MATERIALS AT EQUILBRIUM

Instructed by
Professor Antoine Allanore

Notes compiled and edited by
Michael Gibson and Derek Kita

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Department of Materials Science and Engineering
Massachusetts Institute of Technology

1 Lecture 1: Introduction and Preliminaries

Welcome to 3.20, Materials at Equilibrium. This course is designed to provide all incoming students with a grounding in equilibrium thermodynamics and an understanding of energy scales. The material in this course is broadly applicable to all field 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 it's environment make up the universe.

$$[\text{environment}] = [\text{universe}] - [\text{system}] \tag{1}$$

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:

$$V = V_1 + V_2 \tag{2}$$

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

$$P \neq P_1 + P_2 \tag{3}$$

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 equiliibrium, 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.

6. Boundaries: Conditions that are defined for a system. These strongly depend on the system of interest. Boundaries can have properties such as: permeable (open to mass flow, changing n), 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 sufficicently slow processes, have the same pressure as its surroundings.

In thermodynamics, we will look at the transfer of energy and other extensive variables at 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 system processes during arbitrary processes. Last, we will use these constitutive relationships to look at a special set of processes; phase transitions, and derive laws for how the conditions under which these phase transitions should occur have to 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 thr 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, that U is a function of only the extensive thermodynamic variables (U is a state variable), and that all types of energy exchange that can change the internal state of the system can be represented as work terms represent changes in U. We discuss this final assumption next.

2 Lecture 2: Heat and Work

Let's look at one form of energy transfer: work. A differential amount of work is equal to the force dotted with the displacement:

$$\delta W = \vec{F} \cdot d\vec{r} \tag{5}$$

The formalism for work is $\delta W_i = y_i dx_i$, where y_i is the force (intensive) and dx_i is the response (extensive). Combined, (y_i, x_i) is a **conjugate pair**.

2.1 Two examples of work

Example 1: Deformation of a material: The work resulting from a change in strain energy is

$$\delta W = V\bar{\bar{\sigma}} \cdot d\bar{\bar{\epsilon}} \tag{6}$$

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 [Pa]=[N/m^2], the strain ϵ is dimensionless, and volume element results in a quantity of [N$\cdot$ m] = [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 $\sigma_{11} = \sigma_{22} = \sigma_{33} = -P$.

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

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 $V(d\epsilon_{11} + d\epsilon_{22} + d\epsilon_{33}) = dV$:

$$\delta W_{\text{pressure}} = -PdV \tag{8}$$

To solve these, we need an equation of state $P(V)$ or $\sigma(\epsilon)$. We also have

$$\frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}} = c_{ijkl} \tag{9}$$

where c_{ijkl} is the generalized elastic compliance. 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 define the work done upon the system.

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:

$$\delta W = Vdq \tag{10}$$

Also, $q = D \cdot A$ where D, the electric displacement, is equal to $\varepsilon_0\mathcal{E} + \frac{\mathcal{P}}{A \cdot l}$. $\mathcal{P}$ 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:

$$\begin{aligned} \delta W &= \mathcal{E}l \cdot d(A(\varepsilon_0\mathcal{E} + \frac{\mathcal{P}}{lA})) \\ &= \mathcal{E}lA \cdot d(\varepsilon_0\mathcal{E} + \frac{\mathcal{P}}{lA}) \\ &= V\varepsilon_0\mathcal{E}d\mathcal{E} + \mathcal{E}d\mathcal{P} \end{aligned} \tag{11}$$

Note how the δW nicely seperates into a response that is independent of the system and one that is determined by the material properties of the system. Some energy, $V\varepsilon_0\mathcal{E}d\mathcal{E}$, 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 elecric 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 commmon to all work terms which appear in the internal energy. A differential amount of done upon a system can thus be written as a sum over orthogonal work terms:

$$\delta W = \sum_i y_i dx_i \tag{12}$$

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. [1] 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 are 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 path independent; it is only a function of the endpoints.
- exact 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.

This is illustratted below with two examples.

[1] For 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) and we will allow the environment to replenish the energy in our batteries. 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,

$$\Delta E_{\text{system}} + \Delta E_{\text{field}} = 0 \tag{13}$$

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):

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

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:

$$\vec{F} = -\vec{\nabla}\vec{E} - f_{\text{friction}}|\vec{e_v}|$$
$$\int \vec{F}\delta\vec{r} = -mg\Delta h - fL_{\text{path}}$$

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 underlieing 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:

$$\delta W_{\text{incomplete}} = \delta W_x + \delta W_z = F_x\dot{d}x + F_z\dot{d}z$$

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 $\int \delta W_x + \delta W_z = \int F_x dx F_z dz = 0$ 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 to due to heat flow into a system.

2.3 Heat

Heat is energy transferred between two bodies not due to work or mass transfer. [2] 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 exhanged between the system and the surroundings is 0; $\delta Q = 0$. The first postulate of thermodynamics is

$$\boxed{dU = \delta W + \delta Q} \tag{15}$$

where again, the work terms can be written as $\delta W = \sum_i y_i dx_i$.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, δ, but the sum of the two as dU. We illustrated this with an example:

Example: Consider a simple system with all variables fixed except for the volume, like a piston. It then evolves "slowly" through a series of equilibrium states.[3]

$$W = -\int P dV \tag{16}$$

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 constant temperature), we have an expression

[2] Historically, people used to think heat was transferred between bodies via the flow of an invisibile 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 invisble liquid, flowed from hot to cold bodies. All caloric theories assumed that calor was conserved. Sir Benjamin Thompson (AKA 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.

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

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 a 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, $T = 298K$.

$$\begin{aligned} W_a &= -nRT \int \frac{dV}{V} \\ &= -nRT \ln(\frac{V_f}{V_i}) \\ &= nRT \ln(2) \\ &= 1717 \frac{\mathrm{J}}{\mathrm{mol}} \end{aligned} \tag{18}$$

Let's now consider a separate path b 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 a. For the constant volume pressure change, there will be no work done since $dV = 0$ and $W = -PdV$. Therefore all the work will come from the initial constant pressure process, or isobaric compression.

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

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 Lecture - September 8, 2014

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: $dU = \delta Q + \sum y_i dx_i$. We now want to quantify the first term, or quantify heat exchange. We do this by defining the *heat capacity* for a system as:

$$C_{\text{path}}(T) = \frac{(\delta Q)_{\text{path}}}{dT}$$
$$c_{\text{path}}(T) = \frac{C_{\text{path}}}{N}$$

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.[4] If we consider a simple system[5] with state variables (P, V) or (V, T), we can define

$$c_p = \frac{1}{N}\frac{(\delta Q)_p}{dT}$$
$$c_v = \frac{1}{N}\frac{(\delta Q)_v}{dT}$$

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, that the heat capacity increases with increasing molecular weight; this is general. Next, that $c_p > c_v$ 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 it, we get three degrees of freedom, so:

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

[4]This convention is used throughout: system quantities are uppercase, molar quantities are lowercase

[5]In a simple system, work can only be done on the system via PdV terms.

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 are 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, the two 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:

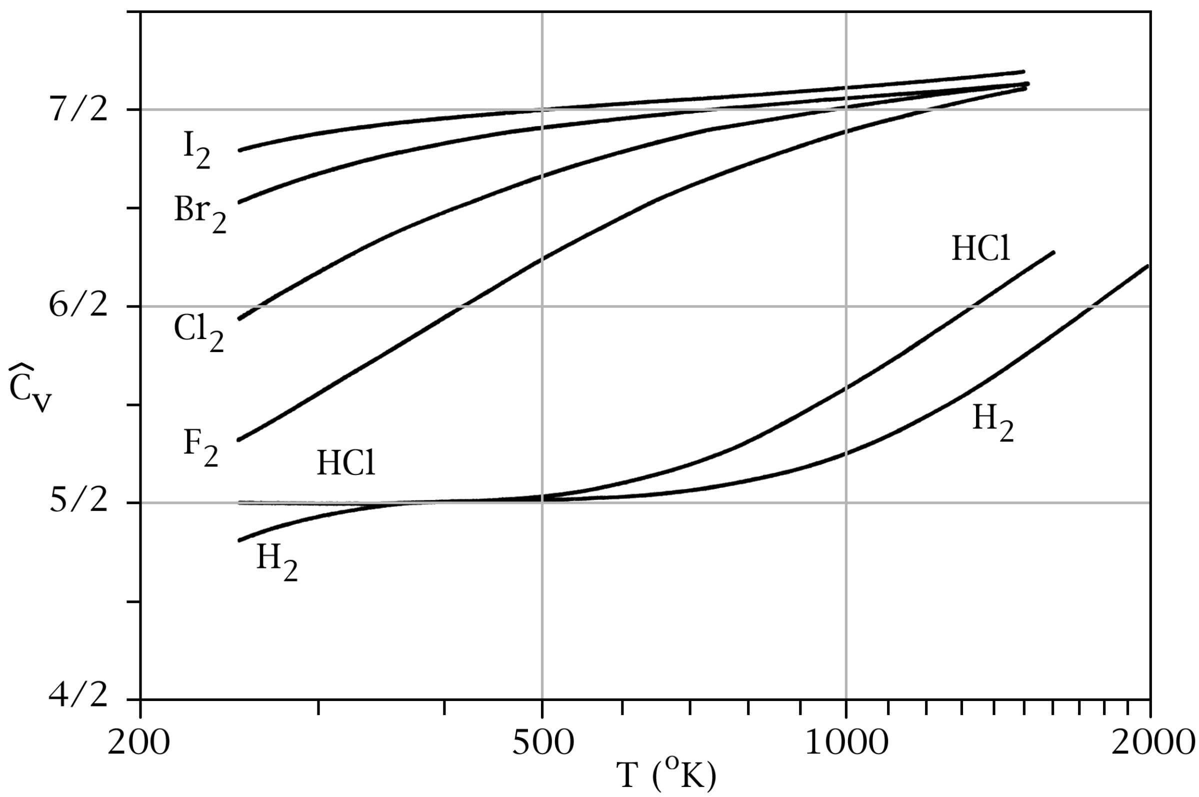


Figure 1: The specific heats of diatomic gases (normalized by R) as a function of temperature. The temperature at which the vibrational modes are excited is a function of the stiffness of the bond, with hydrogen exhibiting especially stiff bonds, and thus a late transition temperature.

$$\begin{aligned} C_p &= C_v + R \\ &= \frac{7}{2}R = 29\text{J/mol/K} \end{aligned}$$

(b) Solids: At room temp., for an element, Dulong and Petit (1819) observed that

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

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 equiparition, c_v should be $6\frac{R}{2} = 3R$. For a non-metallic salt such as Mg, 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 3 R. 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 discontinutities in Fe's diagram at 1550 °C because at this point it melts. Same with Hg, which becomes a gas at low T. For H_2O 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 meaure in the lab. It would be convenient to have a energy function for which c_p is the derivative of the free energy with respect to temperature. The **enthalpy**, H, is this function.

$$H = U + PV$$
$$dH = dU + VdP + PdV$$

and substitute $dU = \delta Q - PdV$

$$dH = \delta Q + VdP$$
$$(dH)_p = \delta Q$$

Note how the enthalpy is naturally expressed with pressure held constant than volume held constant. Because H is defined in terms of state functions, the enthalpy is also a state funcitno. It is the state function that describes the heat change at constant pressure. It is thus the natural energy for discussing **calorimetry**, which is a major experiemental technique. H is often called the "heat" content.

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

$$(dH)_p = nC_p(dT)_p$$
$$\frac{\partial H}{\partial T}|_p = C_p$$

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

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

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 funciton 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[6]. Unlike T or P, there technically is no absolute zero for H or U. As such, we often reference these state functions to their *standard states*. Under the this convention, $H = 0$ for a pure element at atmospheric pressure ($P_0 = 101325$ Pa) and 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; heat is often 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 $900^0 < T < 1400^0$ it is in the γ (FCC) phase, and from 1400→1500°C Fe is the δ (BCC2) phase. Above 1500°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' discontinuitites are barely visible on the left curve. This

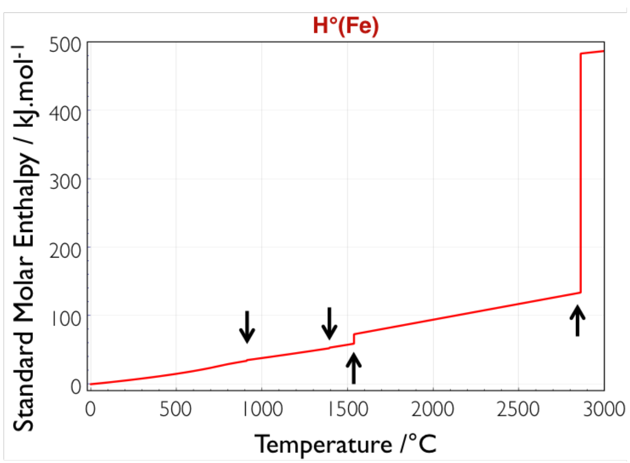


Figure 2: $H°(T)$ for Fe over two temperature scales.

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

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

an element.

$$\Delta H_{\text{fusion}} \text{ in J/mol } \approx 9T_{\text{fusion}} \text{ in K} \tag{21}$$

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 the enthalpy of vaporization is proportional to the boiling temperature.[7]

$$\Delta H_{\text{vap}} \approx 90T_{\text{vap}} \tag{22}$$

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/mol.[8]

Now, what is the relative contribution of the PdV 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 $\rightarrow$ phase II. In a metal, $V_{molar} \approx 10$ cm^3/ mol = 10^-5 m^3/ mol and a good upper bound on the volume change is 10% ΔV. At atmospheric pressure, P°= 10^5 Pa, so $P\Delta V = 10^5 \cdot 10^{-6} = 0.1$ J/mol. Note the use of J/mol instead of kJ/mol here: *the energy scale associated with pressure-volume effects can only moderately perturb the energetics of condensed-matter phase transitions, expect 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*:
At room temperature and pressure:

$$2Fe^{\alpha}_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow Fe_2O^{\alpha}_{3(s)} + (\Delta Q)_p \tag{23}$$

with $(\Delta Q)_p$ = -1963 kcal/mol.

$$\Delta_v H = \Delta H^0_{Fe_2O_3} - \Delta H^0_{Fe} - \frac{3}{2}\Delta H^0_{O_2} \tag{24}$$

and

$$\begin{aligned} \Delta H^0_{Fe_2O_3} &= -820.5\text{kJ/mol} \\ \Delta H^0_{CO} &= -110.52\text{kJ/mol} \\ \Delta H^0_{CO_2} &= -393.51 \cdot \text{kJ/mol} \end{aligned}$$

[7]As we will learn later, these rules imply that the entropies of melting and boiling are approximately equivalent for all of the elements.

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

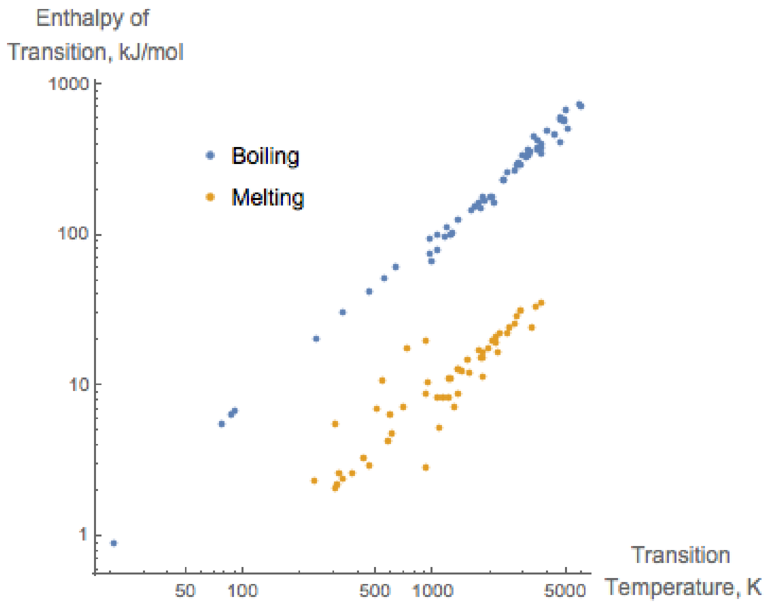


Figure 3: Elemental phase transition temperatures and enthalpies on a log-log scale. The slope of this correlation (on a linear scale) gives the characteristic entropy of these phase transitions. The correlation is stronger for boiling as compared to melting because the liquid→gas transition's entropy 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.

There are plenty of references to get these values, such as Janaf tables. Examples include FactSage & Thermocalc and they provide H^0, G^0, C_p^0, etc.

$$\begin{aligned}
C_{(s)} + O_{2(g)} &\rightleftharpoons CO_{2(g)} \\
\Delta_r H^0 &= -393.52\text{kJ/mol} \\
C_{(s)} + \frac{1}{2}O_{2(g)} &\rightleftharpoons CO_{(g)} \\
\Delta_r H^0 &= -110.52\text{kJ/mol} \\
C_{(s)} + CO_{2(g)} &\rightleftharpoons 2CO_{(g)} \\
\Delta_r H^0 &= +180\text{kJ/mol}
\end{aligned}$$

The ΔH only tells you how much heat is exchanged, it doesn't tell you which reaction is *going to happen*. Exothermic reactions release heat, which 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 Lecture - September 9, 2014

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 of an ideal gas is:[9]

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

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 $P = 4.4$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:

$$\begin{aligned} dU_{\text{gas}} &= \delta Q + \delta W = \delta W \\ &= -PdV \\ &= nC_V dT = -PdV \end{aligned}$$

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 defintion of dV above gives the final temperature in terms of the initial

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

temperature and the ratio of the pressures:

$$nC_V dT = -nRdT + RT\frac{dP}{P}$$
$$(\frac{T_2}{T_1})^{C_P/R} = \frac{P_2}{P_1}$$
$$T_2 = T_1(\frac{P_1}{P_2})^{R/C_P}$$

For the bike tube, this gives $T_2 = 206\text{K} = -67°\text{C}$. Why didn't we actually reach this temperature? Well, the gas flowed through a nozzle instead of simply isotropically expanding, 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:

$$dU_{\text{valve}} = U_{\text{in}}dn - U_{\text{out}}dn + \delta Q \tag{25}$$

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. δQ is zero because the process is adiabatic, so:

$$dU_{\text{valve}} = \delta W = dn(P_{\text{in}}v_{\text{in}} - P_{\text{out}}v_{\text{out}}) \tag{26}$$

Equating these two definitions of dU_{valve} gives:

$$(U_{\text{in}} - U_{\text{out}}) = (P_{\text{in}}V_{\text{in}} - P_{\text{out}}V_{\text{out}})^{10}$$

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 interpet 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, or refer to **Callen pg. 95**.

In general, we categorize processes in the following way:

[10] This 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 asssumption, it's general.

(I) Continuous and at equilibrium with environment (reversible). See Figure 2.

(II) Continuous but not necessarily at equilibrium with environment. This is considered quasi-static. Can be both reversible and irreversible. See Figure 3.

(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.

4.2 Quasistatic Piston

We now consider a piston slowly compressing a gas. See Callen Figure 5. For our path,

$$\sum_{i=1}^{2} \frac{\delta Q_i}{T} = \text{constant} \tag{27}$$

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

Let's assume that $dS = \frac{\delta Q}{T}$.
Process 1: Let's take a reservoir that is adiabatically isolated with T_1. Let's transfer δQ 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 $dS_1 = dS_2 \neq \frac{\delta Q}{T}$.

Second Law of Thermodynamics: There exists a state function (property S) for which holds (closed system)

$$dS_{\text{system}} \geq \frac{\delta Q}{T} \tag{28}$$

it fixes the direction of change. Forward ($1 \to 2$) if $dS_f \geq \frac{\delta Q_f}{T}$ or backward ($2 \to 1$) if $dS_b \geq \frac{\delta Q_b}{T}$.

If a process is reversible (quasi-static), then we have $dS = \frac{\delta Q}{T}$. If it is irreversible, $dS > \frac{\delta Q}{T}$ (or $dS_{\text{rev}} + \xi$ where $\xi > 0$). The first law said that U exists and

$$dU = \delta Q + \sum y_i dx_i \tag{29}$$

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

$$dS \geq \frac{\delta Q}{T} \tag{30}$$

Back to the example of two compartments that are connected (one at T_1 and the other at

T_2), see Figure 6, we get

$$\begin{aligned}
\delta Q_1 &= -\delta Q_2 \\
dS_{\text{system}} &= dS_1 + dS_2 \\
dS_{\text{system}} &= \frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} \\
&= \frac{\delta Q_1}{T_1} - \frac{\delta Q_1}{T_2} \\
&= \delta Q_1 (\frac{1}{T_1} - \frac{1}{T_2}) \\
&= \delta Q_1 (\frac{T_2 - T_1}{T_1 T_2}) \geq 0
\end{aligned}$$

If $T_2 > T_1$, $\delta Q_1 > 0$. Or if $T_2 < T_1$, then $\delta Q_1 < 0$. Heat flows from "hot" to "cold".

5 Lecture - September 10, 2014

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

$$dU = \delta Q + \sum y_i dx_i \tag{31}$$

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

$$dS \geq \frac{\delta Q}{T} \tag{32}$$

If the process is reversible then, $TdS = \delta Q$. 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 by increasing the enreopy 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 δQ 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.

$$\delta W_{\text{reversible}} \geq \delta W_{\text{irreversible}} \tag{33}$$

For a reversible path,

$$dU_{\text{reversible}} = \delta Q_{\text{reversible}} + \delta W_{\text{reversible}} \tag{34}$$

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

$$dU_{\text{reversible}} = dU_{\text{irreversible}} = \delta Q_{\text{irreversible}} + \delta W_{\text{irreversible}} \tag{35}$$

Since $TdS > \delta Q_{\text{irreversible}}$ for an irreversible process, we have

$$TdS + \delta W_{\text{reversible}} = \delta Q_{\text{irreversible}} + \delta W_{\text{irreversible}} \tag{36}$$

$$TdS - \delta Q_{\text{irreversible}} = \delta W_{\text{irreversible}} - \delta W_{\text{reversible}} > 0 \tag{37}$$

so

$$\boxed{\delta W_{\text{reversible}} < \delta W_{\text{irreversible}}} \tag{38}$$

Note that our sign convention in these notes is $dU = \delta Q + \delta W$, so negative work is work done by the systems upon the surroundings. The important physical implication is that 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 is bad for efficiency, regardless of whether work is done by a system, or work is performed upon system.

(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 transfering 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[11], and a good written explanation is on wikipedia.

$$\begin{aligned}\Delta U = 0 &= Q + W \\ \Delta S = \oint \frac{\delta Q}{T} &= 0 \\ &= \frac{Q_H}{T_H}\end{aligned}$$

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

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

[11] Sal Khan is an MIT alum!

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

$$\boxed{\eta_{\text{heat} \to \text{work}} = 1 - \frac{T_L}{T_H}} \tag{39}$$

To give a sense of these efficiencies, with $T_H = 100^0$ C $= 373$ K and $T_L = 25$°C $=$ 298 K, $\eta \approx 20\%$. Significant gains in efficiency can be gained by going to higher temperatures: if $T_H = 550$°C, $\eta \approx 63\%$.

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 work used (this is often referred to as the "coefficient of performance", or COP of a heat pump). One can derive that:

$$COP_{\text{heat pump}} = \frac{-Q_H}{W} = \frac{T_H}{T_H - T_L} \tag{40}$$

$$COP_{\text{refrigerator}} = \frac{Q_L}{W} = \frac{T_L}{T_H - T_L} \tag{41}$$

With $T_H = 25$C and $T_C = 0$C, $\eta = 11$.[12]

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.[13]. 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.

We 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 know the temperature dependence of S:

$$C_c = \frac{(\delta Q)_c}{dT} \tag{42}$$

[12]This 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!

[13]See Nature Materials Vol 8 Feb 2009 "An inconvenient truth about thermoelectrics"

Where the subscript c is for "constant path". A reversible process along such a path must have:

$$T(dS)_c = (\delta Q)_c$$
$$(\frac{\partial S}{\partial T})_c = \frac{C_c}{T}$$
$$(\frac{\partial S}{\partial T})_p = \frac{C_p}{T}$$
$$(\frac{\partial S}{\partial T})_v = \frac{C_v}{T}$$

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 0K, in their equilibrium state, as being equal to zero.[14]

$$S_{0\text{K}}^{\text{element}} = 0 \tag{43}$$

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 0K, as $\Delta S_{formation} = 0$: $S_{AB}^{0\text{K}} = 0$. By extension, *at equilibrium, the entropy of all materials at absolute zero is zero.*

Can we reach 0K?

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 t=you could make a series of heat reverviors 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 0K, as it would take an infinite number of cycles to do so. We can illustrate this by looking at the different processes individually:

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

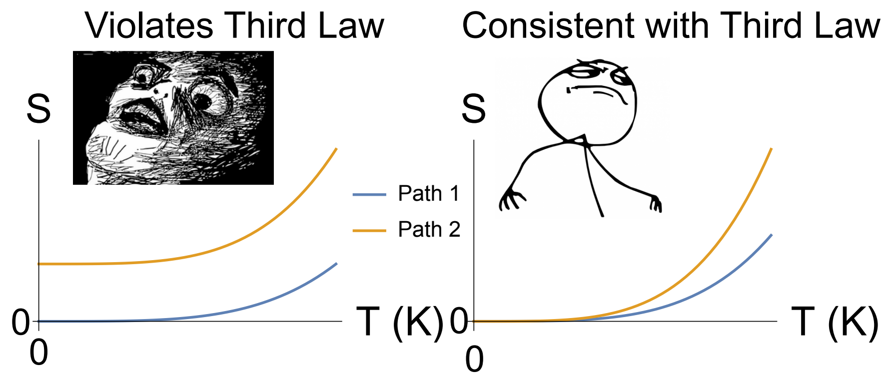


Figure 4: An illustration of entropy as a function of temperature inconsistent and consistent with the third law.

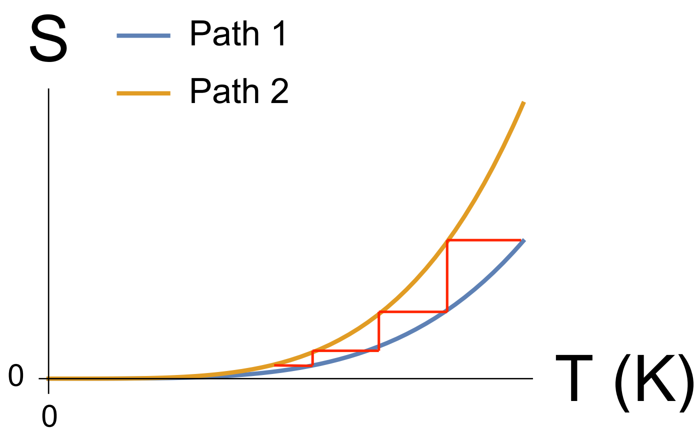


Figure 5: A T-S diagram illustrating the diminishing changes in temperature and entropy in a low-temperature, step-wise isothermal-isentropic cooling process. These changes become so small that an infinite steps are needed to reach 0K.

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

$$T_2/T_1 = \frac{P_1}{P_2}^{R/C_v} \tag{44}$$

But that's kind of silly. You know because it's adiabatic that $dS = 0$ since $\delta Q = 0$

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

$$\Delta S = nR\ln(\frac{V_2}{V_1}) \tag{45}$$

As volume goes up, 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:

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

6 Lecture - September 12, 2014

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

$$dU = TdS + \sum_i Y_i dX_i \tag{47}$$

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:

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

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 a first order homogoneous 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 multipling the size of the system by some parameter, λ, gives λ times the original entropy: $S(\lambda U_\lambda X_i, ...) = \lambda S(U, X_i, ...)$

You'll recognize this as tantamount to stating that the entropy is a first order homogeneous function. A similar argument can be made for the internal energy, which we also know is 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: $U(\lambda S, \lambda X, ...) = \lambda^n U(S, X, ...)$ We can take the derivative of both sides of this equation to get:

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

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

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

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

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

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: $\frac{\partial U(S,X,...)}{\partial S} = T$, $\frac{\partial U(S,X,...)}{\partial X} = Y$, and so on for all of the extensive variables. Remebering that the right hand side is $U(S, X, ...)$, this allows us to show that U is defined as:

$$U(S, X, ...) = TS + \sum_i Y_i X_i \tag{52}$$

This definition is very useful, so it's important we have a rigorous basis for it (which we just showed above!). It is gives 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:

$$H = U + PV \tag{53}$$

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

$$dH = TdS + VdP \tag{54}$$

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 can give an independent definition of dU by taking its total differential:

$$dU(S, X, ...) = TdS + SdT + \sum_i Y_i dX_i + \sum_i X_i dY_i \tag{55}$$

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

$$TdS + \sum_i Y_i dX_i = TdS + SdT + \sum_i Y_i dX_i + \sum_i X_i dY_i$$
$$0 = SdT + \sum_i X_i dY_i$$

This is called a *Gibbs-Duhem equation*. It states that all the intensive variables cannot be varied independently. They have a variety of convenient uses, and we will come back to them 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:

$$N_1 d\mu_1 = -N_2 d\mu_2 \tag{56}$$

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 $T(S, V, N), \mu(S, V, N)$. As the equations of state are the derivates of the free energy, if you know enough of them, you can combine their integrals to get the free energy function as a function of its natural variables referenced to some initial state. For a system where the mole numbers are constant:

$$U(V, S) = \int_{V_0}^{V} \left(\frac{\partial U}{\partial V}\right)_{S_0} dV + \int_{S_0}^{S} \left(\frac{\partial U}{\partial S}\right)_{V} dS = \int_{V_0}^{V} PdV + \int_{S_0}^{S} TdS \tag{57}$$

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).

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. [15]

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.

$$\begin{aligned} U &= TS - PV + \sum_i \mu_i N_i \\ dU &= SdT - VdP + N_i d\mu_i = 0 \end{aligned} \tag{58}$$

For an isolated system, the 1st law says $U_{\text{system}}, V_{\text{system}}$ are constant; we have $dV_{\text{system}} = dU_{\text{system}} = 0$. The 2nd law says $dS_{\text{system}} \geq 0$ (i.e. 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

Lets look at thermal equilibrium (Temperature differences) in a system with two containers I and II that allow energy to flow between them: $dU_I, dU_{II} \neq 0$.

$$\begin{aligned} dU &= 0 = dU_I + dU_{II} \\ dU_I &= -dU_{II} \\ dS &= dS_I + dS_{II} \\ dS &= \frac{dU_I}{T_I} + \frac{dU_{II}}{T_{II}} \text{ (by Massieu/second law)} \\ dS &= dU_I(\frac{1}{T_I} + \frac{1}{T_{II}}) \end{aligned} \tag{59}$$

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 $T_I = T_{II}$.

[15] This 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.

$$\begin{aligned} dU_1 &= -dU_2 \\ dV_1 &= -dV_2 \\ dS &= dU_1(\frac{1}{T_1} + \frac{1}{T_2}) + dV_1(\frac{P_1}{T_1} + \frac{P_2}{T_2}) \end{aligned} \tag{60}$$

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

2.3 Chemical Equilibrium from Mass Flow

Similarly, we can add a μdN term to the energy change (or $-\frac{\mu}{T}dN$ in the entropy representation). We then get an additional term to dS of

$$dS = ... - (\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2})dN_1 \tag{61}$$

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. [16]

In general, we maximize the entropy S by:

- Define the variables which are free to move in the system. For example: can subsystems exchange volume or mass? If so, dV and dN would be appropriate internal variables.
- Write dS as a function of the *internal* variables in the Masseu formulation.
- impose $dS_{\text{system}} = 0$ for all the variations

Thus, given appropriate internal variables, we can directly extract the equilibrium conditions. For energy exchange, $dU_{1\to2}$, we get $T_1 = T_2$. For energy and volume exchange, $dU_{1\to2}$ and $dV_{1\to2}$, we have $T_1 = T_2$ and $P_1 = P_2$. Another example would be charge exchange, $dq_{1\to2}$, which implies a homogenous electrostatic potential: $\phi_1 = \phi_2$.

[16] In terms of kinetics, a gradient of $\frac{\mu}{T}$ generates mass flow (i.e. a diffusional relaxation toward equilibrium).

7 Lecture - September 15, 2014

7.1 Equilibrium under the most general conditions

Mike has not edited this section yet

7.2 Legendre Transforms

The difficulty in working with the internal energy, U, is that it is a natural function of the wrong 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 exchange,[17] 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 of interest.*

How To Take a Legendre Transform

If we want to transform U such that an intensive variable, SY_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 $Y_i \cdot X_i$:

$$\begin{aligned} \phi &= U - Y_i X_i \\ d\phi &= dU - Y_i dX_i - X_i dY_i \end{aligned} \tag{62}$$

where $dU = [...] + y_j dx_j$, so 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:

$$d\phi = \sum_{j \neq i} Y_j dX_j - X_i dY_i \tag{63}$$

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

$$\begin{aligned} dU - TdS + PdV &\leq 0 \\ H &= U + PV \\ dH &= dU + PdV + VdP \\ dH &= TdS + VdP \end{aligned} \tag{64}$$

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

$$\begin{aligned} T &= \frac{\partial H}{\partial S}|_P \\ V &= \frac{\partial H}{\partial P}|_S \end{aligned} \tag{65}$$

[17] You can think of reversible heating as T-S work if you'd like.

Properties of Legendre Transforms

1. $\frac{\partial \phi}{\partial Y_i}_{X_{i \neq j}} = -X_i$; 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 set occurs when U is minimal, so the equilibrium state for a given Legendre transform, ϕ, occurs ϕ 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 corrolary 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.

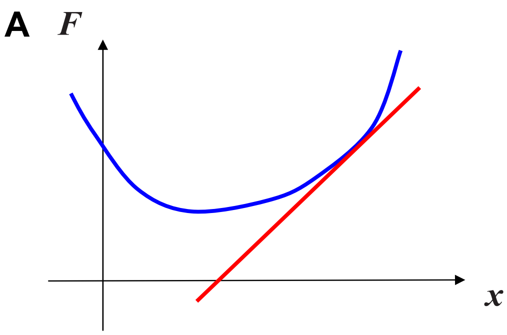
4. The pure double derivatives of ϕ are the negative inverse of the pure double derivatives of U. For example:

$$\begin{aligned} \frac{\partial^2 U}{\partial V^2}_{S,N,\ldots} &= -\frac{\partial P}{\partial V}_{S,N,\ldots} &= (\beta_S V)^{-1} \\ \frac{\partial^2 H}{\partial P^2}_{S,N,\ldots} &= -\frac{\partial V}{\partial P}_{S,N,\ldots} &= -\beta_S V \end{aligned} \tag{66}$$

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 6 [18]:

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

[18] From "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.



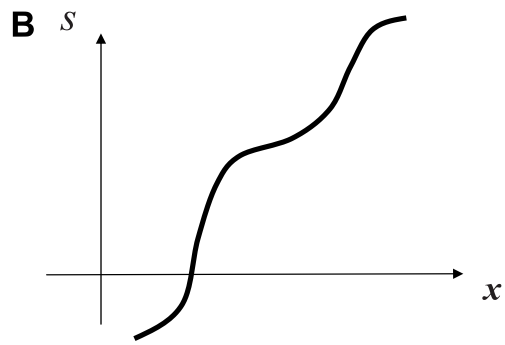


Figure 6: **A** The graph of a convex function F(x). The tangent line at one point is illustrated. **B** The graph of $S(x)$, the slope of a convex function.

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.

7.3 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:

$$\begin{aligned} F &= U - TS \\ dF &= -SdT - PdV \end{aligned} \tag{67}$$

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 **Gibb's Free Energy** is:

$$\begin{aligned} G &= U - TS + PV \\ dG &= -SdT + VdP \end{aligned} \tag{68}$$

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

7.4 A First Look at Manipulating Thermodynamic Functions

Lets now look at a simple system using the Gibb's 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

$$\begin{aligned} dV &= \frac{\partial V}{\partial T}|_P dT + \frac{\partial V}{\partial P}|_T dP \\ &= \alpha_V V dT - V\beta_T dP \end{aligned} \tag{69}$$

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

$$\begin{aligned} dS &= \frac{\partial S}{\partial T}|_P dT + \frac{\partial S}{\partial P}|_T dP \\ &= \frac{c_P}{T} dT + \frac{\partial S}{\partial P}|_T dP \end{aligned} \tag{70}$$

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 double derivative of a function does not depend upon the order in which the derivatives are exchanged.

$$\begin{aligned} \frac{\partial}{\partial P}\left(\left(\frac{\partial G}{\partial T}\right)_P\right)_T &= \frac{\partial}{\partial T}\left(\left(\frac{\partial G}{\partial P}\right)_T\right)_P \\ \frac{\partial}{\partial P}(-S)_T &= \frac{\partial}{\partial T}(V)_P \\ -\left(\frac{\partial S}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_P = \alpha_V V \end{aligned} \tag{71}$$

and from here we can make our substitution into the above

$$dS = \frac{c_P}{T} dT - \alpha_V V dP \tag{72}$$

This should kind of weird you out; 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 experimentally measurable 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.[19]

[19] You 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 Lecture - September 17, 2014

8.1 Maxwell Relations

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

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_{\text{conj}[x]} = \pm\left(\frac{\partial \text{conj}[y]}{\partial \text{conj}[x]}\right)_y} \tag{73}$$

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.

1.1 Maxwell for an Ideal Gas

In general, we know, $dS = \frac{c_P}{T}dT - \alpha_V V dP$. 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:

$$\begin{gathered} d(PV) = nRdT = VdP + PdV \\ \frac{\partial V}{\partial T}|_P = \frac{nR}{P} \end{gathered} \tag{74}$$

Substituting gives:

$$\boxed{dS = -nR\frac{dP}{P} + c_P\frac{dT}{T}} \tag{75}$$

1.2 Magnetic Maxwells

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; we want expressions for $\left(\frac{\partial S}{\partial P}\right)_{T,H}$ and $\left(\frac{\partial S}{\partial H}\right)_{T,P}$. Including magnetic work terms, dU can be expressed as:

$$dU = TdS - PdV + \mu_0 H_0 dM \tag{76}$$

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:

$$\begin{aligned} \phi &= U - TS + PV - \mu_0 H_0 M \\ d\phi &= -SdT + VdP - \mu_0 M dH \end{aligned} \tag{77}$$

This permits us to obtain the following relationships:

$$\begin{aligned} \left(\frac{\partial S}{\partial P}\right)_{T,H} &= -\left(\frac{\partial V}{\partial T}\right)_{P,H} \\ \left(\frac{\partial(\mu_0 M)}{\partial T}\right)_{H,P} &= \left(\frac{\partial S}{\partial H}\right)_{T,P} \end{aligned} \tag{78}$$

8.2 How to do thermo 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.

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

Inverse rule:

$$\left(\frac{\partial f}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial x}{\partial f}\right)_y} \tag{79}$$

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:

$$\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial u}\right)_y \left(\frac{\partial u}{\partial x}\right)_y \tag{80}$$

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:

$$\frac{\partial f}{\partial x}|_y \frac{\partial x}{\partial y}|_f \frac{\partial y}{\partial f}|_x = -1 \tag{81}$$

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

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

$$\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial u}\right)_y \left(\frac{\partial u}{\partial x}\right)_y \tag{82}$$

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).

2.2 Strategy to reduce variables

Thermo derivations are usually 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
i.e. 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:

$$\frac{\partial T}{\partial P}|_H = -\frac{\frac{\partial H}{\partial P}|_T}{\frac{\partial H}{\partial T}|_P} \tag{83}$$

(2) Always bring S to the numerator and turn it into a heat capacity
i.e. from $dH = TdS + VdP$:

$$\begin{aligned}
\left(\frac{\partial H}{\partial P}\right)_T &= T\frac{\partial S}{\partial P} + V \\
\left(\frac{\partial H}{\partial T}\right)_P &= T\left(\frac{\partial S}{\partial T}\right)_P \\
\left(\frac{\partial T}{\partial P}\right)_H &= \frac{-(T\left(\frac{\partial S}{\partial P}\right)_T + V)}{T\left(\frac{\partial S}{\partial T}\right)_P} \\
&= \frac{-(T\left(\frac{\partial S}{\partial P}\right)_T + V)}{c_P} \\
&= \frac{-(-T\alpha_V V + V)}{c_P} \\
&= \frac{V(T\alpha_V - 1)}{c_P}
\end{aligned} \tag{84}$$

(where the above used the Maxwell relationship $\frac{\partial S}{\partial P}|_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha_V V$, 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

$$\begin{aligned}
c_P - c_V &= T[\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V] \\
&= T[\left(\frac{\partial S}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P]
\end{aligned} \tag{85}$$

where in the above I used the relation

$$\left(\frac{\partial f}{\partial x}\right)_g = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \cdot \left(\frac{\partial y}{\partial x}\right)_g \tag{86}$$

continuing, we have

$$\begin{aligned} c_P - c_V &= T\left[\left(\frac{\partial S}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P\right] \\ &= T\left[\left(\frac{\partial S}{\partial P}\right)_T \cdot (\frac{-1}{V\beta_T}) \cdot \left(\frac{\partial V}{\partial T}\right)_P\right] \end{aligned} \tag{87}$$

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

$$\begin{aligned} c_P - c_V &= T\left[\frac{-\alpha_V V}{-\beta_T V}\alpha_V V\right] \\ &= \boxed{TV\left(\frac{\alpha_V^2}{\beta_T}\right)} \end{aligned} \tag{88}$$

2.3 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 pressure dP as a result. What happens to the temperature?

$$\begin{aligned} dS &= \frac{\partial S}{\partial T}|_F dT + \frac{\partial S}{\partial F}|_T dF \\ dU &= TdS + Fdl \end{aligned} \tag{89}$$

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

$$\begin{aligned} \frac{\partial T}{\partial F}|_S &= -\frac{\frac{\partial S}{\partial F}|_T}{\frac{\partial S}{\partial T}|_F} \\ &= -\frac{\frac{\partial S}{\partial F}|_T}{\frac{c_F}{T}} \end{aligned} \tag{90}$$

Now what is $\frac{\partial S}{\partial F}|_T$? We can define a new potential

$$\begin{aligned} \phi &= U - TS - Fl \\ d\phi &= -SdT - ldF \end{aligned} \tag{91}$$

which yields

$$\frac{\partial S}{\partial F}|_T = \frac{\partial l}{\partial T}|_F = \alpha_L \tag{92}$$

The thermal expansion coefficient $\alpha_L = \frac{1}{l}\frac{\partial l}{\partial T}|_F$. Putting this all together,

$$\boxed{\frac{\partial T}{\partial F}|_S = -Tl(\frac{\alpha_L}{c_F})} \tag{93}$$

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

$$\Delta T = -(\Delta \frac{F}{A})(A \cdot l) T \frac{\alpha_L}{c_F} \tag{94}$$

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

8.3 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?

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP \tag{95}$$

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

$$\begin{aligned} \frac{\partial}{\partial P}|_T \cdot U &= T\frac{\partial S}{\partial P}|_T - P\frac{\partial V}{\partial P}|_T \\ &= -T(\alpha_V V) - P(-\beta_T V) \\ &= V(P\beta_T - T\alpha_V) \end{aligned} \tag{96}$$

Similarly,

$$\begin{aligned} \frac{\partial}{\partial T}|_P \cdot U &= T\frac{\partial S}{\partial T}|_P - P\frac{\partial V}{\partial T}|_P \\ &= nc_P - PV\alpha_V \end{aligned} \tag{97}$$

and thus we can write

$$dU = (nc_P - PV\alpha_V)dT + V(P\beta_T - T\alpha_V)dP \tag{98}$$

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.

8.4 A systematic way to think about derivatives

We're starting to build up a large number of derivatives and second derivatives of the free energies, 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. Lets look at the order of some derivatives of $G(T,P) \to dG = -SdT + VdP$:

$$\begin{aligned} \frac{\partial G}{\partial T}|_P &= -S \\ \frac{\partial G}{\partial P}|_T &= V \\ \frac{\partial^2 G}{\partial T^2}|_P &= -\frac{c_P}{T} \\ \frac{\partial^2 G}{\partial P^2}|_T &= -\beta_T V \end{aligned} \tag{99}$$

We can display the order of derivatives as follows:

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 $dU = TdS - PdV + HdM$. The various derivatives of $\phi = U - ST + PV - HM$ result in the following order of (second) derivatives:

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

You can write a similar matrix for any thermodynamic potential you choose. All such matrices are symmetric because of the Maxwell relations. The signs of the off-diagonal terms are controlled 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 of U is convex up with respect to the extensive variables.

9 Lecture - September 24, 2014

Last lecture we asked ourselves what the relationship between the change in volume with respect to temperature at constant magnetization and its derivative at constant magnetic field:

$$\left(\frac{\partial V}{\partial T}\right)_M \rightarrow ? \left(\frac{\partial V}{\partial T}\right)_H \tag{100}$$

We can apply the generalized chain rule, Eq. 82, in this situation:

$$\begin{aligned}\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_M &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_H + \frac{1}{V}\left(\frac{\partial V}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_H \\ &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_H + \frac{1}{V}\left(\frac{\partial V}{\partial M}\right)_T M'(T)\end{aligned} \tag{101}$$

Where we abbreviate $\left(\frac{\partial M}{\partial T}\right)_H$ as $M'(T)$. We know $\left(\frac{\partial V}{\partial M}\right)_T = \left(\frac{\partial V}{\partial H}\right)_T \left(\frac{\partial H}{\partial M}\right)_T = \frac{\gamma}{\chi}$, thus:

$$\alpha_M = \alpha_H + \frac{\gamma}{\chi} M'(T) \tag{102}$$

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?

$$\begin{aligned}\alpha_V &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \\ &= -\frac{1}{V}\left(\frac{\partial S}{\partial P}\right)_T \text{ (Maxwell)} \\ &= -\frac{1}{V}\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T \text{ (Chain Rule, Eq. 80)} \\ &= \beta_T \left(\frac{\partial S}{\partial V}\right)_T\end{aligned} \tag{103}$$

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.103 makes sense.

Can $\alpha_V < 0$? Yes! Indeed, this is observed in many systems. The basic way in which this happens is when molecules have more degees of freedom when the system is smaller. One examples is in polymers: there are more configurations when the chains in a polymer are bent, thus as temperature increases, polymers tend to shrink!

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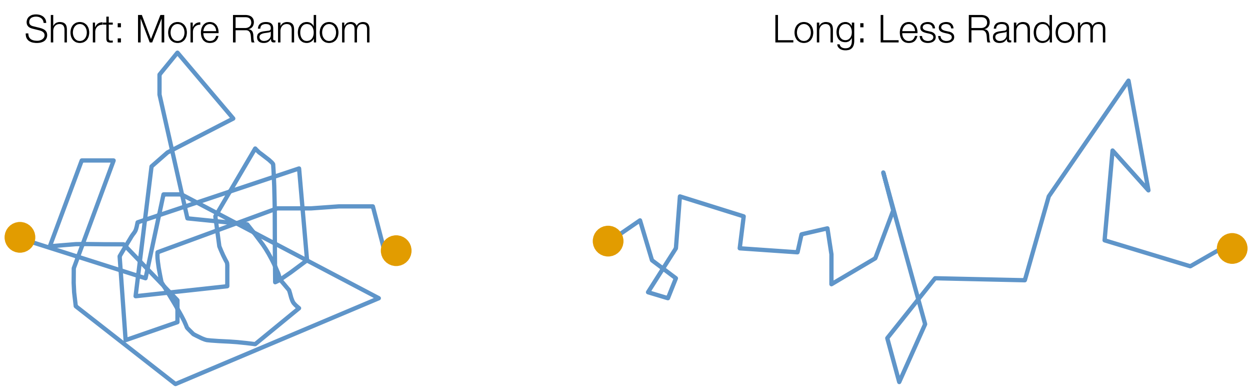

Figure 7: The reason polymers have a negative thermal expansion coefficient is because of entropy: their are more ways for the polymer to wiggle around when it isn't stretched out. We'll get quantitative about this in stat mech

9.1 What you should be able to do by now

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9.2 Checkin: What you should be able to do by now

¿¿¿¿¿¿¿ mikelec9new

(1) Identify work terms, **??**

(2) Construct the relevant thermodynamic potential, 2

(3) Define equilibrium (internal degrees of freedom consistent with boundary conditions)

(4) Define the relevant properties: 4

(5) Relate thermodynamic quantities and thus variations: 2

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9.3 Extending Formalism To Multicomponent systems

Back to open systems, we know =======

9.4 Equilibrium Conditions for Multicomponent Systems

Back to systems where we take the mole numbers into account, we can write dU for a multicomponent system as: ¿¿¿¿¿¿¿ mikelec9new

$$dU = TdS - PdV + \sum_i \mu_i dn_i \tag{104}$$

where $\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{i\neq j}}$ is the chemical potential of a species. If we have a 2-phase system, we will have $S^{(1)}, V^{(1)}, \{n_j\}^{(1)}$ describing the first and $S^{(2)}, V^{(2)}, n_j^{(2)}$ describing the second. We know

$$\begin{aligned} \partial S^{(1)} &= -\partial S^{(2)} \\ \partial V^{(1)} &= -\partial V^{(2)} \\ \partial n_j^{(1)} &= -\partial n_j^{(2)} \end{aligned} \tag{105}$$

where $j = [1, ..., r]$. Meanwhile

$$\begin{aligned} U &= \sum_{\alpha=1}^{v} U^{\alpha} \\ S &= \sum_{\alpha=1}^{v} S^{\alpha} \\ V &= \sum_{\alpha} V^{\alpha} \\ N &= \sum_{\alpha} n^{\alpha} \end{aligned} \tag{106}$$

$$\underset{\cdot}{\mathrm{U}} = \sum_{\alpha} T^{(\alpha)}(\underset{\cdot}{\mathrm{S}})^{\alpha} - P^{(\alpha)}(\underset{\cdot}{\mathrm{V}})^{\alpha} + \sum_{j=1}^{v} \mu_j (\underset{\cdot}{\mathrm{n}}_j)^{\alpha} \tag{107}$$

This is the first order displacement of U. If the system is at equilibrium, $\underset{\cdot}{\mathrm{U}} \geq 0$. If true equilibrium, $\underset{\cdot}{\mathrm{U}}|_{S,V,n} = 0$. For a single homogeneous phase, T, P, μ are constant throughout the phase. Put more generally, the takeaway here is that if the extensive variables are allowed to vary independently of one another (i.e. the exchange of extensive variables between subsystems is uncoupled, ex: charge is not coupled to mass flow like in a battery), 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.
- We can supply a bunch of constraints on the intensive variables of the different phases: they all need to be equal to one another. We derive these constraints in the next section.

If the exchange of extensive variables is coupled, it is the coupled sum of the the intensive variables that needs to be constant throughout a system at equilibrium. For example, if mass flow is coupled to charge exchange, then the electrical potential is coupled to the chemical potential of some species, and its 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.

9.5 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 invalidating (i.e. overspecifying the system) as:

$$f = m - n \tag{108}$$

We call f the degrees of freedom of the system of equations. We define a phase as a part of a system which is measurably distinct in terms of its thermodynamic variables from another part of the subsystem.

When multiple phases are in equilibrium with each other, 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, we increase the vapor pressure of the gas for it to remain in equlibrium 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 itself when the temperature is adjusted. Clearly, there is a non-trival 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 let there by c components in the system. We know that in each phase α, a Gibbs-Duhem equation must hold:

$$S^\alpha \mathrm{dT}^\alpha - V^\alpha \mathrm{dP}^\alpha + \sum_{i=1}^{c} N^\alpha \mathrm{d}\mu_i^\alpha = 0 \tag{109}$$

Hence, for each phase, there are $c+1$ independent intensive variables, which we can write in terms of T^α, P^α, and the $c-1$ independent chemical potentials:μ_i^α. The number of variables is thus the number of phases times $c+1$:

$$m = p(c+1) \tag{110}$$

The number of constraints from the intensive variables being equal to each other in each phase is the number of intensive variables in each phase times the number of phases minus 1:

$$n = (p-1)(c+2) \tag{111}$$

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

$$f = m - n = c - p + 2 \text{ } (T \text{ and } P \text{ can vary}) \tag{112}$$

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

$$f = c - p + 1 \text{ } (P \text{ specified}) \tag{113}$$

If temperature and pressure are both specified, you get:

$$f = c - p \text{ } (T \text{ and } P \text{ specified}) \tag{114}$$

These are all versions of the Gibbs phase rule. It has important implications for the possible shapes of phase diagrams.

9.6 Stability Conditions on the free energy

Here, we use a Taylor expansion to make some insights into the shape of U, and thus its Legendre transforms. U can be expressed as a Taylor expansion in the extensive variables as:

$$(\Delta U)_{S,V,n_j} = dU + d^2U + ... > 0 \tag{115}$$

At equilibrium, we know that $dU = 0$. Therefore $dU \approx d^2U > 0$. Thus, if we know that the second-order terms in a Taylor expansion of U should all be positive to guarantee U is minimal. Very loosely, this is the same as saying that in order for a function, f, to be at a minimum, it must have $f' = 0, f'' > 0$. More concretely, this corresponds to 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 to such perturbations, as illustrated in figure 8.

To illustrate this mathematically, we'll consider composite system with a diathermal wall[20], and then fix S, V, n:

$$\begin{aligned} dS = dS^{(1)} + dS^{(2)} = 0 \\ dV^{(1)} = dV^{(2)} = 0 \\ dn^{(1)} = dn^{(2)} \end{aligned} \tag{116}$$

then the variation in U becomes:

$$\begin{aligned} d^2U &= d^2U^{(1)} + d^2U^{(2)} \\ &= \frac{1}{2}\frac{\partial^2 U}{\partial S^{(1)2}}(dS^{(1)2}) + \frac{1}{2}\frac{\partial^2 U}{\partial S^{(2)2}}(dS^{(2)2}) \end{aligned} \tag{117}$$

[20]Reminder: heat can be exchanged, but n, V, cannot be exchanged.

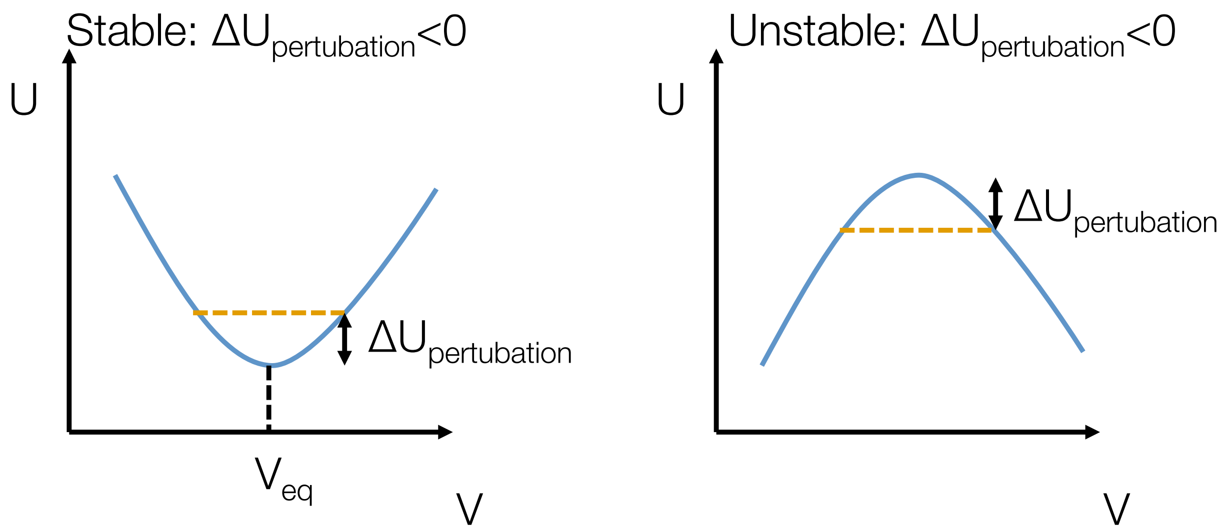

Figure 8: An illustration of a stable and unstable system with respect to volume perturbations. In the unstable case, subsystems can exchange volume and lower the energy of the systems. We call such instabilities to minute perturbations spinodal instabilities, and they evolve by special kinetics, termed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

Substituting in our known derivatives of U:

$$\begin{aligned}\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n} &= \left(\frac{\partial T}{\partial S}\right)_{V,n} = \frac{T}{c_V} \\ \partial^2 U &= \frac{1}{2}(dS^{(1)2})\left[\frac{T^{(1)}}{c_V^{(1)}} + \frac{T^{(2)}}{c_V^{(2)}}\right] \\ T\left[\frac{1}{c_V^{(1)}} + \frac{1}{c_V^{(2)}}\right] &\geq 0\end{aligned} \tag{118}$$

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 variable obey they same conditions; U is concave up with respect to all the extensive variables.

9.7 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. There are similar guarantees on the double derivatives of G. If we imagine that each phase/state of matter has its own free energy curve $G(T)^{\alpha}, G(T)^{\beta}, ...$, 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.

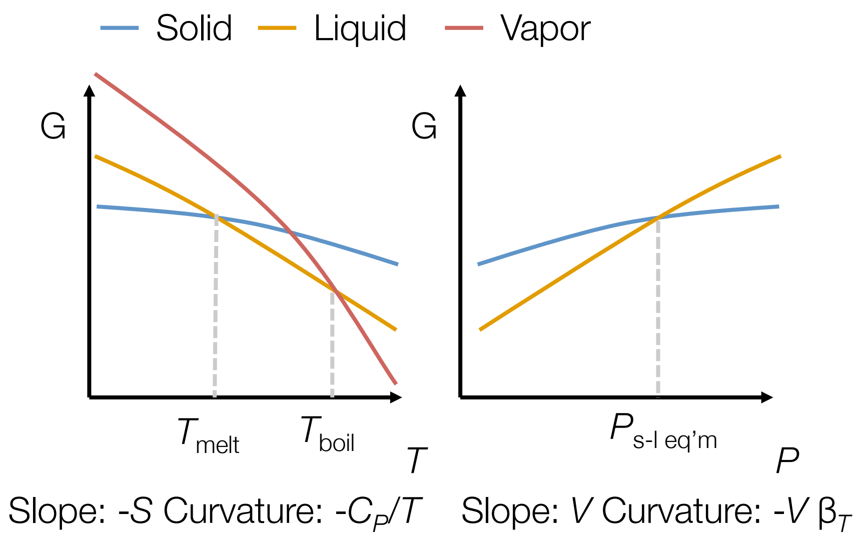

Figure 9: An illustration of thermodynamically consistent curves for the free energy of phases as a function of T and P which obey the stability criteria.

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

$$G^{\alpha} = G^{\beta} \tag{119}$$

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 ($\Delta V_{\phi T}$, $\Delta S_{\phi T}$). G(T)?

$$\begin{aligned}
&\frac{\partial G}{\partial T}|_P = -S \\
&\frac{\partial^2 G}{\partial T^2}|_P = -\frac{\partial S}{\partial T}|_P = -\frac{c_P}{T} < 0 \\
&\frac{\partial G}{\partial P}|_T = V \\
&\frac{\partial^2 G}{\partial P^2}|_T = -\beta_T V < 0
\end{aligned} \tag{120}$$

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 the $G(T)$ get steeper from solid to liquid to vapor and are all negative, because $S_{\text{solid}} \ll S_{\text{liquid}} \ll S_{\text{gas}}$.