx_i \quad (31)$$

The 2nd law states that S is also a state function, and for an *isolated system* under any arbitrary process,

$$dS \geq \frac{dQ}{T} \quad (32)$$

If the process is reversible then, $T dS = dQ$. The change in the entropy for the entire system must increase ($dS_{\text{system}} \geq 0$). Key properties of entropy:

- (I) S of a system is *not* a conserved quantity; entropy can be removed from a system, even during an irreversible process (This is what a refrigerator does, it irreversibly cools a system, the food, while increasing the entropy of the surroundings).
- (II) S of the *universe* is only conserved during reversible processes. Otherwise, S_{universe} is an increasing quantity (Imagine the case where we stir an isolated bucket with a propeller).
- (III) S of an adiabatic system is constant or increases. This is because the dQ term is zero, so $dS \geq 0$.

5.1 Consequences of the 2nd law:

- (I) Irreversibility and ‘lost work’: For processes with the same initial and final states, the work done by a system upon its surroundings during a reversible process is greater than or equal to the work done by a system during an irreversible process:

$$dW_{\text{reversible}} < dW_{\text{irreversible}} \quad (33)$$

We prove Eq. 33 below. For a reversible path,

$$dU_{\text{reversible}} = dQ_{\text{reversible}} + dW_{\text{reversible}} \quad (34)$$

and the second law allows us to replace $dQ_{\text{reversible}}$ by $T dS$. For an irreversible path, U is a state function, so dU is the same:

$$dU_{\text{reversible}} = dU_{\text{irreversible}} = dQ_{\text{irreversible}} + dW_{\text{irreversible}} \quad (35)$$

Since $T dS > dQ_{\text{irreversible}}$ for an irreversible process, we have

$$T dS + dW_{\text{reversible}} = dQ_{\text{irreversible}} + dW_{\text{irreversible}} \quad (36)$$

$$T dS - dQ_{\text{irreversible}} = dW_{\text{irreversible}} - dW_{\text{reversible}} > 0 \quad (37)$$

so

$$dW_{\text{reversible}} < dW_{\text{irreversible}} \quad (38)$$

Note that our sign convention in these notes is $dU = dQ + dW$, so negative work is work done by the systems upon the surroundings. The important physical implication is that if you want to extract work from a system, you get the most work out if the work is performed reversibly. Work that is not obtained from a process due to irreversibilities is sometimes called *lost work*. Similarly, and perhaps more intuitively, if you want to do work upon a system, you will expend the least energy if the work is done reversibly:

The dissipation inherent in irreversible processes reduces efficiency, regardless of whether work is done by a system, or work is performed upon system. ¹⁵

- (II) Limits to heat-work conversion: Since a reversible process leads to the highest efficiencies, it is then logical to use a reversible process to set a limit on the amount of work that we can get from a heat source, i.e. by reversibly transferring heat from hot to cold. One can consider any process to do so, here we consider a non-specific process. The steps are worked out, but not explained. An animated explanation can be found on [Khan Academy](#)¹⁶, and a good written explanation is on [wikipedia](#).

$$\begin{aligned}\Delta S &= \oint \frac{dQ}{T} = 0 \\ \Delta S &= \frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0 \\ Q_H &= \frac{-T_L}{T_H} Q_L\end{aligned}$$

$$\begin{aligned}\Delta U &= 0 = Q + W \\ Q_H + Q_L &= -W \\ Q_H - Q_H \frac{T_L}{T_H} &= -W \\ Q_H \left(1 - \frac{T_L}{T_H}\right) &= -W\end{aligned}$$

This gives us the Carnot efficiency $\eta = \frac{-W}{Q_H}$ and

$$\boxed{\eta_{\text{heat} \rightarrow \text{work}} = 1 - \frac{T_L}{T_H}} \quad (39)$$

To give a sense of these efficiencies, with $T_H = 100^\circ\text{C} = 373\text{ K}$ and $T_L = 25^\circ\text{C} = 298\text{ K}$, $\eta \approx 20\%$. Significant gains in efficiency can be gained by going to higher temperatures:

¹⁵This has significant implications for the operation of batteries, fuel cells, and the materials production, wherein we are generally aiming to make things as reversible as possible.

¹⁶Sal Khan is an MIT alum!

if $T_H = 550^\circ\text{C}$, $\eta \approx 63\%$. Carnot is a big deal, as most of our energy still comes from making heat and converting it to electricity. Increasing the operating temperatures of the turbines used to create electricity from heat is thus a huge opportunity for making more energy with the same amount of fuel, and an active area of materials research.

We can also use work to move heat. This process is also limited by the second law, but is characterized by a different efficiency. Moving heat from hot to cold is spontaneous, so we are usually concerned with how much heat we can move from cold to hot. When making something that is already warm warmer, we have a heat pump and when making something cold colder, we have a refrigerator (or an air conditioner). The logical way to characterize such an efficiency is the amount of heat moved per unit energy input into the machine (this is often referred to as the “coefficient of performance”, or COP of a heat pump). One can derive that:

$$\text{COP}_{\text{heat pump}} = \frac{-Q_H}{W} = \frac{T_H}{T_H - T_L} \quad (40)$$

$$\text{COP}_{\text{refrigerator}} = \frac{Q_L}{W} = \frac{T_L}{T_H - T_L} \quad (41)$$

With $T_H = 25^\circ\text{C}$ and $T_L = 0^\circ\text{C}$, $\text{COP}_{\text{refridgerator}} = 11$.¹⁷

Note that in the above derivation, no reference was made to a specific mechanism: *the Carnot limit applies any time heat is being converted to work*. One example of an exotic device that does this is a thermoelectric. One can apply some basic thermoelectric theory to show that thermoelectrics will never be as efficient as steam engines unless the thermoelectric figure of merit, ZT , increases by around an order of magnitude.¹⁸. This is not to say that thermoelectrics are a bad topic to research, but that one should not believe that they will replace a conventional heat engine for turning heat into energy, unless the given application prohibits the use of a heat engine.

Now that we have an expression for a differential change in entropy, we can compute entropy changes from arbitrary processes, $\Delta S_{\text{process}}$. We that, for an arbitrary reversible path, c , the entropy change is:

$$dS = \frac{(dQ)_c}{T} \quad (42)$$

¹⁷This counterintuitively means that burning a fire is actually an extremely inefficient way to heat a home. You could get an order of magnitude more bang-for-your-Joule if you could convert that chemical energy to work, and use a heat pump!

¹⁸See [Nature Materials Vol 8 Feb 2009 “An inconvenient truth about thermoelectrics”](#)

Thus:

$$\begin{aligned} T(dS)_c &= (dQ)_c \\ \left(\frac{\partial S}{\partial T}\right)_c &= \frac{C_c}{T} \\ \left(\frac{\partial S}{\partial T}\right)_p &= \frac{C_p}{T} \\ \left(\frac{\partial S}{\partial T}\right)_v &= \frac{C_v}{T} \end{aligned}$$

Ultimately, because temperature has an absolute zero, entropy should also have some reference value when $T = 0$ K. How do we come up with a reference entropy S ? Nernst got the Nobel prize for it in 1920.

5.2 The 3rd law

As the temperature approaches zero, the magnitude of the entropy change in any reversible process is zero.

We can then fix the entropy of the elements at 0 K, in their equilibrium state, as being equal to zero.¹⁹

$$S_{0K}^{\text{element}} = 0 \quad (43)$$

Because entropy is a state function, the entropy along different paths must converge to the same value as a system is cooled to absolute zero; the curves must look like the right of Figure 4. Because compounds can be reversibly formed from their constituent elements, the entropy of any compounds must also be zero at 0 K, as $\Delta S_{\text{formation}} = 0$: $S_{0K}^{AB} = 0$. By extension, *at equilibrium, the entropy of all materials at absolute zero is zero.*

Can we reach 0 K?

Consider trying to cool a material by extracting heat from the material and dumping it into a hotter reservoir. We would first need to extract the heat during a process when the material is in contact with the environment (say, through an isothermal compression), and then perform an adiabatic process on the material such that no heat flows in, and we are in a position to repeat the previous heat removal process (say, via an adiabatic expansion). Of course, this would only work if you could make a series of heat reservoirs at lower and lower temperatures. See Figure 5. We can reduce the temperature by cycling between isothermal compression and isentropic (adiabatic) expansion, but we can never practically use this method to get to 0 K, as it would take an infinite number of cycles to do so. We can illustrate this by looking at the different processes individually:

¹⁹We will show the physical meaning behind the third law during statistical mechanics. For now, we take it as a postulate.

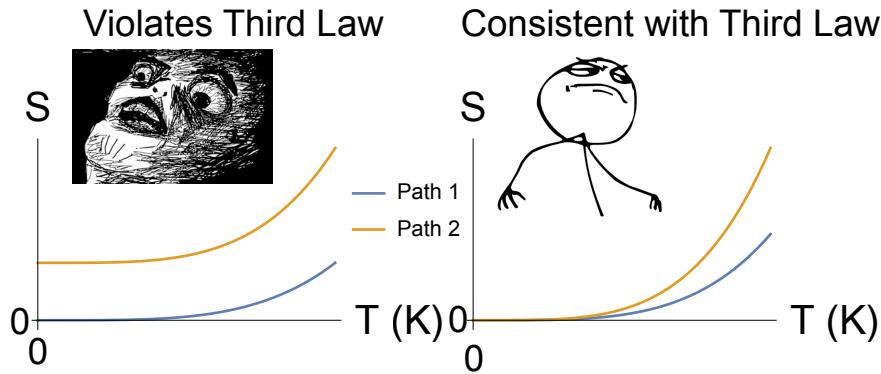


Figure 4: An illustration of entropy as a function of temperature inconsistent and consistent with the third law.

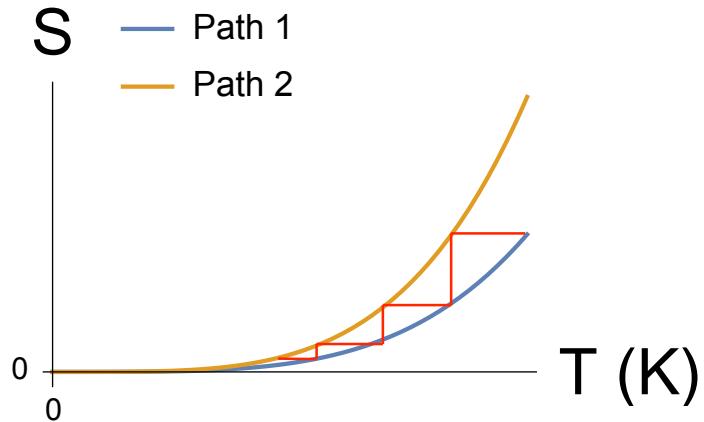


Figure 5: A T-S diagram illustrating the diminishing changes in temperature and entropy in a low-temperature, step-wise isothermal-isentropic cooling process. These changes become so small that an infinite steps are needed to reach 0 K.

- (I) Adiabatic expansion of an ideal gas. How much does the entropy change? You could try integrating the heat capacity along the path:

$$T_2/T_1 = \frac{P_1}{P_2}^{R/C_v} \quad (44)$$

However, such an integration would be a very inefficient way to calculate the entropy change. Instead, you could realize that the process is adiabatic, so ($dQ = 0$), meaning $dS = 0$.

- (II) Isothermal reversible expansion of an ideal gas. $dS = \frac{dQ}{T} = -\frac{dW}{T} = \frac{P dV}{T} = nR \frac{dV}{V}$ (Know this since $U = U(T)$, and T constant means $\Delta U = 0 = Q + W$): chr

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) \quad (45)$$

As system's volume increases, entropy will too.

- (III) Arbitrary change of an ideal gas. Since S is a state function, we only need to find the reversible path. We can break it up:

$$dS = dS_{\text{isobaric}} + dS_{\text{isothermal}} = C_p \frac{dT}{T} - R \frac{dP}{P} \quad (46)$$

6 The Fundamental Equation, Properties of U , Equilibrium Conditions

Now that the entropy has been defined, we are ready to start thinking about U in terms of equilibrium processes, where we can replace dQ by TdS . In this case, an arbitrary change in the state of our system can be represented as:

$$dU = T dS + \sum_i Y_i dX_i \quad (47)$$

The above equation is sometimes called the *combined first and second law*. It is also called the *fundamental equation of physical chemistry*, because it is used to derive the rest of thermodynamics. Performing equilibrium thermodynamics in terms of dU and its transformations is called the Legendre formulation of thermodynamics. One can equivalently formulate thermodynamics in terms of changes in the entropy of a system during arbitrary, reversible processes:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \sum_i \frac{\mu_i}{T} dN_i \quad (48)$$

Energetic calculations are usually easier to do in the Legendre formulation, which is posed in terms of energy. The Massieu formulation is easier to use to think about the reversibility of processes, as it is posed in terms of entropy.

The combined first and second law leads to some powerful representations and insights into the properties of U .

6.1 Mathematical Properties of U

1.1 U is first order homogeneous of the extensive variables, as is S

The entropy is extensive (i.e. one can add the entropy of subsystems to obtain the entropy of a composite system). It also means that multiplying the size of the system by some parameter, λ , gives λ times the original entropy: $S(\lambda U, \lambda X_i, \dots) = \lambda S(U, X_i, \dots)$

This states that the entropy is a first order homogeneous function. A similar argument can be made for the internal energy, which is also extensive. While one can make a somewhat hand-waving argument about integrating the internal energy to get a definition of U instead of just dU , an elegant way to arrive at the same relationship is to make use of the fact that the internal energy is a first order homogeneous function. Hence, the purpose of discussing first order homogeneous functions is to avoid the physically murky reasoning that you need to introduce to integrate dU to get U .

1.2 U can be defined in terms of a sum of the conjugate pairs

We derive this definition below. The result is sometimes called the *Euler Relation*.

A general definition of an n^{th} order homogeneous equation is: $U(\lambda S, \lambda X, \dots) = \lambda^n U(S, X, \dots)$
We can take the derivative of both sides of this equation to get:

$$\frac{\partial}{\partial \lambda} U(\lambda S, \lambda X, \dots) = n \lambda^{n-1} U(S, X, \dots) \quad (49)$$

For $n = 1$, the right hand side is just $U(S, X, \dots)$. We can expand the LHS in terms of its derivatives with respect to the natural variables of U (the extensive variables):

$$\frac{\partial(\lambda S)}{\partial \lambda} \frac{\partial U(\lambda S, \lambda X, \dots)}{\partial(\lambda S)} + \frac{\partial(\lambda X)}{\partial \lambda} \frac{\partial U(\lambda S, \lambda X, \dots)}{\partial(\lambda X)} + \dots = U(S, X, \dots) \quad (50)$$

It's pretty easy to see that $\frac{\partial(\lambda S)}{\partial \lambda} = S$, and $\frac{\partial(\lambda X)}{\partial \lambda} = X$, giving:

$$S \frac{\partial U(\lambda S, \lambda X, \dots)}{\partial(\lambda S)} + X \frac{\partial U(\lambda S, \lambda X, \dots)}{\partial(\lambda X)} + \dots = U(S, X, \dots) \quad (51)$$

Now, this next part seems trivial, but it's actually a nice, subtle trick. We used the definition of a homogeneous first order function to get U on the right hand side, so anything on the left hand side is an alternative defintion of U. By setting $\lambda = 1$, we can set each of the remaining derivatives equal to the conjugate forces: $\frac{\partial U(S, X, \dots)}{\partial S} = T$, $\frac{\partial U(S, X, \dots)}{\partial X} = Y$, and so on for all of the extensive variables. Remembering that the right hand side is $U(S, X, \dots)$, this allows us to show that U is defined as:

$$U(S, X, \dots) = TS + \sum_i Y_i X_i \quad (52)$$

This is the **Euler Relation** is very useful, so it's important we have a rigorous basis for it (which we just showed above!). It will give us the Gibbs-Duhem equations, and also allows us to make changes of variables to other free energy functions which have different natural variables, such as the enthalpy, which has natural variables of S and P :

$$H = U + PV \quad (53)$$

Plugging in the combined first and second law and the total differential of PV gives:

$$dH = T dS + V dP \quad (54)$$

Note how the exact differential of dH is naturally written in terms of new variables. We'll go in-depth into this type of transformation, a Legendre transform, and its implications in the next section.

1.3 The Gibbs-Duhem equation: The intensive variables are not independent

The Euler relation (52) can give an independent definition of dU by taking its total differential:

$$dU(S, X, \dots) = T dS + S dT + \sum_i Y_i dX_i + \sum_i X_i dY_i \quad (55)$$

Setting this equal to the definition of dU from the combined first and second law gives:

$$\begin{aligned} T dS + \sum_i Y_i dX_i &= T dS + S dT + \sum_i Y_i dX_i + \sum_i X_i dY_i \\ 0 &= S dT + \sum_i X_i dY_i \end{aligned} \quad (56)$$

This is called a **Gibbs-Duhem equation**. It states that all the intensive variables cannot be varied independently. Eq 56 can be applied in a variety of situations, and we will come back to Eq 56 frequently in the last section of the class. An example of how a Gibbs-Duhem equation might be applied is as follows:

Let's think about how the chemical potential of a binary system changes. In particular, we'll consider the experimentally relevant case where the system is at constant pressure and temperature ($dP = dT = 0$), and we are varying the chemical potential of one component (say by flowing a vapor with different concentrations through the system). Then, the Gibbs-Duhem equation simplifies to:

$$N_1 d\mu_1 = -N_2 d\mu_2 \quad (57)$$

In words, this says that *varying the chemical potential of one component automatically causes the chemical potential of the other component to change in the opposite direction*, and that the rate of this change is related to the mole numbers of the two components in the system. This is a deep and unintuitive truth.

1.4 Equations of state contain partial information about U

Equations of state of U are expressions of the intensive variables in terms of the independent variables. As a thermodynamic state is completely defined by the extensive variables alone, the equations of state provide the relation between the independent, extensive state variables and the dependent, intensive state variables. For example, $P \equiv (\partial U / \partial V)_{S, N_i}$, which implies that P is a function of the entropy and mole numbers at which the derivative was taken: $P = P(S, N, V)$. This expression, $P(S, N, V)$, is one equation of state for a simple system. The others are $T(S, N, V)$, $\mu(S, N, V)$. As the equations of state are the derivatives of the free energy, if you know enough of them, you can combine their integrals to get $U(S, N, V)$. For a system where the mole numbers are constant:

$$U(S, V) = \int_{S_0}^S \left(\frac{\partial U}{\partial S} \right)_V dS + \int_{V_0}^V \left(\frac{\partial U}{\partial V} \right)_{S_0} dV = \int_{S_0}^S T dS + \int_{V_0}^V P dV \quad (58)$$

However, such an integration can only be performed if you have as many independent equations of state as you have free variables, and you know them in terms of the proper variables (S and V in the case of U). This is experimentally difficult.

6.2 Equilibrium and evolution of isolated systems

We now use the Massieu formulation and the second law to derive the conditions of equilibrium for a variety of cases. The conclusion is: *at equilibrium in an isolated, unconstrained system, the intensive variables are homogeneous (constant across the whole system)*. Below, we treat temperature, chemical potential, and pressure individually, but the results are general.²⁰

We consider a system where the possible work terms are exchange of energy, mole numbers, and volume. The chemical potential, μ , is the intensive conjugate of dN which is the change in number of particles.

$$\begin{aligned} U &= TS - PV + \sum_i \mu_i N_i \\ dU &= T dS - P dV + \sum_i \mu_i dN_i = 0 = S dT - V dP + N_i d\mu_i \end{aligned} \quad (59)$$

For an isolated system, the 1st law says U_{system} & V_{system} are constant ($dV_{\text{system}} = dU_{\text{system}} = 0$). The 2nd law says $dS_{\text{system}} \geq 0$. S is maximized over the set of thermodynamic states that are consistent with the constraints on the extensive variables, i.e. the boundaries. The equilibrium state is then the one with maximal S for our boundary conditions.

2.1 Thermal Equilibrium

Let's look at thermal equilibrium in a system with two containers I and II that allow energy to flow between them: $dU_I, dU_{II} \neq 0$.

$$\begin{aligned} dU &= 0 = dU_I + dU_{II} \\ dU_I &= -dU_{II} \\ dS &= dS_I + dS_{II} \\ dS &= \frac{dU_I}{T_I} + \frac{dU_{II}}{T_{II}} \quad (\text{by Massieu/second law}) \\ dS &= dU_I \left(\frac{1}{T_I} - \frac{1}{T_{II}} \right) \end{aligned} \quad (60)$$

Now, if $T_I < T_{II}$ and $dU_I > 0$, then $dS > 0$ and we are **not at equilibrium**. If $T_I > T_{II}$ and $dU_I < 0$, then $dS > 0$ and we are also **not at equilibrium**. Equilibrium then occurs when $\frac{1}{T_I} - \frac{1}{T_{II}} = 0$, or $T_I = T_{II}$.

²⁰This is similar to the discussion in Callen Chapter 4.4

2.2 Mechanical Equilibrium

Consider two compartments of an isolated container separated by an diathermal, moveable wall. The volume of the left side is V_1 and the right is V_2 .

$$\begin{aligned} dU_1 &= -dU_2 \\ dV_1 &= -dV_2 \\ dS &= dU_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + dV_1 \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) \end{aligned} \tag{61}$$

thus S is maximal for $T_1 = T_2$ and $P_1 = P_2$.

2.3 Chemical Equilibrium from Mass Flow

Similarly, we can consider the μdN term in Eq 59 (or $-\frac{\mu}{T} dN$ in the entropy (Massieu) representation). We then get an additional term to dS of

$$dS = \dots - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dN_1 \tag{62}$$

which results in equilibrium so long as $\frac{\mu_1}{T_1} = \frac{\mu_2}{T_2}$. Enforcing thermal equilibrium means that $\mu_1 = \mu_2$. We can see from the signs of dN_1 and dN_2 that matter flows from high μ to lower μ , as we would expect from a potential.²¹

In general, we can maximize the entropy by:

- defining the internal variables which may be exchanged within the system. For example: can subsystems exchange volume or mass? If so, dV and dN would be appropriate internal variables.
- writing dS as a function of these *internal* variables in the Masseu formulation.
- imposing $dS_{\text{system}} = 0$ for all the variations.

Thus, given appropriate internal variables, we can directly extract the equilibrium conditions. For energy exchange, $dU_{1 \rightarrow 2}$, we get $T_1 = T_2$. For energy and volume exchange, $dU_{1 \rightarrow 2}$ and $dV_{1 \rightarrow 2}$, we have $T_1 = T_2$ and $P_1 = P_2$. Another example would be charge exchange, $dq_{1 \rightarrow 2}$, which implies a homogenous electrostatic potential: $\phi_1 = \phi_2$.

²¹Diffusion is thus caused by a gradient of $\frac{\mu}{T}$ (i.e. a diffusional relaxation toward equilibrium).

7 Legendre Transforms

7.1 Legendre Transforms

The difficulty in working with the internal energy, U , is that it is a natural function of an awkward set of variables: V is the natural, ‘independent’ variable of U for P-V work, whereas systems are usually kept at constant pressure, and S is the natural ‘independent’ variable of U for reversible heat exchange²², but systems are usually kept at constant temperature. What we seek is an alternative formulation of the internal energy which has the appropriate intensive variables as its natural, ‘independent’ variables. *Taking the Legendre transform is a general procedure to ‘switch’ which variables are the natural variables in your thermodynamic potential to match the system and boundaries of interest.*

How To Take a Legendre Transform

If we want to transform U such that an intensive variable, Y_i , is the natural variable of the new, transformed potential, which we will call ϕ , then we define ϕ as the difference of U and the product $Y_i \cdot X_i$:

$$\begin{aligned}\phi &= U - Y_i X_i \\ d\phi &= dU - Y_i dX_i - X_i dY_i\end{aligned}\tag{63}$$

where $dU = [...] + Y_j dX_j$. Note that if U is composed of a sum of extensive variables times their intensives conjugates, $U = \sum_j Y_j X_j$, then $\phi = \sum_{j \neq i} Y_j X_j$. The total derivative of ϕ is then given by:

$$d\phi = \sum_{j \neq i} Y_j dX_j - X_i dY_i\tag{64}$$

This has the desired property that Y_i is a natural variable of ϕ , $\phi = f(X_{j \neq i}, Y_i)$. Let’s look at an example of an isobaric, isentropic ($dS = 0$) system, considering the **enthalpy**, H :

$$\begin{aligned}dU &= T dS - P dV \\ H &= U + PV \\ dH &= dU + P dV + V dP \\ dH &= T dS + V dP\end{aligned}\tag{65}$$

and we can retrieve the following relations from $dH(S, P) = (\frac{\partial H}{\partial S})_P dS + (\frac{\partial H}{\partial P})_S dP$:

$$\begin{aligned}T &= \left(\frac{\partial H}{\partial S}\right)_P \\ V &= \left(\frac{\partial H}{\partial P}\right)_S\end{aligned}\tag{66}$$

²²You can think of reversible heating as T-S work if you’d like.

Properties of Legendre Transforms

1. $\left(\frac{\partial\phi}{\partial Y_i}\right)_{X_{i \neq j}} = -X_i$; the derivative of ϕ with respect to the appropriate intensive variable is minus its conjugate extensive variable.
2. ϕ has analogous extremal properties to U : Just as the equilibrium state when all of the extensive variables are constant occurs when U is minimal, so *the equilibrium state for a given Legendre transform, ϕ , occurs when ϕ is minimal under the appropriate boundary conditions*. For example, the equilibrium state at constant temperature and pressure is the state with minimal Gibbs free energy, the equilibrium state at constant entropy and pressure is the state with minimal enthalpy, etc.
3. A corollary to (2) is that the choice of boundary conditions is arbitrary: each equilibrium state corresponds to a minimum in the appropriate free energy for the final set of state variables. To give a concrete example, if we take a system at constant temperature and pressure and allow it to equilibrate, the Gibbs free energy will be minimal. But, this equilibrium state will also have some well-defined volume and entropy at equilibrium. If, instead, we allowed a system to equilibrate at the volume and entropy which correspond to the equilibrium state from above (i.e. we minimize the internal energy for the analogous state), it will also have some temperature and pressure at equilibrium, and this T and P will correspond to the T and P that we originally minimized the Gibbs free energy for.
4. The pure double derivatives of ϕ are the negative inverse of the pure double derivatives of U . For example:

$$\begin{aligned} \frac{\partial^2 U}{\partial V^2}_{S,N,\dots} &= -\frac{\partial P}{\partial V}_{S,N,\dots} = (\beta_S V)^{-1} \\ \frac{\partial^2 H}{\partial P^2}_{S,N,\dots} &= -\frac{\partial V}{\partial P}_{S,N,\dots} = -\beta_S V \end{aligned} \tag{67}$$

Why do Legendre transforms work? (Optional)

The Legendre transform works because it is an effective switch of coordinate systems, and we don't lose any information in doing this switch of coordinates. This change of coordinates is possible because U is a convex function of the extensive variables, and because U is a 'smooth' function of these variables (there are no discontinuities in the first derivative of U). Therefore, there is a one-to-one mapping between the first derivative of U with respect to the extensive variables and the extensive variable itself, as shown in the Figure 6²³:

The one-to-one mapping of the slope of U with respect to its extensive variables and the extensive variables themselves means we can construct a new function from U that has the slope as its natural variable with no loss of information; all the original thermodynamic information contained in U is also contained in its Legendre transforms, although in a different form.

²³From "Making sense of the Legendre transform", RKP Zia et al. Am. J. Phys. 2007, which is a really good read if you desire a deeper understanding of Legendre transforms.

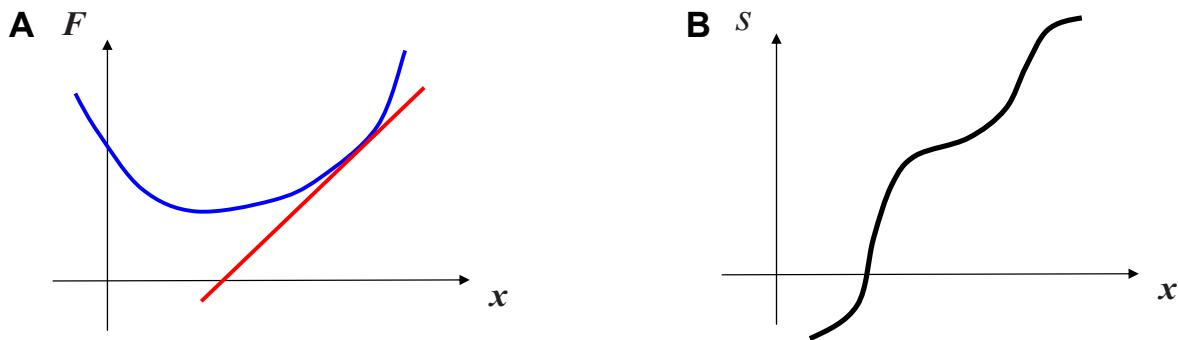


Figure 6: **A** The graph of a convex function $F(x)$. The tangent line at one point is illustrated. **B** The graph of $S(x)$, the slope of a convex function.

7.2 Named Free Energies

There are several other common Legendre transforms which have names. It would be wise to memorize these. The **Helmholtz Free Energy** is:

$$\begin{aligned} F &= U - TS \\ dF &= -S dT - P dV \end{aligned} \tag{68}$$

If we have a system where the temperature and volume are set experimentally, it makes sense to consider $F(T, V)$ since we will only need to minimize F ($dF \leq 0$, $dV = 0$, $dT = 0$). Similarly, the **Gibbs Free Energy** is:

$$\begin{aligned} G &= U - TS + PV \\ dG &= -S dT + V dP \end{aligned} \tag{69}$$

and we will have $dG \leq 0$ for a system where the temperature and pressure are set experimentally.

7.3 A First Look at Manipulating Thermodynamic Functions

Let's now look at a simple system using the Gibbs free energy $G(T, P)$. First, we know from the above that $S = -(\frac{\partial G}{\partial T})_P$ and $V = (\frac{\partial G}{\partial P})_T$. The change in volume is

$$\begin{aligned} dV &= \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP \\ &= \alpha_V V dT - V \beta_T dP \end{aligned} \tag{70}$$

Table 1: Some thermodynamic potentials for simple systems

T.D. potential	Differential	Natural variables	Maxwell's
U	$dU = T \cdot dS - P \cdot dV$	$U(S, V)$	$(\frac{\partial T}{\partial V})_S = -(\frac{\partial P}{\partial S})_V$
F=U-TS	$dF = -S \cdot dT - P \cdot dV$	$F(T, V)$	$(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V$
H=U+PV	$dH = T \cdot dS + V \cdot dP$	$H(S, P)$	$(\frac{\partial T}{\partial P})_S = (\frac{\partial V}{\partial S})_P$
G=U-TS+PV=H-TS	$dG = -S \cdot dT + V \cdot dP$	$G(T, P)$	$-(\frac{\partial S}{\partial P})_T = (\frac{\partial V}{\partial T})_P$

since $\alpha_V = \frac{1}{V} (\frac{\partial V}{\partial T})_P$ is the volumetric thermal expansion and $\beta_T = -\frac{1}{V} (\frac{\partial V}{\partial P})_T$ is the compressibility. Likewise, the change in entropy is

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \\ &= \frac{c_P}{T} dT + \left(\frac{\partial S}{\partial P} \right)_T dP \end{aligned} \tag{71}$$

It's not really obvious what $(\frac{\partial S}{\partial P})_T$ is. We can use a **Maxwell Relation** to gain some insight. For this, we note that the second derivative of a function does not depend upon the order in which the derivatives are exchanged.

$$\begin{aligned} \frac{\partial}{\partial P} \left(\left(\frac{\partial G}{\partial T} \right)_P \right)_T &= \frac{\partial}{\partial T} \left(\left(\frac{\partial G}{\partial P} \right)_T \right)_P \\ \frac{\partial}{\partial P} (-S)_T &= \frac{\partial}{\partial T} (V)_P \\ -\left(\frac{\partial S}{\partial P} \right)_T &= \left(\frac{\partial V}{\partial T} \right)_P = \alpha_V V \end{aligned} \tag{72}$$

and from here we can make our substitution into the above

$$dS = \frac{c_P}{T} dT - \alpha_V V dP \tag{73}$$

This might seem a bit strange. The change in entropy with respect to pressure at a constant temperature is equal to minus the thermal expansion coefficient. This is not intuitive, but it pops right out of the mathematical structure of thermodynamics. Maxwell relations can be useful in this way, as they allow us to express difficult-to-measure quantities in terms of easily measurable experimental quantities. Further, they allow us to reason about the sign of quantities which we might not otherwise have much intuition about. We can now say with certainty that except in cases where the thermal expansion coefficient is negative, the entropy of a substance decreases when you compress it.²⁴

²⁴You can think of this heuristically as being true because the number of microstates becomes smaller as you confine a group of particles to a smaller space.

8 Maxwell Relations, Manipulating Potentials

Previously we discussed **Maxwell relations**, which allow us to swap a derivative in terms of some thermodynamic variables x and y for a derivative in terms of the conjugates of x and y . They may be defined generally as

$$\left(\frac{\partial x}{\partial y} \right)_{\text{conj}[x]} = \pm \left(\frac{\partial \text{conj}[y]}{\partial \text{conj}[x]} \right)_y \quad (74)$$

The \pm in the above expression happens because the sign flips whenever you take a Legendre transform. The general procedure to create a Maxwell relation is then to:

1. Legendre transform your potential so that the natural variables of the free energy are the variables you want in the denominator of the expression.
2. Equate the double partial derivatives.

We now review some applications of Maxwell relations.

0.1 Maxwell relations for an Ideal Gas

In general, $dS = \frac{c_P}{T} dT - \alpha_V V dP$. However, we can apply this in the case of an ideal gas to get a concrete expression for the change in entropy under changes in temperature and pressure:

$$\begin{aligned} d(PV) &= nR dT = V dP + P dV \\ \left(\frac{\partial V}{\partial T} \right)_P &= \frac{nR}{P} \end{aligned} \quad (75)$$

Substituting gives:

$$dS = -nR \frac{dP}{P} + c_P \frac{dT}{T} \quad (76)$$

0.2 Magnetic Maxwell relations

One can perform Maxwell relations including other work terms too. We demonstrate this here. In particular, let's say we wanted expressions relating the behavior of entropy in a magnetic field to other quantities that are more easily measured, say $(\frac{\partial S}{\partial P})_{T,H}$ and $(\frac{\partial S}{\partial H})_{T,P}$. Including magnetic work terms, dU can be expressed as:

$$dU = T dS - P dV + \mu_0 \mathcal{H}_0 dM \quad (77)$$

Here we have $U(S, V, M)$, but we need a thermodynamic potential expressed as a natural function of T, P, H to perform the desired Maxwell relations, i.e. we want $\phi(T, P, H)$. First,

we perform a Legendre Transform:

$$\begin{aligned}\phi &= U - TS + PV - \mu_0 \mathcal{H}_0 \mathcal{M} \\ d\phi &= -S dT + V dP - \mu_0 \mathcal{M} d\mathcal{H}\end{aligned}\quad (78)$$

This permits us to obtain the following relationships:

$$\begin{aligned}\left(\frac{\partial S}{\partial P}\right)_{T,H} &= -\left(\frac{\partial V}{\partial T}\right)_{P,H} \\ \left(\frac{\partial(\mu_0 M)}{\partial T}\right)_{H,P} &= \left(\frac{\partial S}{\partial H}\right)_{T,P}\end{aligned}\quad (79)$$

8.1 How to perform thermodynamic derivations

We first give some general relationships from calculus that are useful in manipulating thermodynamic variables, and then we give you a general way to think about deriving quantities in thermodynamics.

1.1 Very useful relationships of $f(x, y)$

Inverse rule:

$$\left(\frac{\partial f}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial x}{\partial f}\right)_y} \quad (80)$$

This relation is useful for getting things to the numerator from the denominator. This relationship only holds for well-behaved functions, but luckily thermodynamic functions are well-behaved.

Chain rule:

$$\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial u}\right)_y \left(\frac{\partial u}{\partial x}\right)_y \quad (81)$$

This is good if you can't take a derivative of f with respect to X , but you can take the derivative of u with respect to X (and hopefully of f with respect to u).

Triplet rule:

$$\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x = -1 \quad (82)$$

This is good for changing paths: you get to hold different variables constant when taking the other two derivatives

Another, unnamed rule (Mike calls it the generalized chain rule):

$$\left(\frac{\partial f}{\partial x}\right)_g = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \cdot \left(\frac{\partial y}{\partial x}\right)_g \quad (83)$$

This is also good for changing paths, especially for heat capacity paths (this was the relation we used to derive the relationship between C_p and C_V).

1.2 Strategy to reduce variables

Thermodynamic derivations are usually all about simplifying messy derivatives. The object of these derivations is to simplify them by substituting in known materials parameters. Hence, these guidelines are all about how to manipulate the derivatives so that you can start to substitute in known materials parameters.

- (1) Bring the thermodynamic potentials to the numerator.

e.g. given Joule-Thompson expansion (isenthalpic), we can remove the constraint of a derivative at constant enthalpy (which we don't know how to take) by using the triplet rule:

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} \quad (84)$$

- (2) Always bring S to the numerator and turn it into a heat capacity.

e.g. from $dH = TdS + VdP$:

$$\begin{aligned} \left(\frac{\partial H}{\partial P}\right)_T &= T \left(\frac{\partial S}{\partial P}\right)_T + V \\ \left(\frac{\partial H}{\partial T}\right)_P &= T \left(\frac{\partial S}{\partial T}\right)_P \\ \left(\frac{\partial T}{\partial P}\right)_H &= \frac{-(T \left(\frac{\partial S}{\partial P}\right)_T + V)}{T \left(\frac{\partial S}{\partial T}\right)_P} \\ &= \frac{-(T \left(\frac{\partial S}{\partial P}\right)_T + V)}{c_P} \\ &= \frac{-(-T\alpha_V V + V)}{c_P} \\ &= \frac{V(T\alpha_V - 1)}{c_P} \end{aligned} \quad (85)$$

(where the above used the Maxwell relationship $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha_V V$, and for an ideal gas we would have $\alpha_V = T^{-1}$, resulting in $\left(\frac{\partial T}{\partial P}\right)_H = 0$)

- (3) If needed, bring the volume to the numerator and turn it into a derivative of (T,P).
- (4) Relate heat capacities to what you know.

$$\begin{aligned} c_P - c_V &= T \left[\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V \right] \\ &= T \left[\left(\frac{\partial S}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P \right] \end{aligned} \quad (86)$$

In the above I used the relation

$$\left(\frac{\partial f}{\partial x}\right)_g = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \cdot \left(\frac{\partial y}{\partial x}\right)_g \quad (87)$$

continuing, we have

$$\begin{aligned} c_P - c_V &= T \left[\left(\frac{\partial S}{\partial P} \right)_T \cdot \left(\frac{\partial P}{\partial V} \right)_T \cdot \left(\frac{\partial V}{\partial T} \right)_P \right] \\ &= T \left[\left(\frac{\partial S}{\partial P} \right)_T \cdot \left(\frac{-1}{V\beta_T} \right) \cdot \left(\frac{\partial V}{\partial T} \right)_P \right] \end{aligned} \quad (88)$$

and from the Maxwell relation, $\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P = -\alpha_V V$:

$$\begin{aligned} c_P - c_V &= T \left[\frac{-\alpha_V V}{-\beta_T V} \alpha_V V \right] \\ &= \boxed{TV \left(\frac{\alpha_V^2}{\beta_T} \right)} \end{aligned} \quad (89)$$

1.3 Example: A rod under tension

Consider a rod that doesn't change volume and evolves adiabatically. We apply a force F to each end of the rod and obtain a change in length dl as a result. What happens to the temperature?

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T} \right)_F dT + \left(\frac{\partial S}{\partial F} \right)_T dF \\ dU &= T dS + F dl \end{aligned} \quad (90)$$

From the triplet rule, $\left(\frac{\partial T}{\partial F} \right)_S \left(\frac{\partial F}{\partial S} \right)_T \left(\frac{\partial S}{\partial T} \right)_F = -1$, and thus

$$\begin{aligned} \left(\frac{\partial T}{\partial F} \right)_S &= - \frac{\left(\frac{\partial S}{\partial F} \right)_T}{\left(\frac{\partial S}{\partial T} \right)_F} \\ &= - \frac{\left(\frac{\partial S}{\partial F} \right)_T}{\frac{c_F}{T}} \end{aligned} \quad (91)$$

Now what is $\left(\frac{\partial S}{\partial F} \right)_T$? We can define a new potential

$$\begin{aligned} \phi &= U - TS - Fl \\ d\phi &= -S dT - l dF \end{aligned} \quad (92)$$

which yields (note this was the same as using a Maxwell relation)

$$\left(\frac{\partial S}{\partial F} \right)_T = \left(\frac{\partial l}{\partial T} \right)_F = \alpha_l \quad (93)$$

The thermal expansion coefficient $\alpha_l = \frac{1}{l} \left(\frac{\partial l}{\partial T} \right)_F$. Putting this all together,

$$\boxed{\left(\frac{\partial T}{\partial F} \right)_S = -Tl \left(\frac{\alpha_l}{c_F} \right)} \quad (94)$$

Now all we need is the materials parameters. $c_F \approx c_P \approx 25 \text{ J/molK}$ and $\alpha_l \approx 2 \cdot 10^{-5} \text{ 1/K}$, $\Delta(F/A) \approx 100 \text{ MPa}$:

$$\Delta T = - \left(\Delta \frac{F}{A} \right) (A \cdot l) T \frac{\alpha_l}{c_F} \quad (95)$$

This results in a value of $\Delta T = -0.1 \text{ K}$.

8.2 Natural Variables

A question we may ask after all of this is: "What are the natural variables for $U(S, V)$?" Can we write $U(T, P)$? If so, what are the consequences?

$$dU = \left(\frac{\partial U}{\partial T} \right)_P dT + \left(\frac{\partial U}{\partial P} \right)_T dP \quad (96)$$

now let's take partials of the $U(S, V)$ we already know:

$$\begin{aligned} \left(\frac{\partial U}{\partial P} \right)_T &= T \left(\frac{\partial S}{\partial P} \right)_T - P \left(\frac{\partial V}{\partial P} \right)_T \\ &= -T(\alpha_V V) - P(-\beta_T V) \\ &= V(P\beta_T - T\alpha_V) \end{aligned} \quad (97)$$

Similarly,

$$\begin{aligned} \left(\frac{\partial U}{\partial T} \right)_P &= T \left(\frac{\partial S}{\partial T} \right)_P - P \left(\frac{\partial V}{\partial T} \right)_P \\ &= nc_P - PV\alpha_V \end{aligned} \quad (98)$$

and thus we can write

$$dU = (nc_P - PV\alpha_V) dT + V(P\beta_T - T\alpha_V) dP \quad (99)$$

Clearly, it is possible to think about dU in terms of variations in the intensive variables, but it's much more natural to think of dU in terms of dV and dS .

8.3 A systematic way to think about derivatives

We're starting to build up a large number of derivatives and second derivatives of the various thermodynamic potentials, it would be nice to have systematic way of representing and thinking of these derivatives. It turns out you can represent these derivatives as matrices.

Let's look at some derivatives of $G(T, P) \rightarrow dG = -S dT + V dP$:

$$\begin{aligned} \left(\frac{\partial G}{\partial T} \right)_P &= -S \\ \left(\frac{\partial G}{\partial P} \right)_T &= V \\ \left(\frac{\partial^2 G}{\partial T^2} \right)_P &= -\frac{c_P}{T} \\ \left(\frac{\partial^2 G}{\partial P^2} \right)_T &= -\beta_T V \end{aligned} \tag{100}$$

We can display these derivatives as follows:

Table 2: The derivatives of G

G	$\frac{\partial}{\partial T}$	$\frac{\partial}{\partial P}$
$\frac{\partial}{\partial T}$	$-\frac{c_P}{T}$	$\alpha_V V$
$\frac{\partial}{\partial P}$	$\alpha_V V$	$-\beta_T V$

If we add a *magnetic field* our energy becomes $dU = T dS - P dV + \mathcal{H} d\mathcal{M}$. The various derivatives of $\phi = U - ST + PV - \mathcal{H}\mathcal{M}$ result in the following order of (second) derivatives: You can write a similar matrix for any thermodynamic potential you choose. All such

Table 3: The derivatives of $\phi = U - ST + PV - \mathcal{H}\mathcal{M}$

ϕ	$\frac{\partial}{\partial T}$	$\frac{\partial}{\partial P}$	$\frac{\partial}{\partial \mathcal{H}}$
$\frac{\partial}{\partial T}$	$-\frac{c_P}{T}$	$\alpha_V \cdot V$	$-\frac{\partial \mathcal{M}}{\partial T}$
$\frac{\partial}{\partial P}$	$\alpha_V \cdot V$	$-\beta_T \cdot V$	$V \cdot \gamma$
$\frac{\partial}{\partial \mathcal{H}}$	$-\frac{\partial \mathcal{M}}{\partial T}$	$V \cdot \gamma$	$-V \cdot \chi$

matrices are symmetric because of the Maxwell relations. The signs of the off-diagonal terms are a result of the Legendre transforms needed to get to the potential of interest. The signs of the diagonal terms are positive if the thermodynamic variable of interest is extensive, and negative if the variable of interest is intensive. This is because of the properties of the Legendre transform, and ultimately because U is convex up with respect to the extensive variables.

9 Practice Derivations, Phase Rule, Phase Stability

Last lecture we started to look at the difference the path makes in some thermodynamic quantities, such as the heat capacity. Here, we consider another path change: what is the relationship between the change in volume with respect to temperature at constant magnetization and the same quantity at constant magnetic field?

$$\left(\frac{\partial V}{\partial T}\right)_M \rightarrow ? \left(\frac{\partial V}{\partial T}\right)_H \quad (101)$$

We can apply the generalized chain rule, Eq. 83, in this situation:

$$\begin{aligned} \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_M &= \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_H + \frac{1}{V} \left(\frac{\partial V}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_H \\ &= \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_H + \frac{1}{V} \left(\frac{\partial V}{\partial M}\right)_T M'(T) \end{aligned} \quad (102)$$

Where we abbreviate $\left(\frac{\partial M}{\partial T}\right)_H$ as $M'(T)$. We know $\left(\frac{\partial V}{\partial M}\right)_T = \left(\frac{\partial V}{\partial H}\right)_T \left(\frac{\partial H}{\partial M}\right)_T$, letting $\gamma = \left(\frac{\partial V}{\partial H}\right)_T$ (called the *magnetostriction*) and $\chi = \left(\frac{\partial M}{\partial H}\right)_T$ gives: $\left(\frac{\partial V}{\partial M}\right)_T = \frac{\gamma}{\chi}$. Thus:

$$\alpha_M = \alpha_H + \frac{\gamma}{\chi} M'(T) \quad (103)$$

Mostly materials are either paramagnetic or ferromagnetic, so $\chi > 0$. For a ferromagnet, the magnetization is relatively constant until when T gets close to the Curie temperature, T_C , at which it falls rapidly to zero. Thus, we can assume $M'(T) < 0$.

What about thermal expansion?

$$\begin{aligned} \alpha_V &= \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \\ &= -\frac{1}{V} \left(\frac{\partial S}{\partial P}\right)_T \text{ (Maxwell)} \\ &= -\frac{1}{V} \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T \text{ (Chain Rule, Eq. 81)} \\ &= \beta_T \left(\frac{\partial S}{\partial V}\right)_T \end{aligned} \quad (104)$$

As we'll see in stat mech, S is a measure of the number of states the system can occupy. As the volume goes up, the number of states should go up, so the entropy should also go up, so Eq. 104 makes sense. However, there are exceptions, specifically when the thermal expansion coefficient is negative.

Can $\alpha_V < 0$? Yes! Indeed, this is observed in many systems. This happens when molecules gain degrees of freedom as the system size decreases. One examples is in polymers: there are more configurations when the ends of a polymer are closer together (Fig 7). Thus as temperature increases, polymers tend to shrink!

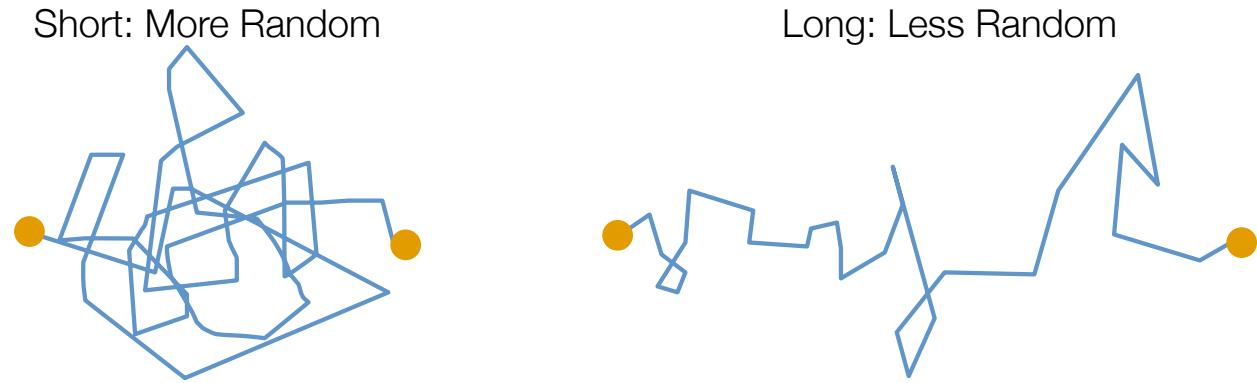


Figure 7: The reason polymers have a negative thermal expansion coefficient is because of entropy: there are more ways for the polymer to wiggle around when it isn't stretched out. We'll get quantitative about this in stat mech.

9.1 Check in: What you should be able to do by now

- (1) Identify work terms
- (2) Construct the relevant thermodynamic potential: see (1)
- (3) Define equilibrium (internal degrees of freedom consistent with boundary conditions)
- (4) Define the relevant properties: see (3)
- (5) Relate thermodynamic quantities and thus variations: see (1)

9.2 Equilibrium Conditions for Multicomponent Systems

Let's return to systems where the mole numbers may change. We can write dU for a multicomponent system as

$$dU = T dS - P dV + \sum_i \mu_i dn_i \quad (105)$$

where $\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j \neq j}$ is the chemical potential of a species. If we have a system with 2 phases, we will have $S^{(1)}, V^{(1)}, \{n_j^{(1)}\}$ describing the first phase and $S^{(2)}, V^{(2)}, \{n_j^{(2)}\}$ describing the second phase. In an isolated system, the two phases can only exchange extensive quantities with each other:

$$\begin{aligned} dS^{(1)} &= -dS^{(2)} \\ dV^{(1)} &= -dV^{(2)} \\ dn_j^{(1)} &= -dn_j^{(2)} \end{aligned} \quad (106)$$

where $j = [1, \dots, r]$. Further, the extensive variables of the system as a whole are the sum of the extensive variables of the different phases

$$\begin{aligned} U &= \sum_{\alpha=1}^2 U^\alpha \\ S &= \sum_{\alpha=1}^2 S^\alpha \\ V &= \sum_{\alpha=1}^2 V^\alpha \\ N &= \sum_{\alpha=1}^2 n^\alpha \end{aligned} \tag{107}$$

$$dU = \sum_{\alpha=1}^2 \left[T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_{j=1}^v \mu_j^\alpha dn_j^\alpha \right] \tag{108}$$

This is the first order displacement of U with respect to exchange of extensive quantities by the two phases. If the system is at equilibrium, $dU \geq 0$. At true equilibrium, $dU|_{S,V,n} = 0$. In order for $dU|_{S,V,n} = 0$ to hold for arbitrary exchanges of extensive variables, T, P, μ must be equal in the two phases. Put more generally, the takeaway here is that if the extensive variables are allowed to vary independently of one another, then the intensive variables in any subsystem must be the same as in any other subsystem; if the pressures aren't equal, then the higher pressure subsystem will expand into the lower pressure subsystem, higher temperature subsystems will exchange heat with lower temperature subsystems, etc. Conceptually this means:

- we always formulate the conditions for equilibrium in terms of the intensive variables.
- each independent phase adds an independent constraint on the way the intensive variables can vary via a Gibbs-Duhem equation for that phase. We derive these constraints in the next section.

If the exchange of extensive variables is coupled, it is the coupled sum of the intensive variables that needs to be constant throughout a system at equilibrium. For example, if mass flow is coupled to charge flow for a given atomic species (i.e. the species exists as an *ion*), then the electrical potential is coupled to the chemical potential of some species, and the *electrochemical potential* is homogeneous. If we denote μ^* as the electrochemical potential, it is easy to show that $\mu^* = \mu + zF\phi$ must be constant across a system, where z is the charge on the species, F is Faraday's constant, and ϕ is the electrical potential.

Exercise: Derive the the conditions for equilibrium in a system where charge and mass exchange are coupled between two systems, i.e. derive that $\mu^{*,1} = \mu^{*,2}$

9.3 Constraints from equilibrium of heterogeneous systems: the Gibbs phase rule

For a system of n well-behaved algebraic equations with m variables, we may define the number of variables which can be freely assigned without overspecifying the system as:

$$f = m - n \quad (109)$$

We call f the degrees of freedom of the system of equations. We define a phase as follows:

A phase is a part of a system which is homogeneous in its densities of the extensive variables at equilibrium. In practice this simply means that a phase has a well-defined density, composition, and entropy per unit volume. Different phases differ in these quantities at equilibrium.

When multiple phases are in equilibrium with one another, their intensive variables are constrained to vary with one another. One example would be a unary system where the liquid is in equilibrium with its vapor. We know that the temperature and pressure of the gas and liquid need to be the same at equilibrium, and that if we raise the temperature of the liquid, the vapor pressure of the gas must increase for the vapor to remain in equilibrium with the liquid. Note that these are examples of *constraints*: the liquid is *constrained* to be at the same temperature and pressure as the gas, and the vapor pressure is *constrained* to adjust its vapor pressure when the temperature is adjusted. Clearly, there is a non-trivial coupling between the intensive variables in the different phases. **The Gibbs phase rule expresses the number of degrees of freedom for the intensive variables when you have multiple phases at equilibrium.** The derivation of the phase rule thus amounts to counting the possible variations of the intensive variables and then subtracting the constraints upon these variables due to equilibrium among the different phases. As stated above, we formulate the equilibrium between the different phases in terms of their intensive variables.

Let there be p phases and c components in the system. We know that for each phase, α , a Gibbs-Duhem equation must hold:

$$S^\alpha dT^\alpha - V^\alpha dP^\alpha + \sum_{i=1}^c N^\alpha d\mu_i^\alpha = 0^{25} \quad (110)$$

Hence, for each phase, there are $c + 1$ independent intensive variables, e.g. T^α, P^α , and the $c - 1$ independent chemical potentials: μ_i^α . The total number of variables is thus the number of phases times $c + 1$:

$$m = p(c + 1) \quad (111)$$

The number of constraints from the intensive variables being equal to each other in each phase (such as $\mu_i^\alpha = \mu_i^\beta, T^\alpha = T^\beta$) is the number of intensive variables in each phase times

²⁵Note: dividing the Gibbs-Duhem equation by the volume of each phase, V^α , yields a condition formulated in terms of the *densities of the extensive variables*. By our definition of a phase, there exist only as many unique constraints on the variation of the intensive variables for a system as there exist unique phases in said system.

the number of phases minus 1:

$$n = (p - 1)(c + 2) \quad (112)$$

Then the number of independent variations of the intensive variables is thus (if one allows temperature and pressure to vary):

$$f = m - n = c - p + 2 \quad (T \text{ and } P \text{ can vary}) \quad (113)$$

If, instead, one considers a system at constant pressure, you get:

$$f = c - p + 1 \quad (P \text{ specified}) \quad (114)$$

If temperature and pressure are both specified, you get:

$$f = c - p \quad (T \text{ and } P \text{ specified}) \quad (115)$$

These are all versions of the Gibbs phase rule. It has important implications for the possible shapes of phase diagrams, which we will describe in section 2.

9.4 Stability Conditions on the free energy

Here, we use a Taylor expansion to provide constraints on the shape of U . U can be expressed as a Taylor expansion in the extensive variables as:

$$(\Delta U)_{S,V,n_j} = dU + d^2U + \dots \quad (116)$$

In order for the internal energy to be minimal at constant entropy, two conditions must hold: $dU = 0$, and $\Delta U \approx d^2U > 0$. That is, because U is minimal at equilibrium, the second-order terms in a Taylor expansion of U should all be positive. The physical process considered in this Taylor expansion is the case where one subsystem exchanges some amount of an extensive variable with another subsystem, such that the total amount of the extensive variable is conserved. To be at equilibrium, a system must be stable with respect to such perturbations, as illustrated in figure 8.

To illustrate this mathematically, we'll consider a composite system with a diathermal wall²⁶, and then fix S, V, n :

$$\begin{aligned} dS &= dS^{(1)} + dS^{(2)} = 0 \\ dV^{(1)} &= dV^{(2)} = 0 \\ dn^{(1)} &= dn^{(2)} \end{aligned} \quad (117)$$

then the variation in U becomes:

$$\begin{aligned} d^2U &= d^2U^{(1)} + d^2U^{(2)} \\ &= \frac{1}{2} \frac{\partial^2 U}{\partial S^{(1)2}} (dS^{(1)2}) + \frac{1}{2} \frac{\partial^2 U}{\partial S^{(2)2}} (dS^{(2)2}) \end{aligned} \quad (118)$$

²⁶Reminder: heat can be exchanged, but n, V , cannot be exchanged.

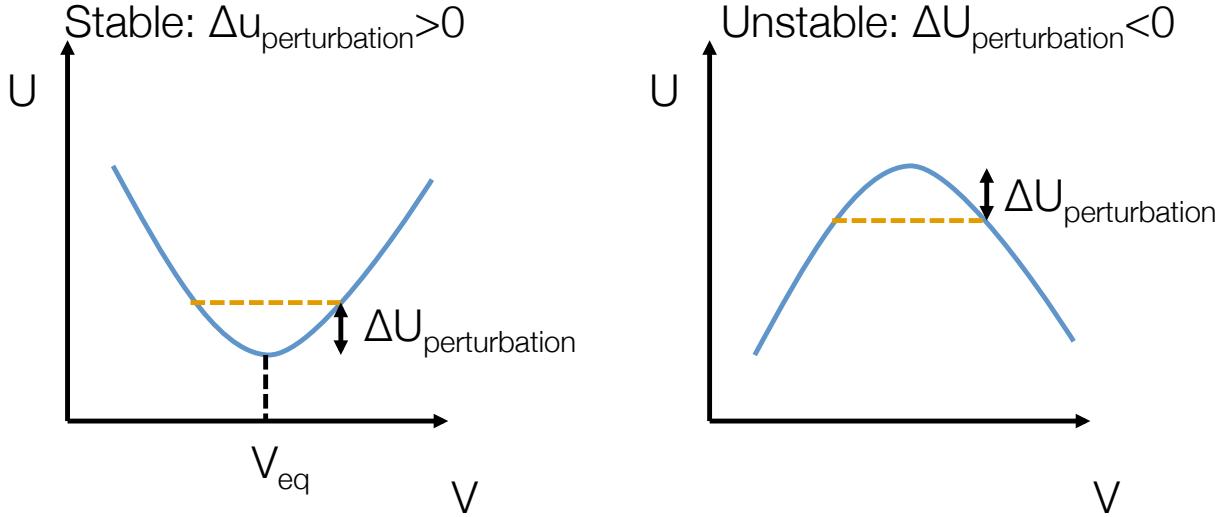


Figure 8: An illustration of a stable and unstable system with respect to volume perturbations. In the unstable case, subsystems can exchange volume and lower the energy of both systems. We call such instabilities to minute perturbations spinodal instabilities. These instabilities evolve by special kinetics, termed spinodal decomposition.

Substituting in our known derivatives of U :

$$\begin{aligned} \left(\frac{\partial^2 U}{\partial S^2} \right)_{V,n} &= \left(\frac{\partial T}{\partial S} \right)_{V,n} = \frac{T}{c_V} \\ \partial^2 U &= \frac{1}{2}(dS^{(1)2}) \left[\frac{T^{(1)}}{c_V^{(1)}} + \frac{T^{(2)}}{c_V^{(2)}} \right] \\ T \left[\frac{1}{c_V^{(1)}} + \frac{1}{c_V^{(2)}} \right] &\geq 0 \end{aligned} \quad (119)$$

Thus we get the result that $c_V \geq 0$. There is nothing special about the heat capacity, all other double derivatives of U with respect to a single extensive variable obey they same conditions; U is concave up with respect to all the extensive variables.

Remember, a Legendre transform causes a change in the sign of the concavity of the free energy with respect to the work terms involved in the transformation (ex: the sign of $\frac{\partial^2 U}{\partial S^2}$ is opposite the sign of $\frac{\partial^2 G}{\partial T^2}$). Therefore, we also just derived the sign of all the unmixed double derivatives of all Legendre transforms.

Exercise: Derive the values of $\frac{\partial^2 G}{\partial T^2}$ and $\frac{\partial^2 H}{\partial P^2}$, prove that they have the proper signs.

Exercise: What should be the sign of $\frac{\partial P}{\partial E}$ for a system at equilibrium?

9.5 Phase stability

G is minimal at equilibrium for a constant T , constant P system, so it would be useful to translate this knowledge of the shape of U to a more experimentally relevant potential. As we discussed above, there are similar guarantees on the second derivatives of G . If we imagine that each phase/state of matter has its own free energy curve $G(T)^\alpha, G(T)^\beta, \dots$, then *the equilibrium free energy is simply the lower envelope of the free energy curves of the possible phases*. This is shown in Figure 9.

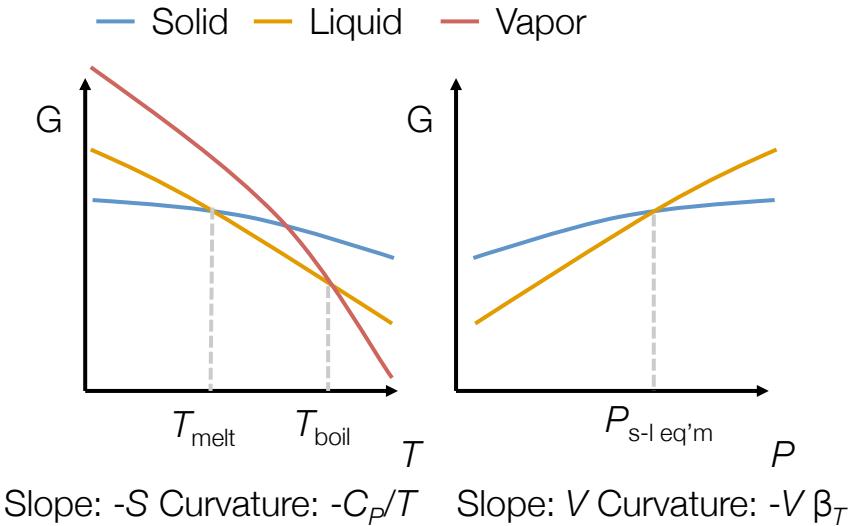


Figure 9: An illustration of thermodynamically consistent curves for the free energy of phases as a function of T and P which obey the stability criteria.

Getting more quantitative, we can follow a similar line of thought as before for U . If there are two possible phases α and β , then at equilibrium between 2 phases, their free energies must be equal as shown in Figure 9

$$G^\alpha = G^\beta \quad (120)$$

We can also read off the first derivatives of G : $\frac{\partial G}{\partial T}|_P = -S$ and $\frac{\partial G}{\partial P}|_T = V$. These hold for both phases. Therefore, as a system passes through a two phase equilibrium, it should exhibit a discontinuity in its volume and entropy ($\Delta V_{\phi T}, \Delta S_{\phi T}$).

$$\begin{aligned} \left(\frac{\partial G}{\partial T} \right)_P &= -S \\ \left(\frac{\partial^2 G}{\partial T^2} \right)_P &= - \left(\frac{\partial S}{\partial T} \right)_P = -\frac{c_P}{T} < 0 \\ \left(\frac{\partial G}{\partial P} \right)_T &= V \\ \left(\frac{\partial^2 G}{\partial P^2} \right)_T &= -\beta_T V < 0 \end{aligned} \quad (121)$$

For example, if we plot $G(T)$ for water, at 1atm of pressure and $G(T)$ for solid water and $G(T)$ for water vapor, we will see that at lower temperatures $G(T)$ for the solid is lowest, then at higher T , $G(T)_{\text{water}}$ becomes lower, and finally at even higher T $G(T)_{\text{vapor}}$ is the lowest. The derivatives of $G(T)$ get steeper from solid to liquid to vapor and are all negative, because $S_{\text{solid}} \ll S_{\text{liquid}} \ll S_{\text{gas}}$. This is shown schematically in Figure 9.

10 Phase Transitions, Phase Diagrams, Clausius-Clapeyron

From last time, we looked at the plot of G vs temperature T for gaseous, liquid, and solid phases, finding that at low- T $G_{\text{solid}} < G_{\text{liquid}} < G_{\text{vapor}}$, at T greater than the melting temperature $G_{\text{liquid}} < G_{\text{solid}} < G_{\text{vapor}}$, and then at T greater than boiling $G_{\text{vapor}} < G_{\text{liquid}} < G_{\text{solid}}$. If we know $\Delta H_{l \rightarrow v} = 44 \text{ kJ/mol}$, $\Delta S_{l \rightarrow v} = 120 \text{ J/mol/K}$ for a certain substance, then what is its boiling temperature, T_B ?

Well, we know that at the boiling point, the free energies of the liquid and vapor phases are equal, or:

$$\Delta G_{l \rightarrow v}(T_B) = 0 \quad (122)$$

As $\Delta G_{l \rightarrow v} = \Delta H_{l \rightarrow v} - T_B \Delta S_{l \rightarrow v}$, the boiling point can be calculated as: $T_B = \frac{\Delta H_{l \rightarrow v}}{\Delta S_{l \rightarrow v}} = 370 \text{ K}$.

One might further be interested in the difference in free energies as a function of temperature (for example, to evaluate the heat released by a supercooled vapor). How does one evaluate $\Delta G_{l \rightarrow v}(T)$? Well, we know that $\Delta S_{l \rightarrow v} = \frac{\Delta H_{l \rightarrow v}}{T_{\phi T}}$ at the phase transformation. If we approximate $\Delta H_{l \rightarrow v}$ and $\Delta S_{l \rightarrow v}$ as constant, we can write:

$$\begin{aligned} \Delta G_{l \rightarrow v}(T) &\approx \Delta H - T \Delta S \\ &= \Delta H_{\phi T} - T \frac{\Delta H_{\phi T}}{T_{\phi T}} = \Delta H_{\phi T} \left(1 - \frac{T}{T_{\phi T}}\right) \end{aligned} \quad (123)$$

Note that this approximation assumes that the heat capacities of the two phases are constant. This may lead to significant errors far from the phase transition if the difference in heat capacities is large.

10.1 Ehrenfest classification of phase transitions

Since free energies curves of individual phases are continuous, the equilibrium free energy curve, which consists of the lower envelope of all of these curves is also continuous. However, the derivatives of the equilibrium free energy envelope will have discontinuities where the different curves intersect, giving rise to a convenient way to describe phase transformations.

The **Ehrenfest Classification of phase transitions** states that phase transitions can be identified by discontinuities in the extensive variables or their derivatives as a function of the intensive variables. First order transitions display discontinuities in the extensive variables themselves (volume, mole number, and entropy), while second order transitions display continuous extensive variables, but exhibit discontinuities in their response functions (i.e. things like compressibilities and heat capacities are discontinuous). One can equivalently think of the Ehrenfest classification in terms of discontinuities in the derivatives of G :

1st order transition: The first derivative of G is discontinuous (S, V, \dots)

2nd order transition: The second derivative of G is discontinuous (but the first derivative is not)

Classifications beyond second order are not usually made because they are not useful in real life, so we don't bother talking about them.

10.2 Elemental Phase Diagrams

A phase diagram is a map of the conditions under which different phases are stable at equilibrium.

As described in sections 2 and 3, the intensive variables are a natural way to describe equilibrium between phases. As such, we will first talk about phase diagrams which have intensive variables as their axes, in particular, we begin with the simple case of T - P phase diagrams for one-component systems, shown in Figure 10 for CO_2 .

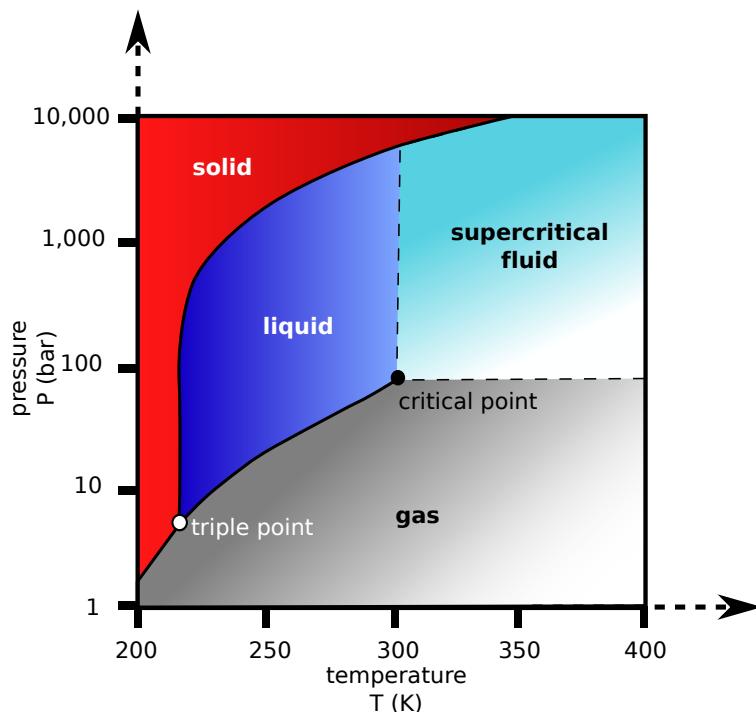


Figure 10: The P - T phase diagram of CO_2 . Image courtesy of [wikimedia commons](#)

The open areas in Figure 10 correspond to single-phase regions, the lines to two-phase regions, and the intersection of the lines to a three phase region, called a triple point. A special point, called a critical point, marks a special case where it is no longer possible to distinguish between the two phases for which there was previously a transition between ²⁷.

Exercise: Prove using the phase rule that for a single-component system, the one-phase regions must be two-dimensional, the two-phase regions must be one-dimensional, and the three-phases regions must occur at a point in T - P space.

One thing that is pretty universal about phase diagrams is that the pressures are really high compared to the pressures we normally think about; note the logarithmic scale in Figure 10, and the fact that 1 bar = 0.1 MPa. We demonstrate why large pressures are needed to effect

²⁷We'll talk more about the meaning of critical points and the interesting physics which occur at criticality in statistical mechanics.

phase stability with an order of magnitude comparison: we'll calculate the work done per mole during a phase transition with some change in volume for 'normal' pressures:

$$\Delta W = P \cdot \Delta V \quad (124)$$

A typical molar volume for an element is $V = 5 \cdot 10^{-6} \text{m}^3/\text{mol}$, and a large change in volume for condensed phases is on the order of 10%, $\Delta V = 5 \cdot 10^{-7} \text{ m}^3/\text{mol}$. A large pressure would be 100 MPa, as this is the order of magnitude when most metals yield. Then $\Delta W = 100 \cdot 10^6 \cdot 5 \cdot 10^{-7} = 50 \text{J/mol} \approx 0.5 \text{ meV}$. Let's compare this to the amount of energy it takes to heat an element by one degree K, $c_V \approx c_P \approx 25 \text{ J/mol/K}$. Therefore, we see that changes of a few degrees K cause the free energy to change the same amount as large changes in volume at rather high pressures. Thus, we expect that in order to appreciably change phase behavior that often takes place via changes of hundreds of degrees K, we will need to apply extremely large pressures, often on the order of tens to hundreds of GPa. This will become more quantitative in the next section.

10.3 Determining Phase Diagrams

Here we demonstrate that the slopes of the lines on phase diagrams are dictated by thermodynamics, and that you can usually guess them pretty well with a bit of knowledge. We know that two phases are at equilibrium at a given temperature and pressure when their free energies are equal, $G_{T,P}^\alpha = G_{T,P}^\beta$. If we change the experimental conditions a bit, the phases will only remain in equilibrium if the free energy change of α is equal to the free energy change of β , $dG_{T,P}^\alpha = dG_{T,P}^\beta$. Expanding this expression gives:

$$-S^\alpha dT + V^\alpha dP = -S^\beta dT + V^\beta dP \quad (125)$$

This can be manipulated to give insight into the slope of the phase boundary in T-P space. Defining the differences in volume and entropy between the two phases and simplifying gives:

$$\begin{aligned} \Delta V^{\alpha \rightarrow \beta} &= V^\beta - V^\alpha \\ \Delta S^{\alpha \rightarrow \beta} &= S^\beta - S^\alpha \end{aligned} \quad (126)$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta S^{\alpha \rightarrow \beta}}{\Delta V^{\alpha \rightarrow \beta}}} \quad (127)$$

This is known as the *Clausius-Clapeyron relation*. It is commonly expressed in terms of the more easily-measured enthalpy changed of the phase transformation, $\Delta H^{\alpha \rightarrow \beta}$. This is possible because at a phase transformation,

$$\Delta G = 0 = \Delta H^{\alpha \rightarrow \beta} - T^{\alpha \rightarrow \beta} \Delta S^{\alpha \rightarrow \beta} \quad (128)$$

so we can eliminate $\Delta S^{\alpha \rightarrow \beta}$:

$$\frac{dP}{dT} = \frac{\Delta H^{\alpha \rightarrow \beta}}{T^{\alpha \rightarrow \beta} \Delta V^{\alpha \rightarrow \beta}} \quad (129)$$

This relation actual tells us a very simple thing: if the temperature changes a bit when two phases are at equilibrium, the resulting difference in free energies is $\Delta S^{\alpha \rightarrow \beta} dP$. If the phases

are to remain at equilibrium, a compensating change in the free energy due to pressure must be made: $-\Delta V^{\alpha \rightarrow \beta} dT$, so the rate at which the pressure changes with respect to temperature along a phase boundary is proportional to the ratio of their conjugates.

10.4 Example: solid to liquid transition

Here we just put some numbers to the Clausius-Clapeyron relationship for liquid-solid relationships so that you can get a feel for some numbers.

$$\begin{aligned}\Delta S &= S_l - S_s \\ \Delta V &= V_l - V_s\end{aligned}\tag{130}$$

How much ΔP is required to raise the melting point of Pb by 10°C ?

$$\begin{aligned}\Delta H_m &= 4810\text{J/mol} \\ T_M &= 600K \\ v_l &= 19.47\text{cm}^3/\text{mol} \\ v_s &= 18.92\text{cm}^3/\text{mol}\end{aligned}\tag{131}$$

and so

$$\begin{aligned}\frac{dP}{dT} &= \frac{\Delta H_M}{T_M \Delta V} \\ \Delta P &= \frac{\Delta H}{T_{M,P=0} \Delta V} \log \frac{T_M}{T_{M,P=0}} = 14.5 \text{ MPa}\end{aligned}\tag{132}$$

Most of the time $\Delta S > 0$ since liquids have higher entropy than solids. If $\Delta V > 0$, $\frac{dP}{dT} > 0$, then the solid/liquid line will have a positive slope. This is the case for most solid-liquid equilibria, as the solid is usually more dense than the liquid. There are some technologically relevant exceptions where $\Delta V < 0$. These mostly occur in directionally-bonded solids, such as [water](#), [Si](#), and [Ge](#), but can occur for metallic elements such as [Ga](#) at low pressures.

Typical slopes: For solid to liquid, we get $\Delta H = 10 \text{ kJ}$, $\Delta V = 1 \text{ cc/mol}$, and the slope is large, with the sign determined by the volume change (+/-). For solid to gas, $\Delta H = 100 \text{ kJ}$, $\Delta V = 10^4 \text{ cc/mol}$ (10 Liters), and the slope is small, but positive.

11 General Clapeyron Relations, Le Chatelier-Braun Principle

Last time we derived the Clausius-Clapeyron relation. Now we would like to find a simplified expression of the Clausius-Clapeyron equation for the condensed phase and vapor equilibrium. We can assume the vapor is an ideal gas $V = \frac{RT}{P}$ and make the approximation $\Delta V \approx V_g$, since the volume of a condensed phase are generally much smaller than the volume of the gas phase.

$$\Delta V = V_v - V_l \approx V_v \quad (133)$$

$$\begin{aligned} \frac{dP}{dT} &= \frac{\Delta H}{T\Delta V} \\ &= P \frac{\Delta H}{RT^2} \\ \frac{dP}{P} &= \frac{dT}{T^2} \frac{\Delta H}{R} \\ \ln(P) &= -\frac{\Delta H}{R} \frac{1}{T} + \text{constant} \end{aligned} \quad (134)$$

The enthalpy is also a function of temperature, so we write it as a function of the relevant heat capacity. Additionally, the heat capacities can all be expanded with respect to temperature.

$$\begin{aligned} \Delta H(T) &= \Delta H_{\phi T}(298) + \Delta C_p(T - 298) \\ c_P^v &= a + bT + \dots \\ c_P^l &= a' + b'T + \dots \\ \Delta c_P &= A' + B'T + \dots \end{aligned} \quad (135)$$

Combining the above results leads to Antoine's equation, a relation with the constants A, B, C that all determine the relationship between temperature and pressure during a phase transition:

$$\log(P) = A - \frac{B}{T + C} \quad (136)$$

Are condensed phases really condensed?²⁸

Take a look at the phase diagram for H_2O in Fig 11. From looking at this phase diagram, one would think that at room temperature and pressure ($10^5 \text{ Pa}, 300 \text{ K}$), water should be a single, liquid phase. Why, then, is there water vapor in the air around us? This is because the phase diagram only considers *unary systems at constant pressure and temperature*, whereas water exists in systems where there are other elements in the vapor above it (air!). Because liquid water at STP has some well-defined chemical potential of H_2O , the vapor above it must have enough H_2O such that it has the same chemical potential.

²⁸(i.e. Why do condensed phases have vapor pressures above them?)

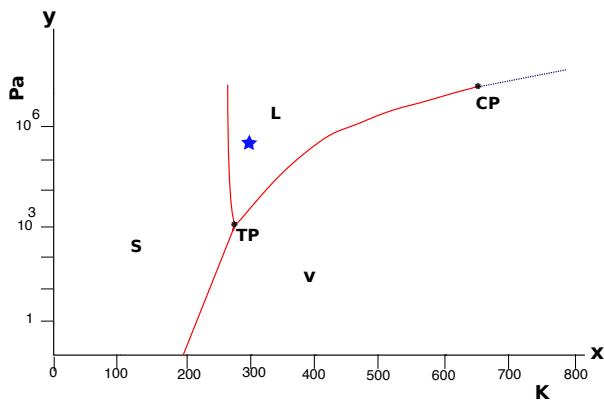


Figure 11: A simplified phase diagram for water. The blue star is room temperature and pressure. Image from [wikimedia commons](#).

The **vapor pressure** is defined as the partial pressure that a substance in the condensed phase will create in the vapor phase in equilibrium with it. Where a partial pressure is defined as:

$$P_i = \frac{n_i}{n_{\text{total}}} P_{\text{total}} \quad (137)$$

Because gases are ideal, if we have a liquid A in a container with some other gas atmosphere, the partial pressure of the vapor A is actually independent of the gas atmosphere. Vapor pressures are only defined by the chemical potentials in the condensed phases, in this case the liquid A .

Example: The equilibrium vapor pressure of H_2O at 25°C is $P_{\text{H}_2\text{O}}^{\text{eq}} = 0.03 \text{ atm}$. At 45°C $P_{\text{H}_2\text{O}}^{\text{eq}} = 0.07$ and at 100°C it is $P_{\text{H}_2\text{O}}^{\text{eq}} = 1$ (boiling point). The relative humidity is expressed by $\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O}}^{\text{eq}}}$. This is actually what people mean when they talk about 80% humidity. The dew point is the temperature at which $P_{\text{H}_2\text{O}}^{\text{eq}}$ drops below the ambient vapor pressure, so that the air becomes supersaturated with H_2O , causing dewy to form.

Note: saturated water vapor does not behave like an ideal gas. If we have a system of 100% pure humid air and we compress the system, the concentration of the water vapor would be above its equilibrium vapor pressure, and so some of the water will condense.

11.1 Le Chatelier-Braun principle

Definition: When a system, initially at equilibrium, is perturbed from its equilibrium state, the system adjusts itself to counteract the effect of the applied change in establishing a new equilibrium.²⁹

²⁹Callen provides a good discussion of this in Ch. 8-4 (p. 210)

Condensation of water from a saturated vapor after a compression is one example of the Le Chatelier-Braun principle: the pressure of the system is increased, and the system responds by forming more of a lower-volume phase, lowering the pressure and counteracting the increase in pressure. The most common examples of this are in chemistry, though. When you add a reactant A to a system which was previously in some equilibrium governed by



then adding some A acts as a *perturbation* to this system, and the system *adjusts itself* by reacting to partly eliminate this additional A, coming to a new equilibrium in the process.³⁰ Thermodynamically, this is tantamount to increasing the chemical potential of A, with the forward reaction then acting to homogenize this perturbation in the chemical potential.³¹

11.2 Generalization of Clausius-Clapeyron

The method used to generate the Clausius-Clapeyron equation can be applied to any two sets of work terms by taking the proper Legendre transform such that the intensive variables of interest are the natural variables for the thermodynamic potential. For example, in the case of the Clausius-Clapeyron equation the intensive variables of interest were T and P, so we took $\phi = U - TS + PV$, which turns out to be the Gibbs free energy. Along a phase boundary, this gave rise to the relation:

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v} \quad (139)$$

A similar relationship can be derived for a magnetic phase transition, taking instead: $\phi = U - TS + PV - \mathcal{HM}$ such that

$$d\phi = -S dT + V dP - \mathcal{M} d\mathcal{H} \quad (140)$$

for the system as a whole. We again consider the case where the system is composed of two phases in equilibrium with one another, and where we want to move along a two-phase equilibrium boundary in $T - \mathcal{H}$ space such that the different thermodynamic potentials are changing at the same rate:

$$d\phi^1 = d\phi^2 \quad (141)$$

$$-S^1 dT + V^1 dP - \mathcal{M}^1 d\mathcal{H} - (-S^2 dT + V^2 dP - \mathcal{M}^2 d\mathcal{H}) = 0 \quad (142)$$

For a system at constant pressure, we can show that:

$$\left(\frac{\partial \mathcal{H}}{\partial T} \right)_P = -\frac{\Delta S}{\Delta \mathcal{M}} \quad (143)$$

³⁰Throwing away the thermo jargon: if you put a bit of A in, some of that A reacts, so the concentration of A becomes less.

³¹Historical note: Le Chatelier and Braun discovered this principle independently, so in 3.20 we give attribution to both of them!

In general, this can be written for any work term as:

$$\left(\frac{\partial Y_j}{\partial T} \right)_{Y_i \neq j} = -\frac{\Delta S}{\Delta X_j} \quad (144)$$

Where the intensive variables are on the left, and the extensive variables are on the right. Due to the weird sign convention with P , Clausius-Clapeyron (C-C) relationships with P have a reversed sign.

11.3 Magnetic-induced phase transformation

Let's put some numbers onto this new C-C relationship to get a sense of how temperature can affect the T - H phase boundary.

$$\begin{aligned} dU &= T dS + \mu_0 \mathcal{H} d\mathcal{M} \\ dG &= -S dT - \mu_0 \mathcal{M} d\mathcal{H} \end{aligned} \quad (145)$$

$$\frac{dT}{d\mathcal{H}} = -\frac{\Delta \mathcal{M}}{\Delta S} \quad (146)$$

$$\Delta \mathcal{M} = \mathcal{M}_{\text{ferro}} - \mathcal{M}_{\text{para}} \approx 4\mu_B \approx 4 \cdot 10^{-5} \text{eV/Tesla} \quad (147)$$

Where we assumed that the magnetization of the ferromagnetic material was 4 Bohr magneton per atom. For spins, we can have two states, so

$$\Delta S = k_B \ln(2) \quad (148)$$

Thus we can estimate our change in temperature with field

$$\frac{dT}{d\mathcal{H}} = -\frac{4 \cdot 10^{-5}}{8.617 \cdot 10^{-5} \cdot \ln(2)} = -0.66 \text{K/Tesla} \quad (149)$$

Note: a Tesla is a *huge* magnetic field, so we see that phase boundaries between magnetic phases are super strongly affected by temperature, making them hard to study well if you don't have good control over T .

11.4 Thermoelasticity

An application of a generalized Clausius-Clapeyron relationship is thermoelasticity. Thermoelasticity, or “superelasticity” is a recoverable strain far beyond what is normally expected for solids³². The phase transformation is typically induced by stress. In the high-T phase, we have the A (austenite) phase. In the low-T phase, we have M (martensite). The stress-strain curves look like those in Fig 12 A.

³²Elastic deformation usually only occurs until around $\epsilon \approx 0.2\%$. Superelasticity permits reversible strains of up to 10%

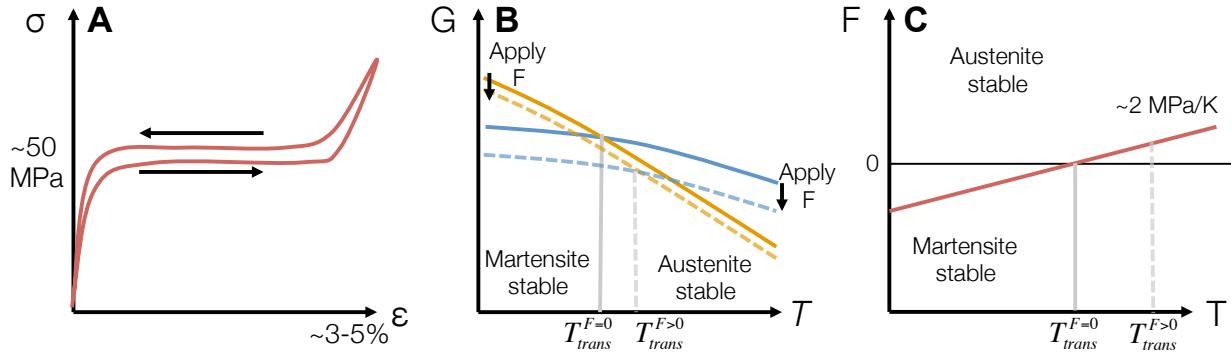


Figure 12: **A** A typical stress-strain curve for a superelastic material. **B** Free energy curves for martensite and austenite as a function of temperature showing how the curves shift upon application of a stress **C** A simplified phase diagram for superelastic materials.

Keep in mind what you see in Fig 12 **A**; a discontinuity in an extensive variable (length/strain) while an intensive variable is constant (force/stress). This is almost always a sign that changing the intensive variable induced a first-order phase transition.³³

If we plot G vs. T , both phases exhibit downward slopes and negative curvature, as in Fig 12 **B**. The higher entropy austenitic phase will have a larger, negative slope, and thus become stable at higher temperature. We want to investigate the effect of force on the temperature of the superelastic transition, so we set up our relevant potential:

$$\begin{aligned} dU &= T dS + F dL \\ G &= U - T \cdot S - F \cdot L \\ L &= - \left(\frac{\partial G}{\partial F} \right)_{T_i} \end{aligned} \tag{150}$$

By applying a force and stretching the material, we move the G vs. T line downwards for both phases, but the the martensitic phase moves down more quickly than the parent phase due to the martensite's larger L . This relative movement is indicated by the dashed lines in Fig. 12B. The interesting thing is that because they don't move at the same rate, you get shifts in the transition temperature due to application of stress; there is a Clausius-Clapeyron effect here. Let's quantify it in the context of a specific system.

Say we're talking about Cu-Al-Zn at $T_0 = 300K$, $V \approx 8 \cdot 10^{-6} \text{ m}^3/\text{mol}$, $\Delta S \approx 1 \text{ J/mol/K}$.

³³Another example is when battery charge-discharge curves exhibit a constant discharge voltage for a large amount of current

Now we write down a version of Clausius-Clapeyron:

$$\begin{aligned} \frac{1}{A} \frac{dF}{dT} &= -\frac{\Delta S}{\Delta L} \frac{1}{A} \\ A\Delta L &= V_m \Delta \epsilon \\ \frac{d\sigma}{dT} &= -\frac{\Delta S}{V_m \Delta \epsilon} = (8 \cdot 10^{-6} \cdot 7.5 \cdot 10^{-3})^{-1} = 1.66 \text{ MPa/K} \end{aligned} \quad (151)$$

The resulting phase diagram is shown in Fig. 12C, it's just a line with a slope given by Equation 151.

In general, what would be the heat involved if we apply a stress?

$$\begin{aligned} H &= U + PV \\ dH &= dQ + V dP + F dl \\ (dH)_p &= (dQ)_p + F dl \end{aligned} \quad (152)$$

Universal enthalpy

$$\begin{aligned} H &= U - \sum y_i x_i \\ H' &= U + PV - Fl \\ (dH') &= (dQ)_p - l dF \end{aligned} \quad (153)$$

11.5 Chemical Clausius-Clapeyron relationships

In this subsection we briefly elaborate on the calculation of the slopes of phase boundaries for phase diagrams relevant to chemistry: Temperature-composition diagrams. We present two alternative derivations that demonstrate the importance of boundary conditions and choice of potential in deriving easily-interpreted results from Clausius-Clapeyron relationships.

Consider a system composed of only A and B atoms. We will, to mimic the processes of traversing a phase diagram, assume that the system is surrounded by a membrane such that whenever an atom of A leaves the system, an atom of B enters the system, i.e. the $dN_A = -dN_B$. We can then write dU as:

$$dU = T dS - P dV + \mu_A dN_A + \mu_B dN_B = T dS - P dV + (\mu_B - \mu_A) dN_B \quad (154)$$

Note that the constraint $dN_A = -dN_B$ means that the system is at constant total numbers of atoms, no matter what processes occur across the boundaries. For simplicity, we'll consider a single mole of atoms total. The system is kept at constant temperature and pressure. In addition, we externally fix the composite chemical potential $(\mu_B - \mu_A)$ by flowing an A/B vapor of varying mole fractions of A and B across the system.

The relevant potential is then:

$$\phi = U - TS + PV - (\mu_B - \mu_A) N_B \quad (155)$$

such that:

$$\begin{aligned} d\phi &= -S dT + V dP - N_B d(\mu_B - \mu_A) \text{ at constant mole number } N_A + N_B \\ &= -S dT + V dP - N_B d\mu_B - N_A d\mu_A \text{ at constant mole number } N_A + N_B \end{aligned} \quad (156)$$

If the system contained within our membrane is a two-phase system, then we can then change the external chemical potential difference by changing the composition of the vapor, and ask how the temperature of the system must change for the system to remain in two-phase equilibrium (at constant pressure). This is equivalent to saying that the change in the molar free energies of the two phases are equal:

$$d\phi_\alpha = d\phi_\beta \quad (157)$$

$$-S_\alpha dT - N_{B,\alpha} d(\mu_B - \mu_A) = -S_\beta dT - N_{B,\beta} d(\mu_B - \mu_A) \quad (158)$$

$$\left(\frac{dT}{d(\mu_B - \mu_A)} \right)_{N_A + N_B, P} = -\frac{\Delta N_{B,\alpha \rightarrow \beta}}{\Delta S_{\alpha \rightarrow \beta}} \quad (159)$$

However, the number of moles of B in the α phase at constant mole number is the composition of phase α when in equilibrium with phase β :

$$\frac{N_{B,\alpha}}{N_{A,\alpha} + N_{B,\alpha}} = X_{B,\alpha}$$

Same with the number of moles in phase β . Thus, we can reduce Eq. 159 to:

$$\left(\frac{dT}{d(\mu_B - \mu_A)} \right)_{N_A + N_B, P} = -\frac{\Delta X_{B,\alpha \rightarrow \beta}}{\Delta S_{\alpha \rightarrow \beta}} \quad (160)$$

$\Delta X_{B,\alpha \rightarrow \beta}$ can be read off of phase diagrams, and $\Delta S_{\alpha \rightarrow \beta}$ (The difference in entropy between a mole of β phase and a mole of α phase) is often easily known or approximated.

An analogous derivation for an open system is as follows: Consider a system composed of only A and B atoms. We will assume that the system is open to exchange of B, but closed to exchange of A , i.e. the $dN_A = 0$. We can then write dU as:

$$dU = T dS - P dV + \mu_B dN_B \quad (161)$$

Note that the constraint $dN_A = 0, dN_B \neq 0$ means that the system is at constant numbers of A atoms, but the total number of atoms changes. For simplicity, we'll consider a single mole of A atoms. The system is kept at constant temperature and pressure. In addition, we externally fix the composite chemical potential of B by flowing a vapor of varying partial pressures of B across the system. The relevant potential is then:

$$\phi = U - TS + PV - \mu_B N_B \quad (162)$$

such that:

$$\begin{aligned} d\phi &= -S dT + V dP - N_B d\mu_B \text{ at constant } N_A \\ &= -S dT + V dP - N_B d\mu_B \text{ at constant } N_A \end{aligned} \quad (163)$$

If the system considered is a two-phase system, then we can change the external chemical potential (via the vapor pressure of B), and ask how the temperature of the system must change for the system to remain in two-phase equilibrium (at constant pressure). This is equivalent to saying that the change in the molar free energies of the two phases are equal:

$$d\phi_\alpha = d\phi_\beta \quad (164)$$

$$-S_\alpha dT - N_{B,\alpha} d\mu_B = -S_\beta dT - N_{B,\beta} d\mu_B \quad (165)$$

$$\left(\frac{dT}{d\mu_B} \right)_{N_A, P} = -\frac{\Delta N_{\alpha \rightarrow \beta}}{\Delta S_{\alpha \rightarrow \beta}} \quad (166)$$

Note that in Eq 166 the term $\Delta N_{\alpha \rightarrow \beta}$ has a very different meaning: it is the number of moles transferred into the system per mole of A atoms during a phase transition from $\alpha \rightarrow \beta$. Similarly, the $\Delta S_{\alpha \rightarrow \beta}$ term is the change in system entropy per mole of A atoms during the same transition.

We can relate Eqs 159 and 166 by expanding Eq. 166 in terms of the underlying molar quantities, writing:

$$N_{B,\alpha} = N_\alpha X_{B,\alpha}, \quad N_{B,\beta} = N_\beta X_{B,\beta}, \quad S_{B,\alpha} = N_\alpha S_{B,\alpha}, \quad S_{B,\beta} = N_\beta S_\beta.$$

This allows us to write:

$$\left(\frac{dT}{d\mu_B} \right)_{N_A, P} = \frac{X_{B,\beta} - \frac{N_\alpha}{N_\beta} X_{B,\alpha}}{S_{B,\beta} - \frac{N_\alpha}{N_\beta} S_{B,\alpha}}. \quad (167)$$

Eq. 167 differs from 159 by factors of $\frac{N_\alpha}{N_\beta}$. The physical origin for the similarity in these expressions but their slight discrepancy is that μ_B varies differently from $\mu_B - \mu_A$, but that their variations within a given phase are connected via a Gibbs-Duhem relation at constant T and P as:

$$d\mu_B = -\frac{N_A}{N_B} d\mu_A$$

For small differences in compositions between α and β , Eqs 159, 166, and 167 are all equivalent, as:

$$\frac{N_\alpha}{N_\beta} = \frac{1 + \frac{X_{B,\alpha}}{1-X_{B,\alpha}}}{1 + \frac{X_{B,\beta}}{1-X_{B,\beta}}}$$

12 Introduction to Solution Theory

We now begin the section on chemical thermodynamics and solution theory. Solution theory is concerned with the thermodynamics of multicomponent systems; it's what happens when the substances we are dealing with are no longer pure.

Readings regarding solution theory will be from *Chemical Thermodynamics of Materials* by Claude H.P. Lupis (a former member of MIT DMSE) and will be posted to Stellar when possible. Readings on specific topics are listed below, under the corresponding heading. In general, Denbigh's *The Principles of Chemical Equilibrium* is also a good reference on these topics. This book is somewhat verbose, but very good if you want a second, different viewpoint.

Phase Diagrams:

Principles of Phase Diagrams in Materials Systems by Paul Gordon is a very thorough reference for phase diagrams. It seems to be out of print and so we will post the chapters as needed.

The ASM Phase Diagram Database is an extremely useful tool for materials scientists. The link is found [here](#). We will look at a lot of phase diagrams from here throughout the last part of this course.

12.1 Adding composition as a work term in G

G is defined as $G = U - TS + PV$. Recognizing that $U = TS - PV + \sum \mu_i N_i$, we see that there are a bunch of chemical work terms we've been leaving out! G can thus be defined as (ignoring other work terms like $\mathcal{H}d\mathcal{M}$, $\mathcal{E}d\mathcal{P}$, etc):

$$G = \sum \mu_i N_i \quad (168)$$

We get a whole new class of properties by taking derivatives of G with respect to the n_i . We call these partial molar quantities, and we can add them to our matrix of derivatives:

Table 4: The derivatives of G

G	$\frac{\partial}{\partial T}$	$\frac{\partial}{\partial P}$	$\frac{\partial}{\partial n_i}$
$\frac{\partial}{\partial T}$	$-\frac{c_P}{T}$	$\alpha_V V$	$-\bar{S}_i$
$\frac{\partial}{\partial P}$	$\alpha_V V$	$-\beta_T V$	\bar{V}_i
$\frac{\partial}{\partial n_i}$	$-\bar{S}_i$	\bar{V}_i	$\frac{\partial \mu_i}{\partial n_i}$

where the extra second derivatives are from

$$\begin{aligned}\frac{\partial^2 G}{\partial T \partial n_i} &= -\frac{\partial S}{\partial n_i} \Big|_{P,T,n_j \neq i} = -\bar{S}_i \\ \frac{\partial^2 G}{\partial P \partial n_i} &= \frac{\partial V}{\partial n_i} = \bar{V}_i\end{aligned}\tag{169}$$

12.2 Solutions, Molar Quantities, and Partial Molar Quantities

Readings: DeHoff's *Thermodynamics in Materials Science* (pgs 197-202) is the best for this. Lupis 2.3.3 also has a decent discussion.

Solutions: A solution is defined as a single phase, α , which has multiple elements. Note that we have not defined whether the solution is in the solid, liquid, or gas state. Solutions can exist in each of these phases, so while it is unintuitive to think of a solid 'solution', solutions definitely occur in the solid state. Disordered solid solutions are often called *alloys*. Ordered solid solutions are called *compounds*. Note that ordered phases are still solutions in the thermodynamic sense; they contain multiple elements; each element just has a tendency to exist at certain crystallographic sites.

Molar Quantities: A *molar quantity* is any extensive property normalized on a molar basis. These are usually written with an underbar; the molar entropy would thus be written $\underline{S} = \frac{S}{N}$. A concrete example is that the molar volume of pure Ni is $\underline{V}_{Ni} = \frac{V}{N} = 7 \text{ cm}^3/\text{mol}$, and that of water is $\underline{V}_{H_2O} = 18 \text{ cm}^3/\text{mol}$. Molar quantities are well-tabulated for the elements. Molar properties can also be defined for solutions; solutions have well-defined extensive variables and mole numbers, so you can divide the extensive variables by the total number of moles in the solution and get a molar property.

Molar quantities are intensive: the molar volume of Ni does not change whether you have one or two moles of Ni. Note that the intensive nature of molar quantities makes it silly to define molar properties of the intensive variables, as the units get messed up: the temperature per mole does not make sense. Molar quantities are very related to (but distinct from) partial molar quantities. We will derive this relationship below.

Partial Molar Quantities:

A *partial molar quantity* (PMQ) is the derivative of any extensive property, X , with respect to the number of moles of a single species, N_i :

$$\bar{X}_i = \left(\frac{\partial X}{\partial N_i} \right)_{T,P,N_j \neq i} \tag{170}$$

PMQ's are written with an overbar. Thus $\bar{S}_i = \left(\frac{\partial S}{\partial N_i} \right)_{T,P,N_j \neq i}$. It is easy to show that the partial molar quantities are intensive properties of the system (i.e. they do not depend on the size of the system). The easiest example of PMQs being intensive is the chemical potential, we already know it is intensive: $\mu_i = \overline{G}_i = \left(\frac{\partial G}{\partial N_i} \right)_{T,P,N_j \neq i}$

The discussion in these notes is meant to be self-contained, but if you need more info, there's

a really good Wikipedia page on these: [Wikipedia page on partial molar quantities](#). We will first discuss a concrete example of PMQs with the partial molar volume of water-ethanol mixtures, and then give a general discussion of the properties of partial molar quantities.

12.3 Ex: Partial Molar Volumes

One common example of a partial molar quantity is a *partial molar volume*. By Eq 170, the definition of the partial molar volume is:

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{n_j \neq i, T, P} \quad (171)$$

In words: \bar{V}_i is the amount that the total volume of a system changes upon addition of a small amount of that substance, normalized by the amount of substance added. Partial molar volumes can be extremely important in technological applications.³⁴

In practice, one way to calculate partial molar volumes is by taking a relatively large solution (say of water) and adding a well-defined, small amount of solute to the solution (say one mole of ethanol). We will discuss a more clever way of measuring partial molar properties later. The partial molar volume is then given (approximately) by the volume change divided by the number of moles added:

$$\bar{V}_{\text{EtOH}} \approx \left(\frac{\Delta V}{\Delta n_{\text{EtOH}}} \right)_{n_{H_2O}, T, P} \quad (172)$$

In this situation, the moles of N_i and the change in volume are small relative to the mole numbers and volume of the system, so Eq. 172 approximates the differential volume change per mole of solute added.

The volume of a solution or compound is generally not the sum of the volume of its constituent elements. For example, shown in Fig. 13 the partial molar volumes of ethanol and water when mixed with one another. As can be seen, for almost all concentrations, the partial molar volume of the constituents is less than the molar volume of the constituents in their pure states (symbolically: $\bar{V}_{\text{EtOH}}(x) < \underline{V}_{\text{EtOH, pure}}$ for all $x < 1$). This means that there is a net contraction when you mix water and ethanol.

This contraction relative to the equivalent mole numbers of the pure constituents can be considered an “excess amount of volume which occurs due to mixing.” This is called the *excess volume of mixing*, and is written symbolically as:

$$\underline{V}_{\text{mix}}^{\text{XS}} = \underline{V}_{\text{solution}}(x) - x_A \underline{V}_A - x_B \underline{V}_B \quad (173)$$

³⁴For example, the change in volume due to lithiation of various battery electrodes causes mechanical degradation of the electrodes. This turns out to be one of the key factors governing the cycling performance of the electrodes, with many next-generation electrodes limited by mechanical degradation. See Woodford et al, JECS 2010 ([link](#))

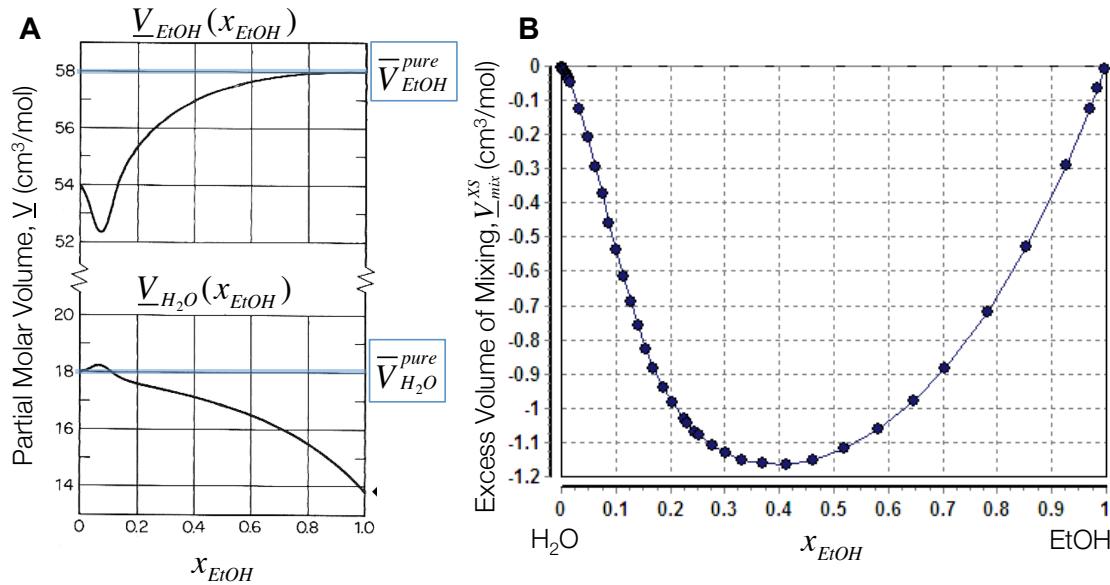


Figure 13: **A** Partial molar volumes of ethanol-water solutions as a function of composition (Moore 1972) **B** The excess volume of ethanol-water solutions as a function of composition, [wikimedia commons](#)

A contraction upon mixing corresponds to a negative excess volume of mixing. Excess properties upon mixing can be defined for any extensive properties of interest, and we will spend a lot of time on them soon.

One could derive the excess volume of mixing by integrating the partial molar volumes and subtracting the reference states. However, it turns out you can just add the partial volumes up weighted by their mole fractions and subtract the reference volumes to get the same answer:

$$\underline{V}_{\text{solution}}(\{x_i\}) = \sum_i x_i \bar{V}_i \quad (174)$$

and so:

$$\underline{V}_{\text{mix}}^{\text{xs}} = \sum_i x_i (\bar{V}_i - \underline{V}_i) \quad (175)$$

Shown in Fig 13B is the excess volume of mixing for water and ethanol. As expected from the previous discussion, it is negative for all compositions.

The ability to sum the individual partial molar quantities to calculate the total molar quantity is a general (and useful) property of partial molar quantities.

12.4 General properties of partial molar quantities

We now discuss general properties of partial molar quantities.

The sum of the partial molar quantities yields the molar quantity of the solution
In general, one might think that we would need to integrate all of the partial molar volumes

one by one with respect to their mole numbers to reach the volume of the solution:

$$V_{\text{solution}} (\{n_i\}) = \int_0^{n_i} \bar{V}_i (n_i, n_j = 0) dn_i + \int_0^{n_j} \bar{V}_j (n_i, n_j) dn_j + \dots \quad (176)$$

More compactly:

$$V_{\text{solution}} (\{n_i\}) = \sum_i \int_0^{n_i} \bar{V}_i (\{n_i\}) dn_i \quad (177)$$

where this sum is carried out in sequence over the components.

However, the volume of the solution is a state function of the composition, so we are free to choose whatever path in composition space we want in integrating these partial molar volumes. The path which makes the most sense is to simply add all of the components at the same time in the proportions found in the final solution. This way, the partial molar volume of each component is constant, and is given by the partial molar volume of the component in the final solution. Then, the volume of the solution is given by:

$$V_{\text{solution}} (\{n_i\}) = \sum_i \bar{V}_i \int_0^{n_i} dn_i \quad (178)$$

Note how we were able to pull the various partial molar volumes, \bar{V}_i , out of the integral because they are constant. This integral is then trivial and gives:

$$V_{\text{solution}} (\{n_i\}) = \sum_i \bar{V}_i n_i \quad (179)$$

Or, taking the molar volume of the solution and converting the n_i to mole fractions:

$$\underline{V}_{\text{solution}} (\{x_i\}) = \sum_i x_i \bar{V}_i \quad (180)$$

The above procedure is valid for an choice of extensive variable and thus all extensive properties of solutions can be written in the general form written in class:

$\underline{X}_{\text{solution}} (\{x_i\}) = \sum_i x_i \bar{X}_i$

(181)

That is, *the total molar quantity is given by a (weighted) sum of the partial molar quantities.*
The partial molar quantities are related by Maxwell relations

With the exception of μ_i , the partial molar quantities are defined as derivatives of some extensive variable with respect to changes in mole number. $\bar{S}_i = \left(\frac{\partial S}{\partial N_i} \right)_{T,P,N_j \neq i}$. However, these extensive variables themselves are defined as derivatives of G : $S = - \left(\frac{\partial G}{\partial T} \right)_{P,N_j \neq i}$. Hence, these partial molar quantities are mixed partial derivatives of G . Therefore a Maxwell relation exists upon switching the order of differentiation:

$$\begin{aligned} \bar{S}_i &= \left(\frac{\partial S}{\partial N_i} \right)_{T,P,N_j \neq i} = - \left(\frac{\partial \mu_i}{\partial T} \right)_{P,N_j} \\ \bar{V}_i &= \left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_j \neq i} = \left(\frac{\partial \mu_i}{\partial P} \right)_{T,N_j} \end{aligned} \quad (182)$$

This gives you a second, nice way of interpreting the meaning of the PMQs: they are also the rate at which the chemical potential changes with respect to changes in the appropriate extensive variable's conjugate. To give an example of such an interpretation, *the partial molar volume is the rate at which the chemical potential of each component changes as you increase the pressure.* This means elements that allow the system to attain a smaller volume are more favorable at higher pressures: the elements which effectively make a solution “bigger” get “squeezed out” of the solution upon application of pressure.

Partial molar quantities can be read from graphs of the molar quantity as a function of composition

A nice property of partial molar quantities is the tangent-intercept rule. It states that if you have a plot of a molar quantity versus composition for an A-B solution, the partial molar quantity for A and B are given by the y-intercepts of the line tangent to the curve: Mathematically, we can write this as, for an arbitrary molar quantity, \bar{Y} :

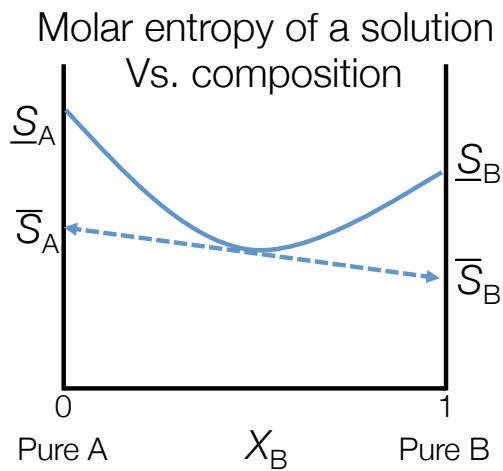


Figure 14: An illustration of the tangent-intercept construction for the partial molar entropy from the molar entropy.

$$\bar{Y}_A(x) = \underline{Y}(x) - (1-x)\frac{\partial \underline{Y}}{\partial x}. \quad (183)$$

This is especially useful for reading the chemical potential off of plots of the free energy versus composition. Fig. 14 demonstrates this construction for an arbitrary partial molar entropy curve. By symmetry arguments, a similar formula applies for the other component.

13 Review of Exam 1 materials

First part of test is True/False questions. An example of a question would be:

“A one component material undergoes a pressure induced phase transformation at $P_{\phi T}$. The material has the same equation of state in both phases. True or False?” (20 questions like this)

There might then be a question like:

“In the α phase, $\beta P = a + b\beta\mu$ (μ is the chemical potential, $\beta = 1/T$), in γ phase, $\beta P = c + d(\beta\mu)^2$. a, b, c, d are positive functions of β , and we know $d > b$, $c < a$. What is the density differences between α and γ at the phase transformation? What $P_{\phi T}$ does the transition happen at?”

Solution: We know that at the phase transformation $\mu_\alpha = \mu_\beta$ and $\beta^{(\alpha)} = \beta^{(\gamma)}$, and $\rho = 1/V$.

13.1 Definitions

- **System:** Any collection of matter that can be uniquely identified and on which you can define macroscopic averages
- **Environment:** Complement of the system

$$[\text{Universe}] = [\text{Environment}] + [\text{System}] \quad (184)$$

- **Extensive Variables:** Variables that scale (linearly) with a system's size (volume, mass, number of particles, ...)
- **Intensive Variables:** Variables that are independent of a system's size (pressure, temperature, chemical potential, ...)
- **Boundaries:** Define a system and its interaction with the environment
- **Adiabatic:** No flow of heat $dQ = 0$ and $PV^\gamma = \text{constant}$, where the γ is determined by

$$\gamma = \frac{c_P}{c_V} = \frac{f+2}{f} \quad (185)$$

- **Conserved quantity:** A quantity dependent on variables that are *constant*. (In this class, we can assume the extensive parameters, except entropy S , are conserved.)
- **Reversible process:** Constant entropy process ($dS = 0$)
- **Isochoric:** Constant volume $dV = 0$

- **Isentropic:** Constant entropy $dS = 0$
- **Isenthalpic:** Constant enthalpy $dH = 0$
- **Isothermal:** Constant temperature $dT = 0$. For an ideal gas, $U = U(T) = nc_V T$ where $c_V = \frac{3}{2}R$ for a monoatomic gas or $c_V = \frac{5}{2}nR$ for a diatomic gas.
- **Isobaric:** Constant pressure $dP = 0$
- **Equations of state:** Expression of intensive parameters in terms of independent extensive parameters (e.g. $T = T(S, V, N, \dots)$)
- **Relative Humidity:** $\frac{P_{H_2O}}{P_{H_2O}^*}$ where the numerator is the partial pressure of water vapor *in the mixture* and the denominator is the *equilibrium vapor pressure* of water.
- **The Fundamental Equation:**

$$dU = T dS - P dV + \sum_i^k \mu_i dn_i + \dots \quad (186)$$

- **Heat Capacity:** The amount of heat that changes with changing temperature. For example:

$$\begin{aligned} c_V &= \left(\frac{\partial Q}{\partial T} \right)_V = \frac{dU}{dT} \\ c_P &= \left(\frac{\partial Q}{\partial T} \right)_P = \frac{dH}{dT} \end{aligned} \quad (187)$$

- **Dulong-Petit:** This is simply the relationships for c_v and c_p for monoatomic and diatomic gases. For monoatomic gases, $c_v = \frac{3}{2}R$, for diatomic gases $c_v = \frac{5}{2}R$, and for both, $c_p = c_v + R$.

13.2 Thermodynamic Laws

- (1) $dU = dW + dQ$. If adiabatic, $dU = dW$
- (2) Reversible: $dS_{\text{system}} = \frac{dQ}{T}$
Irreversible: $dS_{\text{system}} = \frac{dQ}{T}$
- (3) As temperature T approaches zero, the magnitude of entropy change (dS) in any reversible process is zero (Thus heat capacity at $T = 0$ is zero also).

13.3 All the heat capacities, expansion coefficients, etc.

- (i) Coefficient of thermal expansions

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

(188)

(ii) Isothermal compressibility (sometimes denoted by κ_T)

$$\boxed{\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T} \quad (189)$$

(iii) Molar heat capacity at constant pressure (works similarly with volume):

$$\boxed{c_P = \frac{1}{N} \left(\frac{dQ_{\text{rev}}}{dT} \right)_P = \frac{T}{N} \left(\frac{\partial S}{\partial T} \right)_P = T \left(\frac{\partial s}{\partial T} \right)_P} \quad (190)$$

13.4 Maxwell Relations

- (i) Find the appropriate natural variables for the thermodynamic potential of interest (ex: T, P)
- (ii) Convert to the appropriate thermodynamic potential via a Legendre Transform (ex: $T, P \rightarrow G(T, P)$)
- (iii) The Legendre transform should tell you if there is a sign difference between the two second derivatives of the potential with respect to the variables of interest.
- (iv) Match both second derivatives taking the sign difference into account if you need to.

13.5 Gibbs-Duhem

Results from comparing the total derivative of the Euler equation $U = TS - PV + \sum \mu_i N_i$ to the first law.

$$0 = S dT - V dP + \sum N_i d\mu_i \quad (191)$$

13.6 Internal energy U , enthalpy H , Helmholtz F , and Gibbs G

- (i) $H = U + PV$
- (ii) $F = U - TS$
- (iii) $G = U - TS + PV$

13.7 Legendre Transforms:

Given a potential and asked to make the other potentials (i.e. $U(S, X) = X^{-a} e^{bS}$)

- (i) Find the equations of state (relate first derivatives to the conjugate variables you know they should be)
- (ii) To eliminate a variable S of conjugate pair S, T , do $\phi = U - TS$
- (iii) Substitute values from equations of state to make sure new potential is in terms of appropriate variables

13.8 Some useful math identities:

$$\left(\frac{\partial f}{\partial x} \right)_g = \left(\frac{\partial f}{\partial x} \right)_y + \left(\frac{\partial f}{\partial y} \right)_x \cdot \left(\frac{\partial y}{\partial x} \right)_g \quad (192)$$

$$\left(\frac{\partial f}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_f \left(\frac{\partial y}{\partial f} \right)_x = -1 \quad (193)$$

Also just know the chain rule and inverse rule (pretty intuitive).

Variable reduction:

1. Bring your thermodynamic potential to the numerator
2. Bring S to the numerator and turn it into a heat capacity or use a Maxwell Relation
3. If needed, bring your volume to the numerator and turn it into a derivative of T and P .
4. Relate heat capacities to what you know

13.9 Carnot Engines:

Carnot engines really aren't too complicated. The principles are completely derived from the first two principles at reversible equilibrium $dS = 0 = dS_1 + dS_2$ and $dU = 0 = dQ + dW$. The different efficiencies are all just the quantities that *you want to get out of your pump/engine/refridgerator*. Let's begin:

$$\begin{aligned} dS &= dS_1 + dS_2 = 0 \\ \frac{dQ_{1,\text{rev}}}{T_1} &= -\frac{dQ_{2,\text{rev}}}{T_2} \\ dQ_{1,\text{rev}} &= -dQ_{2,\text{rev}} \frac{T_1}{T_2} \end{aligned} \quad (194)$$

and now with the first law

$$\begin{aligned} dU &= dQ_1 + dQ_2 + dW = 0 \\ \left(1 - \frac{T_1}{T_2}\right) dQ_2 &= -dW \end{aligned} \quad (195)$$

Carnot Engine: Here we care about getting work *out* by using a *heat source*, so the efficiency is

$$\mu_{\text{engine}} = \frac{-dW}{dQ_{\text{hot}}} = 1 - \frac{T_L}{T_H} = \frac{T_H - T_C}{T_H} \quad (196)$$

Heat Pump: Here we care about *extracting heat* by *doing work* on the system. The efficiency is then

$$\mu_{\text{pump}} = \frac{-dQ_H}{dW} = \mu_{\text{engine}}^{-1} = \frac{T_H}{T_H - T_C} \quad (197)$$

Refridgerator: Here we want to maximize the amount of heat *leaving* the cold system by *doing work*.

$$\mu_{\text{refridgerator}} = \frac{-dQ_C}{dW} = \frac{-dQ_H \frac{T_C}{T_H}}{-(1 - \frac{T_C}{T_H})dQ_H} = \frac{-T_C}{-(T_H - T_C)} = \frac{T_C}{T_H - T_C} \quad (198)$$

Carnot Cycle (All use reversible work sources)

1. Isothermal expansion with *hot* reservoir contact and reversible work
2. Adiabatic expansion with reversible work to T_C
3. Isothermal compression with *cold* reservoir contact and reversible work
4. Adiabatic compression with reversible work to T_H

13.10 Le Chatelier-Braun principle

Definition: If a system in equilibrium is subjected to constraints which displace the equilibrium, the transformation (reaction) proceeds in such direction as to accommodate the constraints and *partially* nullify their effects.

13.11 Clausius-Clapeyron

The Clausius-Clapeyron equation is a way to characterize phase transformations between two phases of matter (of the same constituent material). Know the *generalized form* (below) and be able to derive it for new systems:

$$\left(\frac{dy_j}{dT} \right)_{y_i \neq j} = -\frac{\Delta S}{\Delta x_j} \quad (199)$$

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}$$

(200)

which, for an ideal gas and where $\Delta V = V_{(g)} - V_{(l)} \approx V_{(g)}$ leads to:

$$\ln \left(\frac{P_f}{P_i} \right) = \frac{\Delta H}{nR} \left[\frac{1}{T_i} - \frac{1}{T_f} \right] \quad (201)$$

Derivation:

$$\begin{aligned}
 d\underline{G}^\alpha &= d\underline{G}^\beta \\
 -\underline{S}^\alpha dT + \underline{V}^\alpha dP &= -\underline{S}^\beta dT + \underline{V}^\beta dP \\
 \Delta \underline{V}^{\alpha \rightarrow \beta} &= \underline{V}^\beta - \underline{V}^\alpha \\
 \Delta \underline{S}^{\alpha \rightarrow \beta} &= \underline{S}^\beta - \underline{S}^\alpha \\
 \Delta \underline{S}^{\alpha \rightarrow \beta} dT + \Delta \underline{V}^{\alpha \rightarrow \beta} dP &= 0 \tag{202} \\
 \frac{dP}{dT} &= \frac{\Delta \underline{S}^{\alpha \rightarrow \beta}}{\Delta \underline{V}^{\alpha \rightarrow \beta}} \\
 \Delta \underline{S}^{\alpha \rightarrow \beta} &= \frac{\Delta \underline{H}^{\alpha \rightarrow \beta}}{T^{\alpha \rightarrow \beta}}
 \end{aligned}$$

plugging in we get the Clapeyron Equation, which defines the slope of our P/T curve:

$$\frac{dP}{dT} = \frac{\Delta \underline{H}^{\alpha \rightarrow \beta}}{T \Delta \underline{V}^{\alpha \rightarrow \beta}} \tag{203}$$

13.12 Raoult's Law:

Given a mixture of ideal liquids, the vapor pressure of each constituent liquid is equal to the vapor pressure of that liquid as a *single component* multiplied by the concentration. Thus, the total vapor pressure of the mixture is

$$P_{\text{vap}} = \chi_A p_A + \chi_B p_B + \dots = \sum_i \chi_i p_i \tag{204}$$

13.13 Phase changes:

You should be able to look at a G vs. T plot and rank the magnitudes of the entropy and heat capacity c_P for the solid, liquid, and gas phases. We can do this because

$$\begin{aligned}
 \frac{\partial G}{\partial T} &= -S \\
 \frac{\partial^2 G}{\partial T^2} &= \frac{-c_P}{T} \tag{205}
 \end{aligned}$$

Gibbs Phase Rule: If there are n phases of r species coexisting at equilibrium and constant temperature and pressure, then there are f degrees of freedom where

$$f = 2 + r - n \tag{206}$$

Binding Energy and Phase Change Rules:

Richard's Rule:

$$\Delta H_{\text{fusion}} = 9T_{\text{fusion}} \quad (207)$$

Trotout's Rule:

$$\Delta H_{\text{vaporization}} = 90T_{\text{vaporization}} \quad (208)$$

For a reaction



the enthalpy of reaction ΔH_r^0 is

$$\Delta H_r^0 = c\Delta H_C^0 + d\Delta H_D^0 - b\Delta H_B^0 - a\Delta H_A^0 \quad (210)$$

Stable equilibrium criteria:

At a relative minimum or maximum, $dU = 0$. Also, $d^2U > 0$, which guarantees a minimum.
At a constant temperature and pressure, two phases are in equilibrium if $G^\alpha = G^\beta$.

13.14 Joule-Thompson Expansion (Throttling)

Two volumes are connected by a valve, with the pressure on one side higher than the other side. The gas escaping from the higher pressure area moves (1) *isenthalpically* ($dH = 0$), (2) *irreversibly* ($dS > 0$), and (3) adiabatically (too fast to allow for heat transfer).

$$\begin{aligned} dH &= \partial Q_{P,N_1,N_2,\dots} \\ Q_{i \rightarrow f} &= H(V_f, P, N) - H(V_i, P, N) \end{aligned} \quad (211)$$

Here's a derivation of an equation useful when dealing with ideal gases that start at different pressures:

$$\begin{aligned} dU &= \partial Q + \partial W = \partial W \\ nc_V \, dT &= -P \, dV \\ V &= nRT/P \\ dV &= \frac{nR}{P} \, dT - nRT \frac{dP}{P^2} \\ (c_V + R) \frac{dT}{T} &= R \frac{dP}{P} \\ \left(\frac{T_2}{T_1}\right)^{cv+R} &= \left(\frac{P_2}{P_1}\right)^R \\ T_2 &= T_1 \left(\frac{P_1}{P_2}\right)^{R/c_P} \\ \mu_{JT} &= \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{c_P}(\alpha T - 1) \end{aligned} \quad (212)$$

and for an ideal gas, $\alpha = T^{-1}$ so $\mu_{JT} = 0$.

13.15 Material Properties (useful 2nd derivatives of energy functions):

$$\text{Thermal Expansion } \alpha: \left(\frac{\partial V}{\partial T} \right)_P = V\alpha \quad (213)$$

$$\text{Compressibility } \beta: \left(\frac{\partial V}{\partial P} \right)_T = -V\beta \quad (214)$$

$$\text{Heat Capacity } c_V: \left(\frac{\partial S}{\partial T} \right)_V = \frac{c_V}{T} \quad (215)$$

$$\text{Heat Capacity } c_P: \left(\frac{\partial S}{\partial T} \right)_P = \frac{c_P}{T} \quad (216)$$

$$\text{Magnetostriction } \gamma: \left(\frac{\partial V}{\partial H} \right)_{T,P} = V\gamma \quad (217)$$

$$\text{Magnetic Susceptibility } \chi: \left(\frac{-\partial M}{\partial H} \right)_{T,P} = -V\chi \quad (218)$$

13.16 Random constants we may need to know:

- $R = 8.314 \text{ Joules mol}^{-1} \text{ K}^{-1}$
- $N_A = 6.022 \times 10^{-23} \text{ mol}$
- $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$

14 Introduction to Statistical Mechanics

In the mixture of such gases by diffusion an increase of entropy would take place, although the process of mixture, dynamically considered, might be absolutely identical in its minutest details (even with respect to the precise path of each atom) with processes which might take place without any increase of entropy. In such respects, **entropy stands strongly contrasted with energy** ... In other words, **the impossibility of an uncompensated decrease of entropy seems to be reduced to improbability.**—

J.W. Gibbs, *On the Equilibrium of Heterogeneous Substances*, p. 167

Sorry! Nothing here right now. Stick to Rickard Armiento's notes, or the various texts listed in the syllabus. We are working on incorporating Prof. Armiento's excellent notes into the course notes directly.

15 Chemical potential as a function of composition

"A vague discomfort at the thought of the chemical potential is still characteristic of a physics education. This intellectual gap is due to the obscurity of the writings of J. Willard Gibbs who discovered and understood the matter 100 years ago." - Charles Kittel, Introduction to Solid State Physics

Readings: All of the below books cover the material in this section, but in different manners. I personally prefer Dehoff's treatment, then Lupis', and last Gaskell's.

R. Dehoff: 8.5-8.6

C. Lupis: 4.1-4.4

S. Gaskell: 8.6,8.7,9.1,9.2,9.3

15.1 Motivation

The chemical potential is homogeneous across a system at equilibrium. Understanding the chemical potential as a function of composition will allow us to understand phase equilibria. Further, when the chemical potential is inhomogeneous, elements diffuse and react down gradients in the chemical potential; the chemical potential is the driving force for chemical kinetics. Hence, if we can model the chemical potential, we have performed the first step in understanding the equilibrium and kinetics of any process where changes or gradients in composition occur such as phase equilibria, diffusion, solidification, etc. We thus need a convenient way to express the chemical potential as a function of composition, temperature, and pressure.³⁵

The first step in creating an interpretable model of chemical potential is to ask how we can measure the chemical potential. There are several ways we can measure the chemical potential well: by measuring vapor pressures, by using electrochemical methods to back out free energy changes, or by using calorimetry to back out free energy changes. Historically, chemical potentials were first measured in the gas phase. Hence, the vocabulary and formalism associated with the chemical potential was developed to have a close association with the gas phase. We trace the evolution of this formalism in hopes of providing insight into what the variety of terms in the formalism mean (as well as to define all of the terms you're likely to encounter in your materials career). As can be seen below, many authors have treated these derivations, and so I will not attempt to reproduce them, but merely to reproduce their results and give my own spin on the interpretation.

³⁵People spend a lot of money and time for such models! In fact, the primary reason software like Thermocalc is useful is because it has an accurate, empirical database for chemical potentials as a function of T , P , and n_i . Generating phase diagrams once you have such a database is relatively trivial.

15.2 Chemical Potential of ideal gases

2.1 μ in a single component ideal gas

The chemical potential of a single-component ideal gas is only a function of temperature and pressure. It can be derived to be (you can do this from simplifying the stat mech partition function, or see Craig Carter's notes ([link](#))):

$$\mu(T, P) = \mu_{\text{ref}}(T, P_{\text{ref}}) + RT \ln \frac{P}{P_{\text{ref}}} \quad (219)$$

letting $P_{\text{ref}} = 1 \text{ atm}$ is customary, assuming this convention we can write:

$$\mu(T, P) = \mu_{\text{ref}}(T) + RT \ln P \quad (P \text{ in units of atm}) \quad (220)$$

This is surprisingly useful, as it allows us to measure the chemical potential above a unary solid or liquid just by measuring the vapor pressure of the gas above it. However, this has limited utility for two reasons. The first: the gas must also be single-component for this to hold, and second: we are limited by the assumption of ideality of the gas. We deal with these two limitations in turn.

2.2 μ in a multicomponent ideal gas

You can also derive that the chemical potential of component i in a mixture of ideal gases is given by (see DeHoff, 8.5, or Craig Carter's notes ([link](#))):

$$\mu_i(T, P_i, P_{\text{total}}) = \mu_i^{\text{ref}}(T, P_{\text{total}}) + RT \ln \frac{P_i}{P_{\text{total}}} \quad (221)$$

where P_i is the partial pressure of a single component: $P_i = x_i P_{\text{total}}$, x_i is the mole fraction of i atoms in the gas, and P_{total} is the total pressure exhibited by the gas mixture. The reference state in this equation for each component is the individual gas at the total pressure of the gas mixture. The difference in chemical potential is thus due solely to the process of mixing the different, initially pure gases at constant total pressure. We see can re-write the chemical potential of component i in terms of its mole fraction:

$$\mu_i(T, P_i, P_{\text{total}}) = \mu_i^{\text{ref}}(T, P_{\text{total}}) + RT \ln x_i \quad (222)$$

Because the reference state already contains P_{total} , the $RT \ln x_i$ term is due solely to the presence of the other gas molecules, even though they don't interact. This term is thus a completely entropic effect. In fact, using $\underline{G}_{\text{solution}} = \sum_i x_i \mu_i$, we see that the $RT \ln x_i$ terms give rise to the ideal entropy of mixing from statistical mechanics (plugging the equation for μ_i above into \underline{G}):

$$\underline{G}_{\text{solution}} = \sum_i x_i \mu_i^{\text{ref}} + RT x_i \ln x_i \quad (223)$$

Terms of the form $RT \ln x_i$ in chemical potentials are thus always due to ideal mixing, whether in solid, liquid, or gas solutions.

15.3 Fugacity and dealing with non-ideal gases

We have removed the constraint of having a single component in the gas phase. It is now time to remove the constraint of ideality (i.e. to include interactions). Once we have developed a formalism for conveniently expressing the chemical potential of non-ideal solutions, this will be easily transferable to the description of condensed phases, where the solutions are frequently not ideal.

In the gas phase, we write the chemical potential of a non-ideal mixture of gases as:

$$d\mu_i(T, P, \{x_j\}) = RT d\ln f_i(T, P, \{x_j\}) \quad (224)$$

where f_i is the **fugacity** of component i , and is a function of T , P and composition. Integration of this differential form for the chemical potential gives us the chemical potential as a function of the fugacity, where we also need a reference state:

$$\mu_i(T, P, \{x_j\}) = \mu_i^{\text{ref}}(T, P_{\text{ref}}) + RT \ln f_i(T, P, \{x_j\}) \quad (225)$$

The reference state is typically the pure substance at one atmosphere and the given temperature. Note that all of the chemical behavior (ideal and non-ideal) for component i is contained in f_i , and that f_i is a function of all of the compositional variables and pressure.

In terms of interpretation, the *fugacity is the effective partial pressure of the gas if the gas were to behave ideally*. Fugacities for pure gases are frequently tabulated as a function of T and P . Hence, one can measure the chemical potential of a pure solid even in non-ideal gas conditions via measurement of the partial pressure above that solid and conversion to a fugacity. Further, fugacities for mixtures of gases generally behave pretty ideally: the fugacity of a single component i in a mixture of gases is usually very close to its mole fraction in the gas times the fugacity of the pure gas at the total pressure of the mixture:

$$f_{i,\text{mixture}}(T, P, \{x_j\}) = x_i f_{i,\text{pure}}(T, P) \quad (226)$$

Hence, using existing, tabulated fugacities, we can accurately estimate the chemical potentials of components in a solid or liquid solution from the corresponding gas phase equilibrium above the condensed phases. The chemical potential is now a readily measureable quantity, and not just an abstract concept.

15.4 Activity: adapting the fugacity formalism to condensed phases

The main difference between chemical studies of gases and those of liquids and solids is that we frequently change the pressure on gases during processing, but we rarely pressurize condensed phases during their processing. Further, the chemical behavior of gases under varying pressure can change significantly, while the chemical behavior of solids and liquids is much less sensitive to pressure: solids and liquids are much less compressible, and don't undergo a non-interacting-to-interacting transition as pressure increases. Hence, for most practical applications, we like to define the reference state for a solid's chemical potential at

the pressure that we are conducting our experiments at. This is in contrast to the fugacity, where the reference chemical potential is defined at 1 atm, and gives rise to a slightly different formula:

$$\mu_i(T, P, \{X_j\}) = \mu_i^{\text{ref}}(T, P) + RT \ln a_i(T, \{X_j\}) \quad (227)$$

this is the formula for the chemical potential as a function of the **activity**, $a_i(T, \{X_j\})$. Note that $\mu_i^{\text{ref}}(T, P)$ is a function of the pressure, and the activity defined for this reference state is not a function of pressure. However, for reasonable pressures, the chemical potential of condensed phases is so weakly dependent on pressure that we can approximate the activity to be equal to the fugacity:

$$a_i = f_i \quad (\text{low } P) \quad (228)$$

The activity is interpreted in a similar way to the fugacity: *activity is the effective concentration of component i in the solution if the solution were to be mixing ideally.* Another way of saying this is that a_i is the concentration component i “acts” as if it possessed in terms of its molar contribution to the free energy above μ_i^{ref} . To demonstrate this, we can again plug into the equation for the molar free energy:

$$\underline{G}_{\text{solution}} = \sum_i x_i \mu_i = \sum_i x_i \mu_i^{\text{ref}} + RT x_i \ln a_i \quad (229)$$

We also see from the above that if the activities are known, it is easy to calculate the free energy change upon mixing, which is the free energy of the solution minus the pure references: $\Delta\underline{G}_{\text{mix}} = \underline{G}_{\text{solution}} - \sum_i x_i \mu_i^{\text{ref}} = RT \sum_i x_i \ln a_i$. A negative free energy of mixing means mixing will be spontaneous, a positive free energy of mixing means the substances will be immiscible.

The activity is often written as an activity coefficient, γ_i , times the concentration of the solute:

$$a_i = \gamma_i x_i \quad (230)$$

This is convenient because when you take the log of this term, it automatically splits up into an ideal mixing contribution, and a term that contains all of the non-idealities (Note: γ_i is generally a function of composition and T ; it's not a constant in general):

$$RT \ln \gamma_i x_i = RT \ln x_i + RT \ln \gamma_i \quad (231)$$

The $RT \ln \gamma_i$ has units of energy and tells us whether the chemical potential of component i is higher or lower than we would expect from just ideal mixing. If the chemical potential is higher than we would expect from just ideal mixing, then there are unfavorable interactions in the solution and if the chemical potential is lower than we would expect from ideal mixing, there are favorable interactions in the solution.³⁶

³⁶The concepts of activity and the activity coefficient are covered well in DeHoff 8.6 and 8.7 (only 4 pages!), and more in depth in Lupis 4.1-4.4.

15.5 Models for activity

We'll now discuss common ways of thinking of the activity. Two of simplest models are those for an ideal (often called **Raoultian**) solution and a simply-interacting **Henrian** solution.

In an ideal solution: $a_i = x_i$. This is the simplest model for the chemical potential of a solution. In a Henrian solution, the activity coefficient is a constant: $a_i = \gamma_i x_i$. Doing the math out, you can see that this corresponds to a constant energy of interaction per solute atom ($\mu_i = \mu_{\text{ideal}} + RT \ln \gamma_i = \mu_{\text{ideal}} + \text{constant}$).

These are both useful models for dilute solutions. Solvents tend to behave in Raoultian (i.e. ideal) manner when a dilute solute is present. Physically, this says that dilute solutes do not affect the chemical potential of the solvent beyond the entropic effects of random mixing. Dilute solutes tend to behave as if none of the other solute atoms are present, because they are too far away from each other (i.e. feel like they are being put into a matrix of pure solvent). Therefore, the energy to add another solute atom is constant, and γ_i is constant.³⁷

In Henrian solutions, $\gamma_i < 1$ means that $\ln \gamma_i < 0$. Thus the solute has an energetically favorable interaction with the solvent. We call this a *negative deviation from ideality*, and these solutes have an enthalpic *and* entropic driving force for dissolution. These solutes are thus more difficult to get rid of during chemical purification than the case of positively deviating solutes. These solutes are often called *negative heat of mixing* as well, because the change in enthalpy upon mixing the solute and solvent together is negative.

Similarly, $\gamma_i > 1$ means that $\ln \gamma_i > 0$. Thus, the solute has an energetically unfavorable interaction with the solvent. We call this a *positive deviation from ideality*, and it actually costs energy to put these solutes into the matrix. It is relatively easy to purify out positive heat of mixing solutes from a matrix, and these solutions tend to phase separate as you cool them down. Lowering the temperature removes the entropic driving force for mixing, and the unfavorable interactions force the constituents apart. The activities as a function of composition are schematized for ideally mixing, negative heat of mixing, and positive heat of mixing binaries in Fig. 15.

³⁷Note: charged solutes, such as salts in water or aliovalent solutes in ceramics, have inherently long-range interactions. Their activity coefficients change very quickly with composition and should not be handled with a Henrian formalism, even in a dilute case.

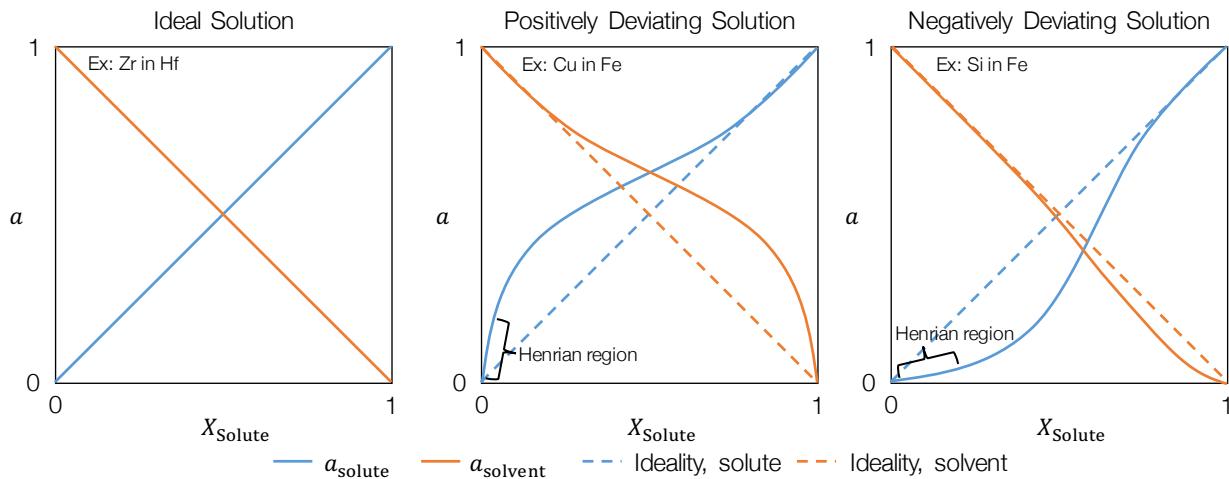


Figure 15: Schematics of activities as a function of composition for various binary liquid systems. In ideal systems (left), the activity is equal to the composition. In positively deviating systems (center), the activity falls above what would be expected from random mixing. In negatively deviating systems, the activity falls below what would be expected from random mixing. Note how the activity curves look like reflections of each other for Cu and Fe; metal-metal mixing is often like this due to the symmetry in bonding. In Si and Fe, the two are chemically dissimilar (they prefer different coordinations, etc), and the mixing is less symmetric. Note the approximately linear regions at dilute solute concentrations: this is where Henry's law applies.

16 Regular Solutions

16.1 The fundamental quantities in solution theory illustrated with Regular solution theory.

In the regular solution model, we make several assumptions:

1. The energy of the system can be described by pairwise bonds only.
2. The atoms mix randomly
3. All atoms have the same coordination

This gives rise to the following expression for the mixing quantities (note: this is written with a convention for the sign of \mathcal{W} which is opposite that from class to be consistent with

the Bragg-Williams model discussed later):

$$\Delta U_{\text{mix}} = X_B (X_B - 1) \mathcal{W} \quad (232)$$

$$\Delta S_{\text{mix}} = -k_B [X_B \text{Log} X_B + (1 - X_B) \text{Log} (1 - X_B)] \quad (233)$$

$$\Delta F_{\text{mix}} = \Delta U_{\text{mix}} - T \Delta S_{\text{mix}} \quad (234)$$

$$= X_B (X_B - 1) \mathcal{W} + T k_B [X_B \text{Log} X_B + (1 - X_B) \text{Log} (1 - X_B)] \quad (235)$$

If we assume that P - V effects are small relative to chemical effects, as is usually the case in condensed matter, then $\Delta G_{\text{mix}} \approx \Delta F_{\text{mix}}$, and so examining the behavior of Eq. 235 should yield all of the information needed to determine the chemical behavior of the system.

We often speak about the **heat of mixing** of a system, ΔH_{mix} . If we ignore P - V effects, then $\Delta H_{\text{mix}} \approx \Delta U_{\text{mix}} = X_B (X_B - 1) \mathcal{W}$ in the regular solution approximation. Therefore, $X_B (X_B - 1) \mathcal{W}$ represents the enthalpy change upon mixing A and B together in a random solution. A positive heat of mixing therefore corresponds to unfavorable bonding (the enthalpy/internal energy *rises* upon mixing), whereas a negative heat of mixing corresponds to a favorable pairwise interaction. Although the form of the heat of mixing is different outside of the regular solution model, it is general that a release of enthalpy upon mixing (i.e. an *exothermic mixing*) corresponds to more favorable interactions in the mixed state than in the unmixed state, and the opposite for endothermic mixing.

In class, we made a distinction between **mixing quantities** and **excess quantities of mixing**. The difference between these two is the reference state. In the case of the mixing quantities, they are defined as the difference between an extensive variable, Y , in the mixed state and those of the pure references:

$$\Delta Y_{\text{mix}} = Y_{\text{mixed}} - \sum_i x_i Y_i^{\text{ref}} \quad (236)$$

Excess quantities of mixing are defined as the difference between an extensive variable, Y , in the mixed state and that of the ideally mixed solution. The excess quantities of mixing are thus the deviations from purely random mixing:

$$\Delta Y_{\text{mix}}^{\text{XS}} = Y_{\text{mixed}} - Y_{\text{mixed}}^{\text{ideal}} \quad (237)$$

In the regular solution approximation, $\Delta S_{\text{mixed}} = \Delta S_{\text{mixed}}^{\text{ideal}}$ so $\Delta S_{\text{mix}}^{\text{XS}} = 0$. Note that in ideal solutions, the extensive variables which are unrelated to the entropy (ex: volume, magnetization, etc) are assumed to be linear superpositions of the pure reference states ($Y_{\text{mixed}}^{\text{ideal}} = \sum_i x_i Y_i^{\text{ref}}$), so $\Delta Y_{\text{mix}}^{\text{XS}} = \Delta Y_{\text{mix}}$ for extensive quantities other than the entropy and related quantities, like G .³⁸

16.2 Illustrating the common tangent construction using regular solution theory with positive heat of mixing systems

The assumptions of pairwise bonding can be easily simulated on a computer. Fig 16 shows such simulations for a positive heat of mixing solution at different compositions and temper-

³⁸ G being related to the entropy by $G = H - TS$, of course.

atures, with solute atoms in black and solvent atoms in green.³⁹ At low temperatures, the system doesn't form a homogeneous solution. Instead, it phase separates. At high enough temperatures, the phases are driven to dissolve by configurational entropy. We can explain this with the free energy curves from the regular solution model.

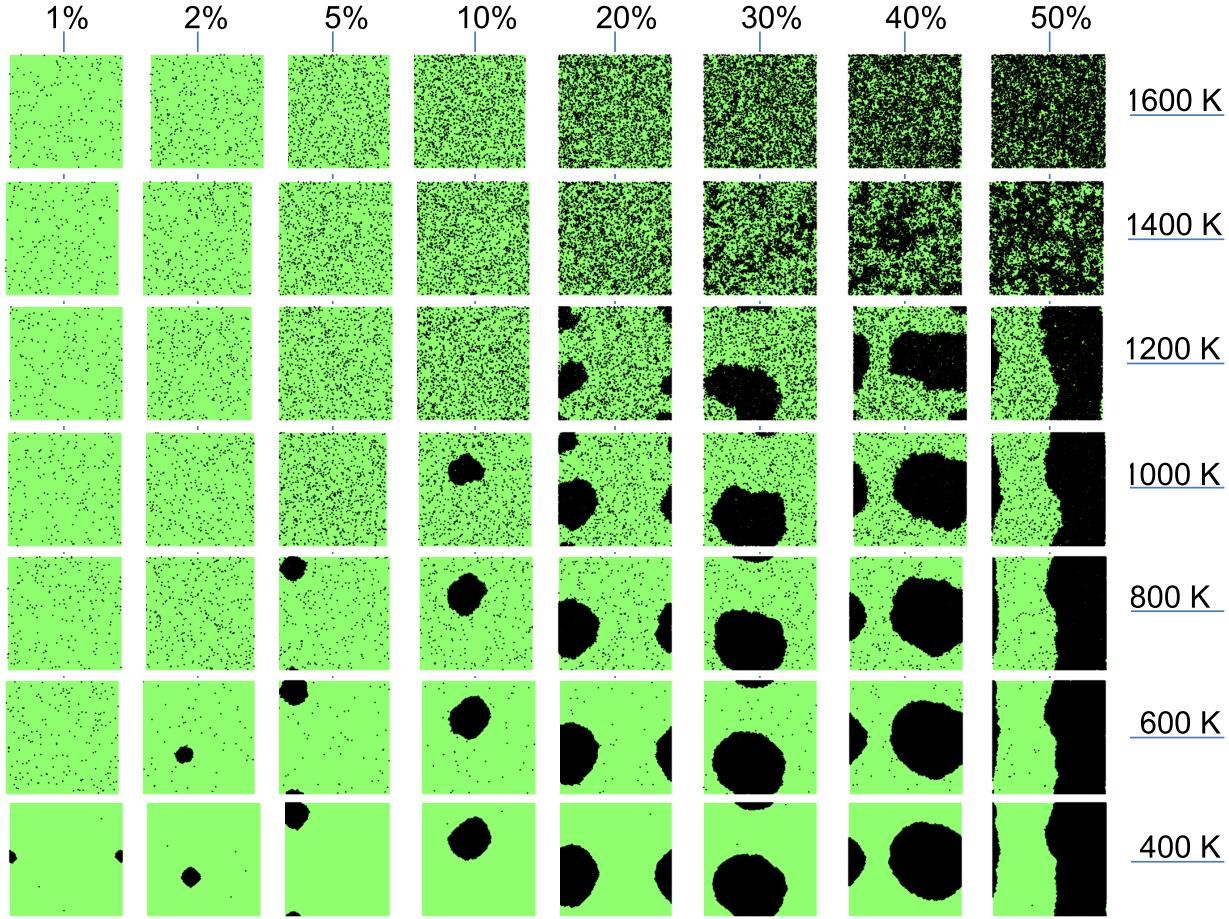


Figure 16: A visual phase diagram for phase separation: snapshots of solute distributions from Monte Carlo simulations of positive heat of mixing systems showing phase separation at low temperatures, clustered solid solutions at intermediate temperatures, and fully random solutions at high temperatures.

The free energy curves for the same positive heat of mixing solution as a function of composition under the regular solution approximation are shown in Fig. 17. Importantly, the molar Gibbs free energy of a combination of two solutions with different compositions, X_1 and X_2 is just given by adding up the free energies of the two solutions times their volume fractions, f_1 and f_2 :

$$G_{\text{two solutions at } X_1 \text{ and } X_2} = f_1 G_{X_1} + f_2 G_{X_2} = f_1 G_{X_1} + (1 - f_1) G_{X_2} \quad (238)$$

³⁹The simulations were performed by Tongjai Chookajorn using Monte Carlo, a formalism based on statistical mechanics.

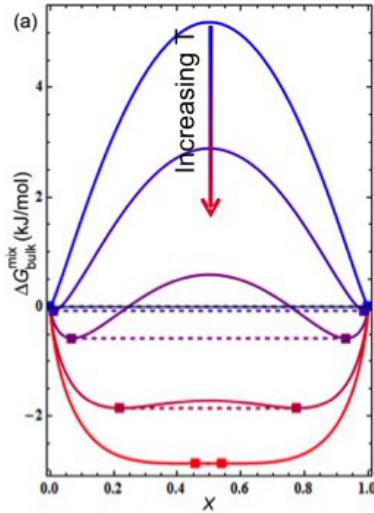


Figure 17: Free energy curves for the regular solution model with a heat of mixing of 30 kJ/mol at various temperatures.

You can think of this as taking linear superpositions of the free energies of two separate solutions. This means that there are points on this curve (marked with squares) where **the solution can lower its free energy by decomposing into two solutions of different composition**. This is exactly the condition for when phase separation will occur at equilibrium: two macroscopic systems would spontaneously form with measurably different thermodynamic properties. This is illustrated by the dotted lines on the figure above.

Thus, the endpoints of these **common tangents** between the curves represent phase boundaries: the unfavorable interactions between A and B cause immiscibility between these endpoints. Solving for these endpoints as a function of temperature gives a phase boundary: the miscibility gap. Fig. 18 shows the solution to the phase boundary in regular solution theory along with microstructures corresponding to each numbered point.

You may notice that the phase boundaries in the simulation seem to be depressed relative to the predictions from regular solution theory (i.e. the microstructures don't quite match up with what you would expect from the phase diagram). This is because of the approximations inherent in the regular solution approximation that are not needed to perform a Monte Carlo simulation. In particular, the solutions exhibit **short range ordering**. Short range order (SRO) is defined statistically: it is a *correlation* between the site occupation at one site and the site occupation at another site (note: random mixing means no correlations between sites, so solutions with SRO are not random).⁴⁰ In this case, the black atoms prefer to be next to each other energetically, so they tend to appear next to each other, even once the precipitates dissolve; they form clusters.

Unsurprisingly, this type of short range order is called **clustering**, and is typical of positive heat of mixing systems. Clustering permits the solution to lower its free energy relative to random mixing. This stabilizes solutions to lower temperatures compared to the regular so-

⁴⁰We'll define short range order more rigorously soon.

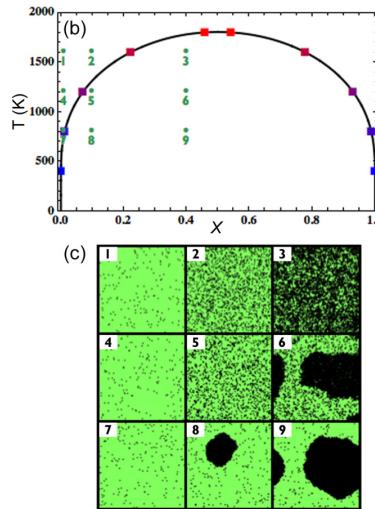


Figure 18: A comparison of the miscibility gap from regular solution theory to Monte Carlo results.

lution's ideal mixing-based estimate. However, clustering, like other forms of SRO, decreases the entropy of a solution, and thus the degree of clustering should decrease with increasing temperature. If you compare the solutions at 1400K and 1600K in the first figure, you can actually see the degree of clustering in the solution decrease at higher temperatures: there are real 'clusters' of solute atoms just above the miscibility gap, and they go away when you heat the solution up more.

In class, we showed that there is a critical temperature, T_{crit} , at which we have full miscibility (a.k.a. the top of the miscibility gap, also called the *upper consolute temperature* by people who like to use big words to sound smart). This occurs when no part of your curve is concave down anymore. In the regular solution model, the $X = 0.5$ point is the last point to remain concave down as a function of temperature (you can see it in the figure above). Solving for the temperature at which $\frac{\partial^2 G}{\partial X^2} = 0$ at $X = 0.5$ gives T_{crit} as a function of the regular solution parameter, \mathcal{W} .

Exercise: Solve for T_{crit} in the regular solution model.

16.3 Negative heat of mixing systems: Taking compound formation into account

What happens if the interactions between A and B atoms are *favorable* instead of unfavorable (i.e. $\mathcal{W} < 0$ such that

$$\Delta H_{\text{mix}} = X_B (X_B - 1) \mathcal{W} < 0?$$

Well, the regular solution in its original form isn't that informative, as both entropy and enthalpy favor mixing. You would simply conclude that A and B are miscible in all proportions. This is most of the story for polymers, for which it is extremely difficult kinetically to form ordered compounds. However, most other materials systems can form ordered compounds. For example, ordered oxide, semiconductor, and metallic compounds are all extremely common. An **ordered compound** in the regular solution view of things is simply a material

which introduces **long-range order** such that it maximizes the number of favorable A-B bonds. The difference between an ordered compound and a solid solution is shown in Fig 19 for the case of a 2D square lattice.

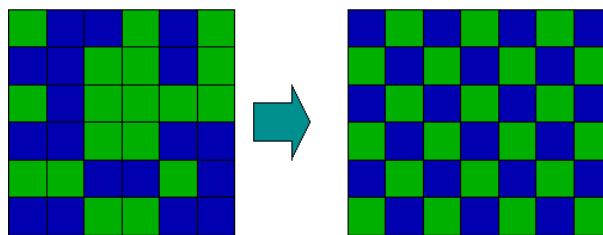


Figure 19: A schematic of ordered compounds versus solid solutions.

16.4 Short-range versus longe-range order

Both short range order and long range order are defined in terms of being able to predict the environment of an atom. Crystals all possess long range order: if I know the position of one atom (and the orientation of the crystal's axes), I know the position of all atoms in the crystal: you just start repeating the unit cell through space. The range over which I can predict atomic positions thus only limited by the size of the defect-free crystal. You could represent this correlation by plotting the radial distribution function (RDF, http://en.wikipedia.org/wiki/Radial_distribution_function) of a crystal. For a perfect crystal, you just get a series of Dirac δ functions at the nearest neighbor distances, as all the atomic distances are perfectly defined. More realistically, for a crystal at non-zero temperature, the RDF's δ functions get 'smeared' out by atomic vibrations. The black line in Fig. 20 is a realistic RDF for FCC Au at 300 K. Long range order may be considered in contrast to **short range order**, which is defined as when knowing the position of one atom gives you information on the positions of atoms nearby, but not necessarily those far away.⁴¹ Short range order is usually characteristic of liquids. For example, taking the same element, Au, in the liquid state yields a very different RDF, shown in red over the crystalline RDF (same source). Notice how the length over which the correlation is not equal to one (called the correlation length of the RDF) is much smaller in the liquid state compared to the solid state: the atomic ordering is *short-ranged*!

Generally, the key distinction is that long range order is a result of crystallography; order in the crystal is inherently long-ranged. Short range order, on the other hand, is only defined only *probabilistically*, and usually over limited length scales on the order of a few atomic distances. Both of these concepts apply to solid solutions and ordered compounds as well.

Compound formation is thus defined crystallographically; it is defined by the existence of preferred sites in the unit cell for each element. There is thus a long range order associated with the positions of the different alloying elements, and the correlation length between

⁴¹Most rigorously, the *correlation length* for longe range order is infinite (or the size of you crystal), whereas for SRO the correlation length is finite (usually a small number of nearest neighbor shells).

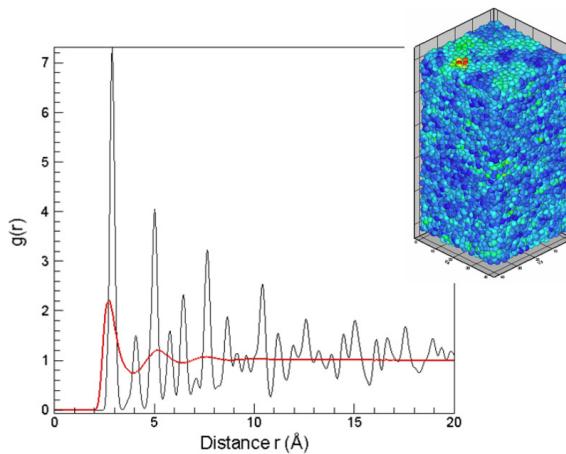


Figure 20: A comparison of radial distribution functions representing short range and long range order in solid (black) and liquid (red) Au. ([source](#))

the positions of the A and B atoms is thus on the order of the length scale of the defect-free crystal. Short range order for alloys, on the other hand, is usually only discussed for solutions. In this case, there are no preferred sites for A or B atoms, but knowing that an A atom sits at one site likely gives you information about the atoms surrounding that atom, as the A atom likely has an energetic preference for the chemical identity of its nearest neighbors. You could quantify this in a similar manner by comparing the radial distribution functions for A and B atoms, and then backing out nearest neighbor probabilities, etc.

16.5 Negative heat of mixing systems and ordering

The problem before us then became to determine when a material wants to form an ordered compound as opposed to a solid solution. However, the appearance of ordering does not mean that the regular solution approximation ceases to have utility for negative heat of mixing couples which form compounds. How do we extend regular solution theory to ordered compounds? Well, we do this with sublattices, which can have different concentrations. Fig 21 shows an example of two rectangular sublattices forming a face-centered lattice.

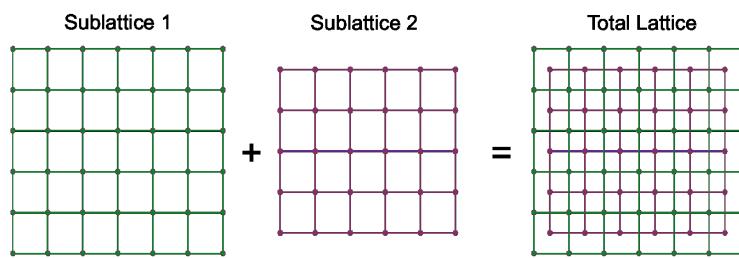


Figure 21: Two sub-lattices forming a new lattice (modified from [here](#)).

Usually, one sub-lattice is very A-rich, and the other is very B-rich, and each sublattice

is primarily or completely bonded to the other sub-lattice. Hence, the partitioning of the elements to the different sublattices maximizes the number of favorable A-B bonds, and is enthalpically favored. However, if the concentrations of A and B on their respective sublattices are near unity, then the configurational entropy on each sublattice is approximately zero, so increased order comes with an entropic penalty.

There should thus be a balance in the competition between the enthalpically favorable and entropically unfavorable contributions to the free energy from the ordering process.

The degree of ordering was quantified by assuming a random solution on each sublattice and defining an order parameter, η , such that when $\eta = 1$ the superlattice is maximally ordered, and when $\eta = 0$, the lattice is just one homogeneous solution. The free energy at a given temperature and composition is minimal with respect to changes in the degree of ordering at equilibrium: $\left(\frac{\partial G}{\partial \eta}\right)_{T,P,\mu_i} = 0$. Another way of saying this is that there is an equilibrium amount of order for a given temperature, pressure, and composition of a phase. This is the same concept as there being an equilibrium amount of vacancies at a given temperature; in this case we are just considering the formation of a different kind of defect (antisite defects) as opposed to vacancies. This allows one to plot (or measure experimentally) the equilibrium order parameter as a function of T .⁴²

⁴²FYI, the model presented in class is the Bragg-Williams model, and is usually used for BCC order-disorder transitions. There is a *Mathematica* notebook from Profesor Emeritus Sam Allen which I have uploaded to Stellar which goes through this model in detail. The Bragg-Williams model is another classical example of the competition between entropy and enthalpy in determining phase behavior as a function of temperature.

17 The Physical Basis of Mixing

This section was heavily influenced by Professor Gerbrand Ceder's lectures on mixing. A lot of credit for the structure and insight in this section goes to him.

In this section, we will elucidate the physical reasons why some pairs of elements mix together to form random solutions and/or compounds, whereas others are immiscible. We will call this general process of allowing two elements to come together *mixing*. It is illustrated in Fig. 22. We will mostly restrict ourselves to the solid state. From a thermodynamic perspective, pairs of elements mix because the free energy of forming the solution is negative relative to the pure state, $\Delta G_{\text{mix}} < 0$. An element is immiscible in another if $\Delta G_{\text{mix}} > 0$. It is useful to split ΔG_{mix} into its component parts, ΔH_{mix} and ΔS_{mix} in order to understand why mixing occurs. We'll begin with ΔH_{mix} , and then address ΔS_{mix} .

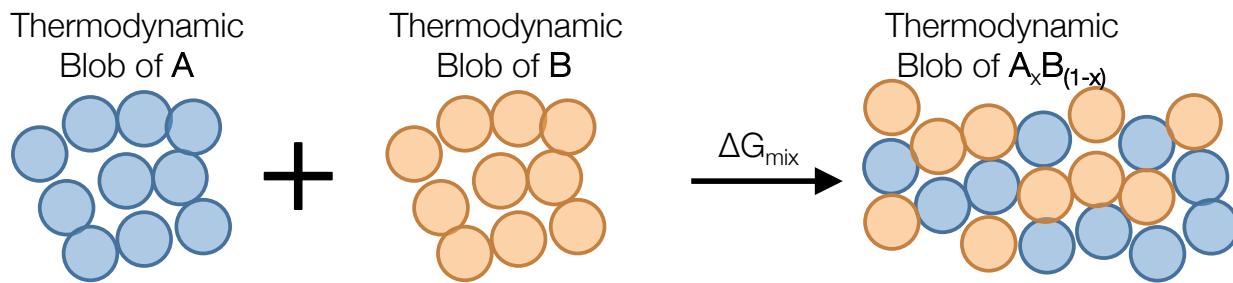


Figure 22: The process of mixing. Note: A_xB_{1-x} can be a compound or a random solid solution. It's depicted as a general blob here to emphasize the generality of the mixing process.

17.1 Energetic Effects on Mixing

As $p\Delta V$ terms are generally negligible in the solid state, we will discuss the energy of mixing, ΔE_{mix} , instead of the enthalpy of mixing. In practice, this is convenient because simulations are often pretty good at calculating energies, by e.g. quantum mechanical methods. In fact, quantum mechanics is used to compute ground state energies of compounds quite often, and there are now large bodies of computed energies of compounds available online, for example at the [Materials Project](#), and the [Open Quantum Materials Database](#). Between these online resources and compendiums of experimentally-determined enthalpies of formation like the [Janaf Tables](#), you will almost never have to determine the enthalpy/energy of formation of a compound. Therefore, this section will try to explain why certain pairs of elements interact the way they do, rather than to provide detailed values. This amounts to the creation and examination of heuristics for mixing.

Some possible heuristic rules for mixing are the following. We'll discuss them in more detail below.

- Size: The hypothesis would be that atoms might mix well if they are the same size; they need to fit together.
- Crystal Structure: The hypothesis would be that elements with the same crystal structure should mix. This turns out to be a bad heuristic. Don't use it.
- Electronegativity (χ): The hypothesis would be that a large difference in electronegativity should drive compound formation due to charge transfer: large $\Delta\chi$ should be associated with large, negative energies of compound formation.
- Valency: One might also hypothesize that there should be some relationship between the number of valence electrons that each mixing element has to promote mixing.
- The Miedema Rules: A set of rules developed by Miedema and co-workers to predict whether transition metals will form compounds or be immiscible which worked astoundingly well. It turns out Miedema got the right result, but got the physical picture entirely wrong, so we won't get into his theory.⁴³

1.1 Is size a good predictor of mixing behavior?

Size is indeed a good predictor of mixing behavior, especially in terms of forming solid solutions: two elements can only coexist in a lattice if they both ‘fit’ in the same sites. More specifically, in metals, Hume-Rothery found that large ranges of solid solubility are only found for pairs of elements whose atomic radii differ by less than 15%.⁴⁴ This behavior comes about because there is an energetic penalty associated with the straining of an atom to fit in a given site. Note that this rule is a necessary but not sufficient condition for solubility: it tells you when dissolution is possible, but doesn't guarantee when it will occur. This is because it only considers *size*, but there's a lot more going on when you mix two things together: bands can hybridize, charge transfer can occur, and chemical bonds can form. These are what one might call chemical effects. Atomic size differences determine miscibility in the absence of chemical effects.

The effects of atomic size are not limited to metals; similar size-based arguments hold for the mixing of other systems where chemical effects are small. For example, when you mix isovalent⁴⁵ oxides, there really isn't any chemistry going on; the cations are separated from one another by the oxygen atoms and the cations' charge remains the same. Therefore, the biggest factor in determining whether two isovalent oxides mix is whether they can fit on the same lattice in terms of their sizes. Similarly, the miscibility of solutions of semiconductor

⁴³For a proper discussion of cohesion in transition metal alloys, and why Miedema got it wrong, see: *A Quantum-Mechanical Critique of the Miedema Rules for Alloy Formation*, D.G. Pettifor, Solid State Physics **40** 1987 ([link](#))

⁴⁴Hume-Rothery developed a series of rules for the mixing behavior of metallic solutions based on the properties of the elements, called the Hume-Rothery rules. The 15% rule is the first Hume-Rothery rule. They're very useful, even if they're a bit primitive compared to quantum mechanics.

⁴⁵Isovalent means *having the same charge*; a isovalent oxides would be CaO and MgO, where both cations have the same charge, +2, as compared to Al₂O₃ and MgO, where the cations have different charges.

compounds with from the same families⁴⁶ is mostly determined by atomic size arguments.

1.2 Is electronegativity a good predictor of mixing behavior?

Of all the heuristics commonly discussed in the literature, electronegativity differences have the largest effects on mixing. It is generally true that larger differences in electronegativity between two elements, are correlated with a greater the tendency for compound formation. Further, $|\chi_A - \chi_B|$ is correlated with more negative the enthalpies of formation, as shown in Fig. 23.

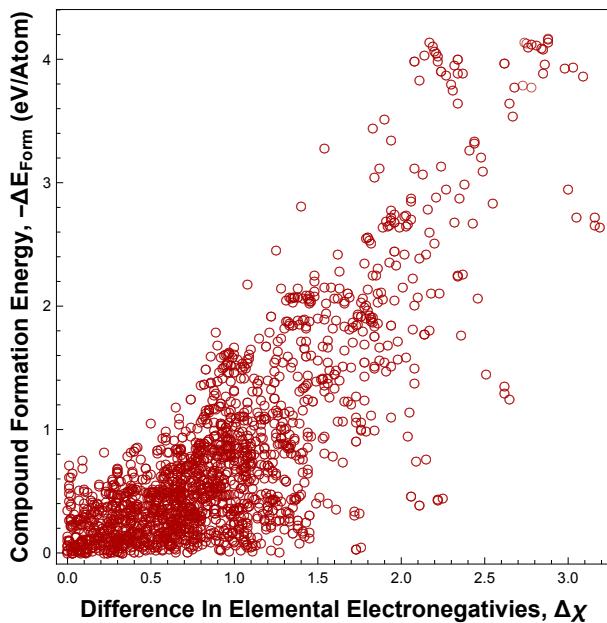


Figure 23: Elemental compound formation energies per atom (the energy to form the compound from the pure constituents), versus the difference in electronegativities for the constituent elements, $|\chi_A - \chi_B|$. Data from the [the materials project](#), via their [RESTful interface](#). (Figure original to these notes, do not distribute.)

There are actually two mechanisms at work in explaining why electronegativity differences are correlated with compound formation. We can explain the mechanism with a bit of band theory and an understanding of what electronegativity means physically. Intuitively, electronegativity is the tendency of an element to pull electrons from its neighboring elements. What this means physically is that a highly electronegative element has low energy, empty states above its Fermi level. Ignoring the effects of hybridization between energy levels, electrons from other elements with higher Fermi levels could lower their energy by occupy those lower energy states. Therefore, when another, less electronegative element (with a higher Fermi level) is brought into contact with a more electronegative one, the electrons from the less electronegative element are transferred to the more electronegative element. This process is shown in Fig. 24. This charge transfer is essentially what happens in ionic

⁴⁶e.g. the alloying of III-V compounds with one another versus alloying a III-V with a II-VI

bonding; the electrons from one element are transferred to the other, filling the lower-energy band up, and emptying the higher energy band.

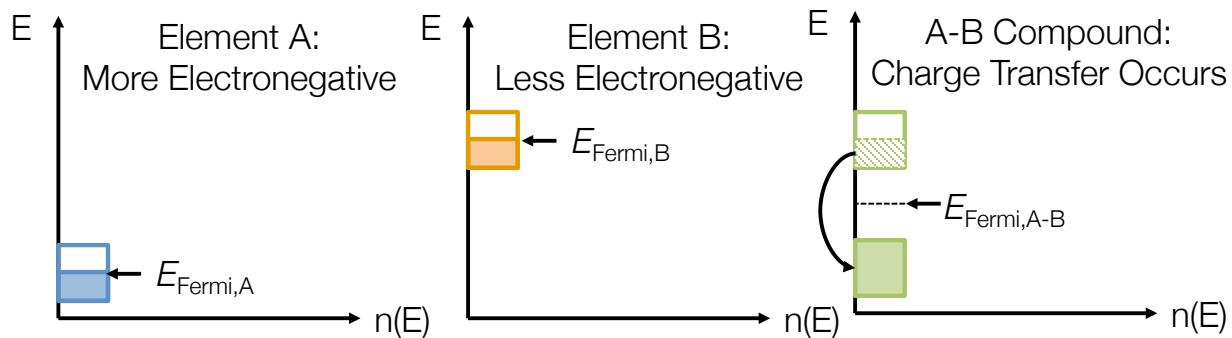


Figure 24: A schematic of charge transfer for the case of large electronegativity differences. The three panels are flipped density-of-states diagrams. The high-energy valence electrons of B are transferred into the empty states above the Fermi level of A. When compounds form, stoichiometry is generally optimized so that maximal charge transfer occurs (e.g. Al donates three electrons when forming an oxide, while O only accepts 2, leading to the Al_2O_3 stoichiometry), meaning the low-energy band is completely filled, and the high energy band is completely empty. This is why ionic compounds are insulators.

The physics are different when compounds form when there are small differences in electronegativity, typically with pairs of transition metals. Note that in this case, we can't ignore hybridization because the bands overlap. Compound formation between pairs of transition metals is also well-predicted by electronegativity differences, but we know from *ab-initio* studies that charge transfer does not occur in transition metal compounds; the bands overlap (and thus hybridize when alloyed), and the valence electrons are not well-localized. Therefore, we know that electrostatics isn't actually driving compound formation in binaries with low $\Delta\chi$; electronegativity differences are a red herring here.

What's actually happening in transition metal alloys is a metallic version of the octet rule; the bands in metals like to have certain occupancy levels. You can derive from tight-binding arguments that the doping energy of a d -band should be maximal when the d -band is half full ($N_d = 5$); think of this as filling all the bonding states in the d -band but none of the antibonding states. The process of band filling in TM's is schematized in Fig 25. Data supporting the band-filling arguments are shown in the lower left-hand panel of Fig. 26.

Thus, when two transition metals are mixed, compounds will form when the two metals can achieve a d -band occupancy of around 5 on average. Therefore, early transition metals with $N_d < 5$ tend to form compounds with late transition metals with $N_d > 5$. As electronegativity is lowest for the early transition metals and highest for the late transition metals, electronegativity is well-correlated with this d -band filling criterion, but electronegativity differences do not cause this phenomenon.

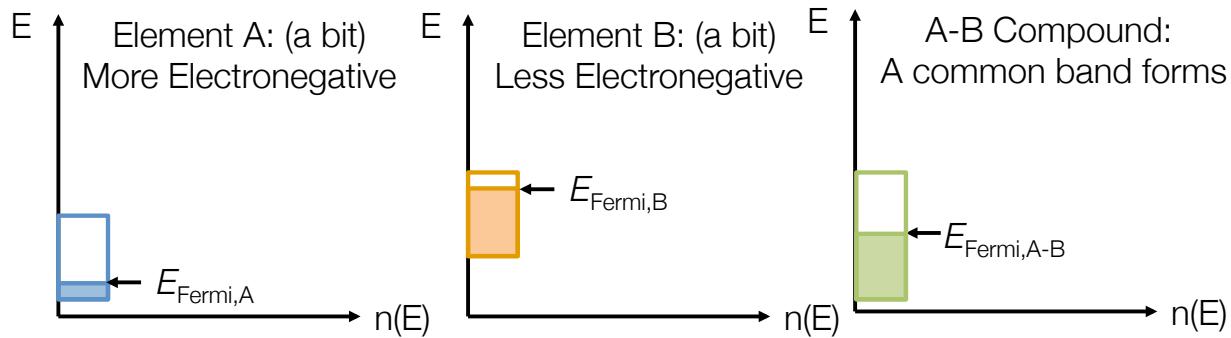


Figure 25: A schematic of band hybridization for the case of small electronegativity differences. The three panels are flipped density-of-states diagrams. The d-band of element A is underfilled, while the that of element B is overfilled. When the two bands hybridize, the filling is much closer to the optimal halfway mark. After Pettifor, DG *Quantum mechanics in alloy design*, in Alloy Phase Stability, eds. Stocks and Gonis, 1989.

1.3 Is Valency a good predictor of mixing behavior?

Valency is in fact a good predictor of mixing, but it's beyond the scope of this course. In fact, the number of valence electrons per atom, called the *electron over atom ratio* n/a , strongly controls cohesion and stability of crystal structures in metals. This is for similar, quantum mechanical reasons as above: n/a controls where the Fermi surface is, and a metal has the lowest energy when the Fermi surface just touches the edge of the first Brillouin zone. As different crystal structures achieve this touching at different n/a , different crystal structures are favored at different n/a . By introducing progressively more alloying element into a crystal structure, you are effectively 'scanning' the Fermi energy by changing the number of valence electrons. In doing so, the metal adopts different crystal structures which optimize the location of the first Brillouin zone relative to the Fermi energy. Thus, n/a arguments (along with size arguments) generally justify the progression of crystal structures within a binary, while band-filling arguments justify whether or not compounds form at all. The influence of the electron-over-atom ratio was first realized empirically by Hume-Rothery, and then explained quantum-mechanically by Mott. A really good discussion of this is in Mott, NF. *Reports on Progress in Physics* 1962 ([link](#)).

17.2 Entropic Effects on Mixing

Knowledge of the internal energy allow us to predict mixing behaviors at low temperatures. At higher temperatures, we must also take into account the entropy of the mixed and unmixed states. There are several types of entropy one could consider:

- Configurational Entropy: the number of different ways you could arrange the molecules on a lattice or in a liquid solution. This is essentially given by site occupation probabilities and correlations. This is the entropy that drives solutions to mix at higher

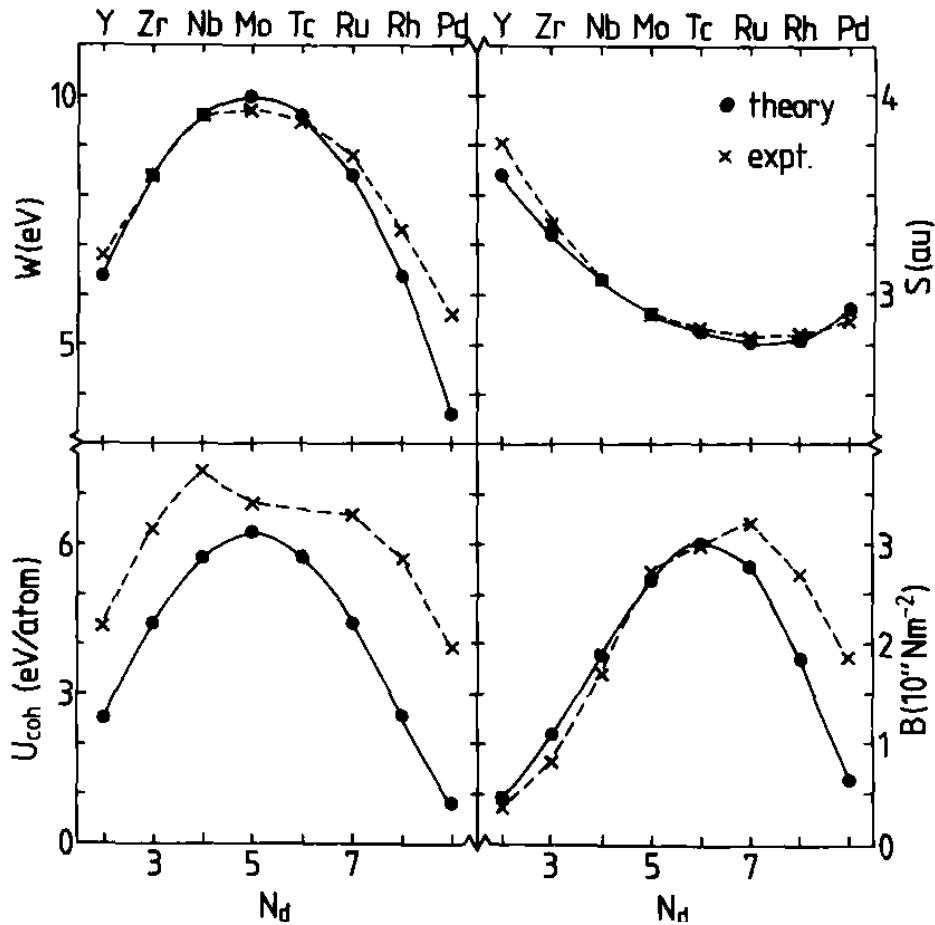


Figure 26: Theoretical predictions of transition metal properties according to tight-binding as a function of the number of d-electrons. The cohesive energy, U_{coh} is in the bottom left. You can see that tight-binding predicts most properties pretty accurately from considering the d-electrons alone. Other properties depicted are the d-band width (top left), Wigner-Seitz radius (top right), and bulk modulus (bottom right). From Pettifor, DG. *Solid State Physics* 1987

temperatures. Other entropies may support or oppose mixing.

- Vibrational Entropy: the frequency/amplitude of vibrations gives more states at each site (Think Debye and Einstein models for the heat capacity).
- Translational Entropy: In the gas phase, the translational entropy is extremely large. Note: in the limit of large vibrations, translational entropy should be the same as vibrational entropy.
- Electronic Entropy: In some systems, the electrons can be thermally excited into many different states. This can end up affecting phase stability.
- Magnetic Entropy: Disordering or ordering of spins gives rise to magnetic entropy.

2.1 Configurational Entropy

This is the entropy that we usually think of when mixing occurs with increasing temperature; it drives solubility limits, as well as order-disorder transformations. To first approximation, the configurational entropy is given by the random mixing entropy:

$$S_{\text{configurational}} = -k_B \sum x_i \ln x_i \quad (239)$$

2.2 Vibrational Entropy

The vibrational entropy should be proportional to the number of vibrational quantum states within $k_B T$ of the ground state. As we know from quantum mechanics and our study of the Einstein model, the spacing of energy levels in a quantum harmonic oscillator is proportional to the frequency of the oscillator, and thus proportional to $\sqrt{k/m}$.

What this tells us is that for a given element and/or composition, (i.e. if m is constant), softer phases should be favored at higher temperatures, as the system gains access to more vibrational states due to their lower spacing between energy levels.

As a rule, BCC phases tend to be softer than FCC/HCP phases, so you would expect to observe closed packed \rightarrow BCC transitions upon heating. This does indeed occur: Zr, Ti, and Hf all exhibit such transitions, as does Fe in the γ to δ transition at very high temperatures.⁴⁷ Some of the alkali metals (e.g. Li and Na), which we traditionally think of as BCC, are actually close-packed below room temperature; their melting temperatures are just so low that their vibrationally-driven transitions occur much earlier than in the more cohesive transition metals. These allotropic phase transitions tend to be very important in microstructure evolution during solidification. For example, Ti and Fe are very weldable metals because they undergo allotropic phases transformations. Thus, vibrational entropy does play an observable and important role in the behavior of materials.⁴⁸

2.3 Electronic Entropy

Please refer to the [wikipedia page on electronic entropy](#). It was authored specifically with this course in mind.

⁴⁷The low-temperature BCC phase, α -Fe, is stabilized by magnetic effects. One can stabilize the FCC by alloying, typically with Ni.

⁴⁸Note: We restricted our discussion to the elements because only the acoustic modes are really proportional to the moduli (and thus the stiffness) of a material, so only the acoustic contribution to the vibrational entropy can be explained from moduli. The optical modes are fairly independent of the moduli. This approximation works for the elements because they have very simple unit cells, and so there aren't optical modes!

18 Bonus Topic: Chemical thermodynamics of polymers

This section will attempt to apply much of what we have learned in 3.20 to systems that we didn't touch as much in class: polymers.⁴⁹ The reason is not because polymers are too complex, but rather because if we taught chemical thermodynamics from the perspective of polymers, it would often be too simple.⁵⁰ By the end of this, you should develop a fairly good intuition for what happens when you blend two polymers together.

Polymer scientists rarely use phase diagrams. This is for several reasons. First, there are way more polymers than there are elements, so the number of polymer phase diagrams would be extremely large. Even such details as the polymer's molecular weight have a significant influence on phase behavior. Second, polymers simply don't mix very well: they tend to phase separate, or be *immiscible* in the language of polymers. Even when they are miscible (e.g. soluble), they never form compounds, so really, there are only two basic phase behaviors for polymers: miscible, and immiscible, with most polymers being immiscible. We'll illustrate this with a simple example.

Consider blends of deuterated and non-deuterated polybutadiene.⁵¹ The only difference between the two polymers being blended is that one polymer has hydrogens that don't have a neutron (called protium), while the other polymer has hydrogen atoms that contain a neutron (called deuterium). These polymers should thus behave identically chemically, and we might naively expect them to form an ideal solution. Compare this expectation to the experimentally-determined phase diagram in Fig 27, where we see that the chemically 'identical' polymers exhibit a miscibility gap up to 333 K (60 °C), which is a fairly high temperature for a polymer. In polymer science, the critical temperature at the top of the miscibility gap is called the upper critical solution temperature, abbreviated UCST. Of course, polymers which differ in their chemistry can be expected to exhibit significantly larger interactions than those between two polymers which differ merely in their isotopes, and so their UCST values are often much higher. So, we see that somehow, our intuition for what drives mixing is off in polymers.

18.1 Why don't polymers mix when we heat them up?

It turns out that the reason polymers don't mix well is because polymers are highly correlated in terms of their atomic positions: each repeat unit is chemically bonded to all of the others, and so the configurational entropy of a polymer chain is greatly reduced relative to the same number of monomers. Thus, the configurational driving force for mixing is greatly reduced

⁴⁹This section was inspired by and draws heavily A.H. Windle's *A metallurgist's guide to polymers*, in Physical Metallurgy, eds. Cahn and Haasen, 1997. Since MIT teaches materials science from a metallurgist's perspective, this article is an especially good intro to polymers for people trained in MIT's department.

⁵⁰The other reason is that polymers often don't come to true equilibrium: those long chains can often make the approach to equilibrium *slow*.

⁵¹Polymer scientists use the term *blend* for what others materials scientists might call mixtures or alloys.

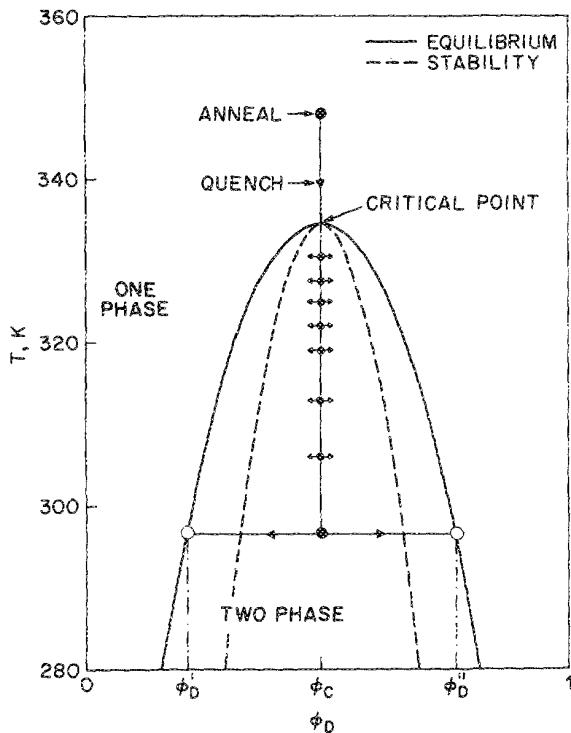


Figure 27: The phase diagram for mixtures of deuterated and protonated polybutadiene with $N_i \approx 3200$ formula units each exhibiting a miscibility gap (UCST) at 60 °C.

as well. More quantitatively, the entropy of mixing of a polymer was given approximately by Flory and Huggins as:

$$\Delta S_{\text{mix}} = -R \left[\frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 \right] \quad (240)$$

where ϕ_i refers to the volume fraction of monomers of component i , and N_i is the number of monomers per polymer chain for polymeric component i . Note the similarity to the ideal entropy of mixing of a molecular solution: $\Delta S = -k_B \sum x_i \ln x_i$; the volume fractions of monomers, ϕ_i , are exactly analogous to the concentrations x_i . However, the entropy terms are divided by the degree of polymerization of each polymer. It's as if each polymer is 'ball' that is ideally mixing instead of each molecular unit ideally mixing. As the degree of polymerization is usually on the order of 1000 or more, *the configurational entropy of mixing of polymers is approximately three orders of magnitude smaller than that of molecular solutions (or even smaller)*.

The natural next step in discussing the mixing of polymers is to define an enthalpy of mixing, such that we can write out the free energy of mixing. Generally, a version of the regular solution approximation is sufficient to describe the enthalpy of mixing of polymers. Polymer scientists like to write the free energy of mixing as:

$$\Delta G_{\text{mix}} = RT \left[\chi \phi_1 \phi_2 + \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 \right] \quad (241)$$

This is called the *Flory-Huggins equation*. Looking closely, you can identify the enthalpy of mixing as:

$$\Delta H_{\text{mix}} = RT\chi\phi_1\phi_2 \quad (242)$$

Again, there is a close analogy here between the concentrations x_i from metallurgical alloy theory and the volume fractions ϕ_i in polymer mixing. In the regular solution approximation, $\Delta H_{\text{mix}} = z\omega x_1 x_2$, so we see that $RT\chi$ is then analogous to the pairwise interactions between polymers, just as $z\omega$ represented the pairwise interactions between alloying elements in regular solution theory. It might at first strike you as silly that polymer scientists write an enthalpic term as proportional to the temperature, as it looks like an entropic term. Indeed, from the perspective clearly separating enthalpies and entropies, this is inconvenient, and χ itself must be temperature-dependent even to model temperature-independent interactions in the blend. However, the Flory-Huggins free energy offers a great convenience for polymer scientists in that it is easily non-dimensionalized:

$$\frac{\Delta G_{\text{mix}}}{RT} = \chi\phi_1\phi_2 + \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 \quad (243)$$

Remember, the phase behavior of a system is not controlled by the absolute scale of the free energy, but by the *shape* of the free energy curves. Thus, this normalization just serves to eliminate temperature as a needed thermodynamic descriptor for polymeric system. There are thus only three variables needed to describe mixing for all polymers that behave according to Flory-Huggins theory: χ, N_1, N_2 . The Flory-Huggins expression is thus useful for polymers because it is so transferable across systems, and the number of systems in the polymer world is very large. As you might be able to infer from this discussion, χ is a very important parameter in polymer science.

So, what is generally the sign of χ ? Well, the chemical adage *like dissolves like* is very useful in understanding miscibility in polymers. Nothing is more like one type of polymer than the same polymer, so they tend to like to stay with themselves rather than with mix: χ is more often positive than negative. Due to the tiny entropic forces for mixing, even small values for χ result in immiscibility, as you will demonstrate in the below exercise.

Exercise: Derive the value of χ from the value of the UCST in Figure 27 using Flory-Huggins theory. Compare this value to values for the heat of mixing for typical metallic and ionic systems.

Now, this isn't to say there aren't polymer systems which exhibit miscibility. Many miscible blends exist. Such systems occur when the side-groups on the chains of the two polymers interact favorably. Interestingly, these systems often phase separate at higher temperatures. The mechanism for this is not too complex, and has its origins in statistical mechanics.

18.2 Why do miscible blends phase separate at high temperatures?

Again, miscibility of polymers occurs due to favorable interactions between polymeric side chains. As the temperature increases, the chains tend to wiggle a lot more, a process termed *reptation*. The contact between the favorable groups on the side chains cannot be maintained

with increasing temperature; the side groups desorb from one another (one could also view this as the polymer activating out of this local energy well to the plethora of states outside of it). This then leads to the interactions becoming unfavorable on average, and the systems phase separate. A related mechanism which can drive polymers to phase separate at higher temperatures is that miscible polymers tend to maximize the degree of contact with the other member of the blend. The polymers thus stretch out in solution to minimize contact with themselves. Per Figure 7, this is a lower entropy conformation, and thus the polymer gains entropy upon coiling back up during the phase separation process. The conformations of the polymers in solution, along with schematics of the UCST and LCST are shown in Figure 28. This should take you off guard; it's entropically-driven phase separation!

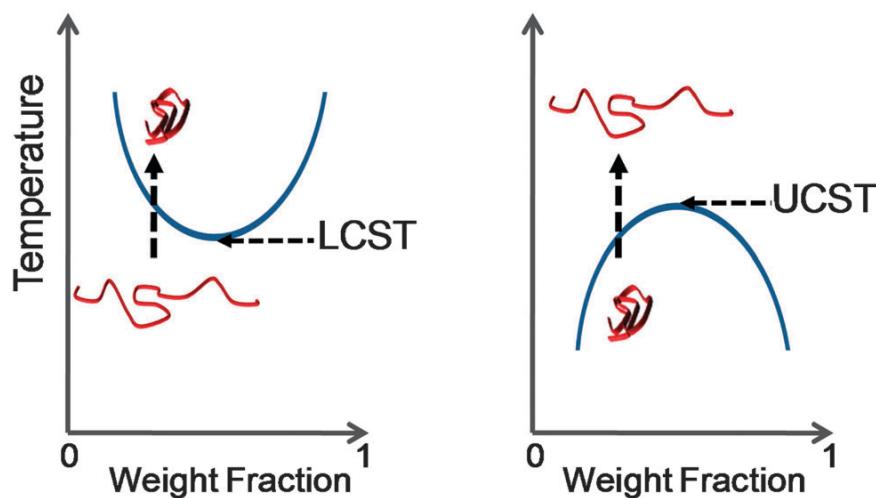


Figure 28: A schematic of the polymer confirmations in LCST and UCST behavior, courtesy of Gibson and O'Reilly, Chem. Soc. Rev., 2013, 42, 7204-7213 ([link](#)).

To finish this discussion, many systems that exhibit both an LCST and a UCST through a combination of both of these effects; entropically-driven phase separation at low temperatures and then entropically-driven mixing at high temperatures (Figure 29). This is about as complex as polymer phase diagrams get as long as we don't get into liquid crystalline phase diagrams.

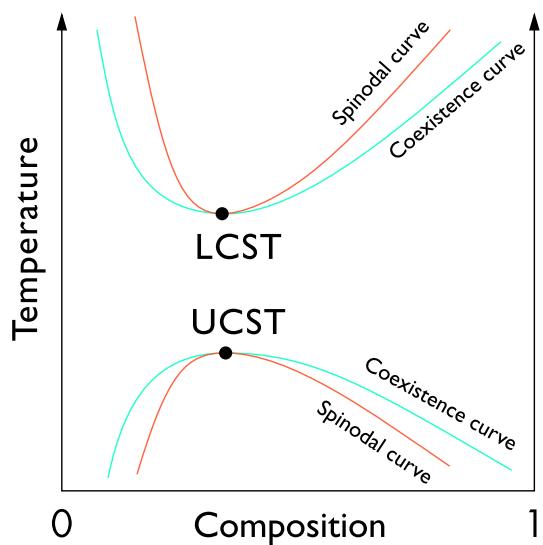


Figure 29: A schematic of a polymer phase diagram exhibiting an LCST and a UCST, courtesy of [wikimedia commons](#).