The purpose of these notes is to provide a succinct discussion of the fundamental principles of equilibrium thermodynamics. The focus is on the mathematical structure of the theory, and the freedom one has to choose the basic thermodynamic variables and the ability to formulate equivalent descriptions. This freedom is essentially of a mathematical nature, but this freedom is also why thermodynamics is so useful in practice, as different experimental situations are most conveniently formulated using precisely those variables and functions that are under control of the experimentalist. The discussion provided here is based on information gleaned from three textbooks, which have far more information than these notes.

Herbert B. Callen: Thermodynamics and an Introduction to Thermostatistics, second edition, 1985 John Wiley and Sons, ISBN-0-471-86256-8, abbreviated (HC). This is a classic, very readable textbook that has a beautiful coherent discussion of the basic principles of thermodynamics.

Myron Tribus: Thermostatics and Thermodynamics, 1961, Van Nostrand, abbreviated (MT). This book has a very complete discussion on the freedom to choose variables in thermodynamics, and the statistical underpinnings of the theory. The book discusses a simple algorithm in terms of Jacobians that allows one to calculate any partial derivative for multicomponent systems in terms of elementary, ‘easily’ measurable quantities. It also discusses in detail how all thermodynamic properties can be obtained from ‘easily’ obtainable (or tabulated) quantities.

Michel Le Bellac, Fabrice Mortessagne, G. George Batrouni, Equilibrium and non-equilibrium statistical thermodynamics, 2004, Cambridge University Press, ISBN 0-521-82143-6 (BMB). This is a modern quite readable but fairly advanced text, which has concise discussions of thermodynamics and quantum statistical mechanics, including non-equilibrium processes.

In the following I provide a list of the basic definitions and postulates of equilibrium thermodynamics. These postulates no doubt would need adjustment in order to apply to any type of thermodynamical system. The goal is to elucidate the basic structure of thermodynamics, without striving for completeness.

Definitions and Postulates:

1. A macroscopic system, viewed in isolation, has a definite and precise total energy, $U$, subject to microscopic conservation laws.
2. There exist so-called equilibrium states that from the thermodynamic perspective are characterized completely by their total energy $U$, the volume $V$ and the mole numbers $n = n_1, n_2, \ldots, n_r$ of the chemical components.

3. It is possible to connect the equilibrium states $A(U_A, V, n) \leftrightarrow B(U_B, V, n)$, by transforming either $A$ to $B$ or $B$ to $A$ using exclusively mechanical work (that can be measured quantitatively), enclosing the states in an adiabatic environment:

$$w_{A \rightarrow B} = U_B - U_A$$

4. It is possible to transform state $A$ to $B$ (or conversely) by other processes. The mechanical work $w_{A \rightarrow B}$ can be measured. In addition the process involves heat in general, such that $q_{A \rightarrow B} = (U_B - U_A) - w_{A \rightarrow B}$, or $q_{A \rightarrow B} + w_{A \rightarrow B} = (U_B - U_A)$. The energy difference only depends on the equilibrium states, not on the process.

5. Systems can be partitioned into subsystems using walls. Walls can be:
   a. fixed vs. moveable (allowing $V$ to vary among component systems)
   b. adiabatic vs. diathermal (allowing heat to flow among component systems)
   c. impermeable vs. permeable to specific chemical compounds (allowing redistribution of matter among component systems)

6. Quantities for a system of subsystems can be extensive or intensive:
   a. Extensive (or additive) quantities for the total system are the sums of the quantities for the individual subsystems, e.g. $U$, $V$, $n$
   b. Intensive quantities can only be defined for the subsystems individually (e.g. $T$, $p$, $\mu$, to be defined later on).

7. To describe the system in relation to an environment, surroundings or reservoir, some nomenclature is useful. A reservoir is a particular environment such that the temperature and/or pressure and/or chemical potential can be kept constant and is under control of the experimentalist. One distinguishes:
   a. Open systems can exchange both matter and energy with the surroundings.
   b. Isolated systems can exchange neither matter nor energy with the surroundings.
   c. Closed systems can exchange energy but not matter with their surroundings.

To discuss the ‘Basic Problem of Thermodynamics’ (following HC), consider a system, which in its totality is a isolated and has a fixed volume (i.e. no exchange of energy, matter, fixed volume). This isolated system is partitioned into two compartments that are separated by a wall, which in the initial state is fixed, adiabatic and impermeable. Both subsystems are in equilibrium and described by $U^{(i)}, V^{(i)}, n^{(i)}, i = 1, 2$. The wall is said to pose an internal constraint. The essential problem of thermodynamics is to predict the new equilibrium situation if one or more of the internal constraints are removed. Hence, what are the new values for $U^{(i)}, V^{(i)}, n^{(i)}, i = 1, 2$ if the wall is made moveable, and/or adiabatic, and/or permeable? Upon the lifting of the constraint typically a new equilibrium situation
will establish itself (the alternative is eternal oscillation), and to calculate the new equilibrium situation one postulates the existence of an extremum principle: ‘some’ quantity is maximized by the new equilibrium situation. This quantity is called entropy, and it is postulated to have the following properties:

**Postulates and properties concerning Entropy**

I. For any system in equilibrium (all equilibrium states) there exists a positive, continuous and differentiable entropy function \( S(U,V,n) \), which is an increasing function of \( U \), for fixed \( V,n \) (for an exception see BMB problem 3.8.2)

II. For a system consisting of \( M \) subsystems, \( S \) is additive or extensive,
\[
S_{\text{total}} = \sum_m S_m(U_m,V_m,n_m)
\]

III. If the global isolated system is initially divided by internal constraints and one or more of the constraints are lifted, the entropy of the final new equilibrium state must be greater than or equal to the initial entropy. The new subsystem values \( U_m,V_m,n_m \) are such that \( S_{\text{tot}}^{\text{new}} \geq S_{\text{tot}}^{\text{initial}} \), entropy cannot decrease (following BMB). The values assumed by the extensive subsystem parameters after the lifting of the initial constraint(s) are such that the entropy is maximized over the allowed manifold of equilibrium states (allowed according to the still remaining constraints).

IV. For a single component system (no phase separation) the entropy is a concave function of the extensive variables. Concave means that a straight line connecting two points on the curve is always below the curve:
\[
f(\lambda x_1 + (1-\lambda) x_2) \geq \lambda f(x_1) + (1-\lambda) f(x_2), \quad 0 \leq \lambda \leq 1.
\]
It is also said that the entropy is locally concave (or piecewise concave). Concavity implies that the second derivatives of the entropy are negative (or zero) everywhere and in any direction.

V. The entropy is bound from below (and its minimum is attained at the 0 of absolute temperature, to be defined).

**Definition of temperature, pressure and chemical potentials based on entropy.**

I will give the definitions for a single system. If the system consists of a number of subsystems separated by walls, each in thermodynamic equilibrium, the definitions hold for each subsystem separately, and only involve the extensive quantities for the subsystem.

Temperature \( T \):
\[
\left( \frac{\partial S}{\partial U} \right)_{V,n} = \frac{1}{T} \geq 0
\]

Pressure \( P \):
\[
\left( \frac{\partial S}{\partial V} \right)_{U,n} = \frac{P}{T} \geq 0
\]
Chemical potential $\mu_i : \left( \frac{\partial S}{\partial n_i} \right)_{U,V,n^{(\neq i)}} = -\frac{\mu_i}{T}$

**Definition of different types of (idealized) processes for a isolated system:**

- A *quasistatic* process $A \rightarrow B$ maintains internal equilibrium during the transformation from A to B. It is necessarily an infinitesimal, ‘impossibly’ slow process. Not all infinitesimal processes are quasistatic, e.g. letting a gas expand through a tiny hole may be thought of as infinitesimal but is not quasi-static.

- A *reversible* process $A \rightarrow B$ is quasistatic but in addition the change in entropy in the transformation is zero, and therefore the reverse process $B \rightarrow A$ is also possible (for the isolated system).

- An *irreversible* process is a general (not necessarily infinitesimal) process in which there is an increase in entropy. An example of a quasistatic but irreversible process would be the thermal equilibration of two subsystems connected by a nearly adiabatic wall that just barely conducts heat. The process could not run in reverse.

The above definitions and postulates are all that is needed to define the subject of thermodynamics. Other functions can be defined in terms of the already defined quantities, and the derivation of relations and the discussion of thermal equilibrium in all of its different guises is mostly a matter of turning the crank of mathematics, which does not mean it is trivial. In the following we will discuss some of the mathematics in some detail. I will also provide some handouts that discuss things nicely from a general perspective. Before we go on it may be good to provide some comments to make the above rather abstract exposition more palatable, and to convince the reader that this indeed summarizes (in essence) the principles of thermodynamics. Let me refer to the book by Callen in particular for more extensive discussion. Below, I will repeat the postulates and insert more discussion.

**Definitions and Postulates:**

1. *A macroscopic system, viewed in isolation, has a definite and precise total energy, $U$, subject to microscopic conservation laws.*

   This postulate has its most profound basis in the microscopic laws of physics. One can use either classical or quantum mechanics. In either case the system as a whole evolves in time and it satisfies the law of conservation of energy. This is true only for so-called conservative systems (the definition is circular), but this suffices as the associated Hamiltonians describe the fundamental laws of nature.

2. *There exist so-called equilibrium states that from the thermodynamic perspective are characterized completely by their total energy $U$, the volume $V$ and the mole numbers $n = n_1, n_2, \ldots, n_r$ of the chemical components.*
This statement states that macroscopic states exist, which can be described or characterized uniquely by amazingly few variables. In the above definition, all of these variables are chosen to be extensive. This is but one possibility, and it leads to the so-called entropic representation of thermodynamics, which is what we are discussing. One macroscopic state would have many microscopic realizations (e.g. stating position and momenta of each particle, i.e. a configuration in a classical context). Equilibrium states do not change with time (in contrast to microstates, which are perennially hustling about), and in practice such states are often metastable, meaning they change on a very long timescale, and can ‘therefore’ be viewed to be equilibrium states. It does not seem possible to give an unambiguous definition of an equilibrium state vs. metastable state. Equilibrium states are defined in the sense that they satisfy the postulates of equilibrium thermodynamics! (HC). Since the equilibrium states are defined in terms of the variables \( U, V, n \) it follows that it does not matter how these states are prepared. If the values of the variables are the same, the macroscopic state is the same. For many systems the process of preparation does matter (e.g. systems showing hysteresis, or glassy materials, see HC), and this means that such systems are not in thermodynamic equilibrium. It is also important that equilibrium thermodynamics only refers to the properties of equilibrium states, and does not immediately apply to the non-equilibrium processes that might connect various equilibrium states.

3. It is possible to connect the equilibrium states \( A(U_A, V, n) \leftrightarrow B(U_B, V, n) \), by transforming either \( A \) to \( B \) or \( B \) to \( A \) using exclusively mechanical work (that can be measured quantitatively), enclosing the states in an adiabatic environment:

\[
W_{A \rightarrow B} = U_B - U_A
\]

This observation was first made by Joule. It is important that we can easily quantify mechanical work (e.g. pV work or electrical work), and that we can perform work on a system isolated from the rest of the world. This type of experiment is the quintessential process to measure the change in energy between equilibrium states \( A \) and \( B \), and it is vital to keep heat out of the equation. Most transformations changing an equilibrium system \( A \) into equilibrium system \( B \) would involve an increase in entropy, and hence cannot be reversed under adiabatic conditions. To obtain the energy difference it suffices if the process can be carried out one way or the other. Let me note that in the available textbooks I do not find a corresponding discussion about changing \( V \) or \( n \). It would seem to be required that one would have procedures to change \( V \) and \( n \) and to know the corresponding change in \( U \), in order to keep track of all of the variables that define the state.

4. It is possible to transform state \( A \) to \( B \) (or conversely) by other processes. The mechanical work \( W_{A \rightarrow B} \) can be measured. In addition the process involves heat in
general, such that \( q_{A \rightarrow B} = (U_B - U_A) - w_{A \rightarrow B} \), or \( q_{A \rightarrow B} + w_{A \rightarrow B} = (U_B - U_A) \). The energy difference only depends on the equilibrium states, not on the process.

Here we have reached the first law of thermodynamics. The processes described under 3) are needed to define/measure the change in energy associated with the transformation \( A \rightarrow B \). The states themselves are unique (from 1), and any other process that affects the same transformation must preserve this difference in energy (as a postulate that has been painstakingly confirmed experimentally). Whatever difference in energy is not supplied (or taken out) by work is accounted for by heat. The mechanical work can always be measured. We then infer the quantity of heat. It is perhaps interesting to note that from the above definitions it is self-evident that work and heat depend on the particulars of the process, and can therefore not be functions of state (or from a mathematical perspective: they are inexact (Pfaff) differentials). Of course, as we leave the realm of discussing the fundamentals, heat can be measured in other ways, e.g. it is the basis of calorimetry. You might note that to calibrate the calorimeter a more basic process is needed involving mechanical work in the final analysis.

5. **Systems can be partitioned into subsystems using walls.** Walls can be
   a. **adiabatic vs. diathermal** (allowing heat to flow among component systems)
   b. **fixed vs. moveable** (allowing \( V \) to vary among component systems)
   c. **impermeable vs. permeable to specific chemical compounds** (allowing redistribution of matter among component systems)

The use of walls is a good way to impose constraints and is an essential ingredient of much of formal thermodynamic analysis. Changing a wall from adiabatic to diathermal enables heat flow and the subsystems will equilibrate to reach equal temperature. That is when the heat flow stops, and entropy would have reached a maximum. The volume and the number of particles for each subsystem would be unchanged. If the wall is changed from a fixed to a moveable wall, the wall will start to move until the pressure is equal on both sides. As one subsystem does \( P \)\( V \) work on the other it follows that both the volumes and the energies of the subsystems change. If the moveable wall would be kept adiabatic, there is no unique solution for the temperatures of the subsystems, and the system would keep oscillating. In every textbook therefore (but for illuminating discussion see Callen 2.7), a moveable wall is also taken to be diathermal. Then the system equilibrates until all subsystems have equal temperature and pressure. The final constraint to be considered is the flow of particles. If particles flow also the energy content changes, and moreover a permeable wall, of course, always allows the transfer of heat. In this case the system equilibrates such that the temperature and the chemical potential of each chemical species (that is allowed to migrate) is equal in every subsystem. If all constraints are lifted the situation is as if there are no walls at all. Still there are imaginary boundaries that allow one to calculate the number of particles for each subsystem, there is a volume and one might assign energy to each subsystem. The assignment of energy is problematic as it depends on interactions between particles, possibly from different subsystems. In a
thermodynamic system at equilibrium the temperature, pressure and chemical potentials would be homogenous throughout.

6. Quantities for a system of subsystems can be extensive or intensive:
   d. Extensive (or additive) quantities for the total system are the sums of the quantities for the individual subsystems, e.g. $U, V, n$
   e. Intensive quantities can only be defined for the subsystems individually (e.g. $T, p, \mu$, to be defined later on).

As we shall see below some very powerful results follow from the notion of extensivity of the entropy. It can also be noted that entropy is a function of purely extensive quantities and as the entropy function reaches its maximum one finds equality of the intensive variables in the system ($T, P, \mu_i$). Extensive variables are always associated with their conjugate intensive variables, e.g. $P & V$, $n_i & \mu_i$, $U & T$ or $S & T$, and most thermodynamic quantities are expressed as functions of either the intensive or extensive partner of a pair. This is not necessarily true however.

Let us next turn to the entropy function. Let us first verify the physical plausibility of the maximum entropy criterion for equilibrium states, together with the definitions of the partial derivatives of entropy. This weak criterion of plausibility would not be a particularly good reason to use the postulates as formulated. In subsequent sections we will analyse what is implied by the mathematical properties of entropy. This will help to elucidate the full power of the formulation.

**Physical plausibility of the maximum entropy criterion and the definitions of temperature, pressure and chemical potentials based on entropy.**

The partial derivatives where given by

Temperature $T$:

$$\left(\frac{\partial S}{\partial U}\right)_{P,n} = \frac{1}{T} \geq 0$$

Pressure $P$:

$$\left(\frac{\partial S}{\partial V}\right)_{U,n} = \frac{P}{T} \geq 0$$

Chemical potential $\mu_i$:

$$\left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_i} = -\frac{\mu_i}{T}$$

and it then follows that a change in entropy would be given by

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

This equation can alternately be written as an equation for $dU$

$$dU = TdS - PdV + \sum_i \mu_i dn_i$$
This equation should look familiar as a basic relation in thermodynamics. It demonstrates that the above definitions agree with the usual definitions in thermodynamics. Let us also demonstrate the maximum entropy principle for the basic equilibrium situations.

If we consider a system consisting of two subsystems separated initially by an adiabatic, fixed, impermeable wall, where each subsystem is characterized by its separate values \( U_i, V_i, n_i, T_i, P_i, \mu_i \), \( i = 1, 2 \) and the total change in \( S \) is the sum over the two subsystems, \( dS = dS_1 + dS_2 \).

i) Analysis temperature: If we change the wall from adiabatic to diathermal, heat can flow between the subsystems, changing the internal energies of the subsystems, but preserving total energy

\[ dU_2 = -dU_1 \]

Hence

\[ dS = \frac{1}{T_1} dU_1 + \frac{1}{T_2} dU_2 = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 \rightarrow 0 \]

Hence heat flows until \( S \) reaches its extremum (maximum), which occurs when the temperatures are equal. Moreover, when the temperatures are not equal, e.g.

\[ T_1 < T_2 \rightarrow \left( \frac{1}{T_1} - \frac{1}{T_2} \right) > 0 \]

it follows \( dU_1 > 0 \) as entropy cannot decrease. The subsystem at the lower temperature gains energy, or, heat flows from hot to cold. All as it should be.

ii) Analysis pressure. As discussed before we should now change the wall into a diathermal, movable wall, and hence energy and volume can be repartitioned among subsystems, but preserving their totals:

\[ dU_2 = -dU_1; \quad dV_2 = -dV_1; \]

\[ dS = \left( \frac{1}{T_1} dU_1 + \frac{P_1}{T_1} dV_1 \right) + \left( \frac{1}{T_2} dU_2 + \frac{P_2}{T_2} dV_2 \right) \]

\[ = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left( \frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 \rightarrow 0 \]

It follows that \( S \) reaches its extremum if both the temperatures and the pressures are equal. If we assume equal temperatures, then, if \( P_1 > P_2 \), it follows that \( dV_1 > 0 \) as \( S \) cannot decrease, in agreement with common sense that the volume increases on the high pressure side.

iii) Analysis chemical potential. Now we change the wall to be diathermal and permeable, allowing energy and the number of particles to redistribute. We find

\[ dU_2 = -dU_1; \quad dn_2 = -dn_1; \]

\[ dS = \left( \frac{1}{T_1} dU_1 - \frac{\mu_1}{T_1} dn_1 \right) + \left( \frac{1}{T_2} dU_2 - \frac{\mu_2}{T_2} dn_2 \right) \]

\[ = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 - \left( \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dn_1 \rightarrow 0 \]
and it follows that energy and particles redistribute until both the temperature and the chemical potential is equal on both sides of the wall. If $\mu_1 > \mu_2$, assuming the temperatures are equal, it follows that $dn_i < 0$ (because $dS$ cannot decrease), and it follows that particles flow from region with high chemical potential to regions with low chemical potential, in accordance with the usual definitions.

Let us now continue the discussion focusing on the mathematical properties of the entropy function. It will be seen that these mathematical properties are underlying the rest of the formulation of thermodynamics, in particular the definition of the various chemical potentials, $U$, $H$, $A$ and $G$, and their so-called natural variables. We will be discussing so-called Legendre transformations, and eventually also consider the plethora of partial derivatives you might have encountered in your study of thermodynamics.

**Mathematical properties of Entropy:**

*Entropy is an extensive, semipositive, continuous and differentiable (except for isolated points) function of the extensive variables $U$, $V$ and $n$, which is locally concave, the lowest possible value of which is zero (attained at zero temperature).*

Let us divorce this yet more from its physical annotations to be able to better focus on the mathematics, and consider a function of two variables $f(x,y)$, with similar properties as the entropy function. Extensivity means that if all the variables are scaled by the same parameter $\lambda$, the function value itself is also scaled by $\lambda$, it is known as first-order homogeneity in mathematics. Let me note here that when discussing extensivity, one usually thinks of doubling or tripling the size of the system, which just amounts to adding duplicates. With a little bit of work one can turn this into continuous scaling or first-order homogeneity. Hence we have

$$f(\lambda x, \lambda y) = \lambda f(x, y).$$

Differentiating with respect to $\lambda$ we find

$$\frac{\partial f(\lambda x, \lambda y)}{\partial (\lambda x)} \frac{\partial (\lambda x)}{\partial \lambda} + \frac{\partial f(\lambda x, \lambda y)}{\partial (\lambda y)} \frac{\partial (\lambda y)}{\partial \lambda} = f(x, y)$$

$$x \frac{\partial f(\lambda x, \lambda y)}{\partial (\lambda x)} + y \frac{\partial f(\lambda x, \lambda y)}{\partial (\lambda y)} = f(x, y)$$

This equation is true for all $\lambda$, in particular at $\lambda = 1$, where we obtain,

$$x \frac{\partial f}{\partial x}(x, y) + y \frac{\partial f}{\partial y}(x, y) = f(x, y)$$

Here we use the conventional mathematical notation in which taking a partial derivative implies that all other variables of the function are taken to be constant. This innocent looking equation is quite remarkable. It says that if we know the partial first derivatives of the function at some point $(x,y)$ we actually also know the value of the function at that point. If we know the first-order partial derivatives of the function for all $(x,y)$ the
function is immediately known (no need to integrate). Let us consider some examples of first-order homogeneous functions, their partial derivatives and the reconstructed function

\[ f(x, y) = \frac{x^2}{y} + y^{3/4}x^{1/4} \rightarrow x^* \left( \frac{2x}{y} + \frac{1}{4}y^{3/4}x^{-3/4} \right) + y^* \left( -\frac{x^2}{y^2} + \frac{3}{4}y^{-1/4}x^{1/4} \right) \]

\[ = \left( \frac{2x^2}{y} - \frac{x^2}{y} \right) + y^{3/4}x^{1/4} \left( \frac{1}{4} + \frac{3}{4} \right) = f(x, y) \]

or in general for any first-order homogenous product

\[ f(x, y) = x^a y^{1-a} \rightarrow x a x^{a-1} y^{1-a} + y(1-a)x^a y^{-a} = x^a y^{1-a} \]

If the variables make up the argument \( z(x,y) \) in a more general function like \( e^z \) or \( \sin(z) \), the overall argument of the function would need to have overall rank zero to satisfy the first-order homogenous property. Such a function would then need to be multiplied by a proper first-order product function. An example would be

\[ f(x, y) = xe^{y/x} \rightarrow x^*(e^{y/x} + x(-\frac{y}{x^2})e^{y/x}) + y^*(x(\frac{1}{x})e^{y/x}) \]

\[ = (x - y + y)e^{y/x} = xe^{y/x} \]

These examples give you some idea of the type of multivariate functions that can be first-order homogenous. Let us examine some other properties. For the differential of any function \( f(x, y) \) we can always write

\[ df = \left( \frac{\partial f}{\partial x} \right)_y dx + \left( \frac{\partial f}{\partial y} \right)_x dy \]

and if we use the special form of a first-order homogenous function

\[ f = \left( \frac{\partial f}{\partial x} \right)_y x + \left( \frac{\partial f}{\partial y} \right)_x y \]

we obtain

\[ df = \left[ \left( \frac{\partial^2 f}{\partial x^2} \right)x + \left( \frac{\partial^2 f}{\partial x \partial y} \right)y \right] dx + \left[ \left( \frac{\partial^2 f}{\partial x \partial y} \right)x + \left( \frac{\partial^2 f}{\partial y^2} \right)y + \left( \frac{\partial f}{\partial y} \right) \right] dy \]

since these two expressions for \( df \) have to be equal for any \( dx, dy \), we find

\[ x \left( \frac{\partial^2 f}{\partial x^2} \right) + y \left( \frac{\partial^2 f}{\partial x \partial y} \right) = 0 \]

\[ x \left( \frac{\partial^2 f}{\partial x \partial y} \right) + y \left( \frac{\partial^2 f}{\partial y^2} \right) = 0 \]

\[ x^2 \left( \frac{\partial^2 f}{\partial x^2} \right) - y^2 \left( \frac{\partial^2 f}{\partial y^2} \right) = 0 \]

It follows that if we know one of the partial second-order derivatives, we know all of them in the case of a first-order homogenous product, at least in the case of two variables. This illustrates again that these functions are special indeed. As an example, it is easily verified that indeed these differential relations are satisfied for the quite general first-order homogenous function \( x^a y^{1-a} \).
Let us return to thermodynamics and consider the implications for the entropy function

\[ S = S(U, V, n) \]

\[ dS = \left( \frac{\partial S}{\partial U} \right)_{U,V,n} dU + \left( \frac{\partial S}{\partial V} \right)_{U,n} dV + \sum_i \left( \frac{\partial S}{\partial n_i} \right)_{U,V,n} dn_i \]

\[ dS = \frac{1}{T} dU + \frac{P}{T} dV - \sum_i \frac{\mu_i}{T} dn_i \]

Here I used the definitions for the partial derivatives of the entropy, as they were mentioned before. Because of the first-order homogeneity (or extensivity) of entropy, from the knowledge of the partial derivatives in the expression for we can immediately write for the entropy function

\[ S = \frac{1}{T} U + \frac{P}{T} V - \sum_i \frac{\mu_i}{T} n_i \]

This equation can alternatively be written as an expression for the internal energy \( U \)

\[ U = TS - PV + \sum_i \mu_i n_i \]

Taking the previous formula for \( dS \), it is also straightforward to convert that into an equation for \( dU \):

\[ dU = TdS - PdV + \sum_i \mu_i dn_i \]

This agrees with a formula that will be familiar to you from a previous thermodynamics class (as I mentioned before). From the differential for \( dU \) we find

\[ \left( \frac{\partial U}{\partial S} \right)_{U,V,n} = T; \quad \left( \frac{\partial U}{\partial V} \right)_{S,n} = -P; \quad \left( \frac{\partial U}{\partial n_i} \right)_{S,V,n} = -\mu_i; \]

and since \( S, V \) and \( n \) are all extensive quantities we note that \( U(S, V, n) \) is a first-order homogenous function, and therefore knowledge of the partial derivatives immediately allows us to go from the expression for \( dU \) back to the expression for \( U \).

Let me emphasize the import of these results. If we would have an explicit form for the function \( S(U, V, n) \) we have access to all possible thermodynamic information. In particular this would mean that we would know the \((2+r)\) partial derivatives (for \( r \) chemical compounds) and would be able to obtain expressions for

\[ \frac{1}{T}(U, V, n); \quad \frac{P}{T}(U, V, n); \quad -\frac{\mu_i}{T}(U, V, n) \]

Complete knowledge of all of these \((2+r)\) functions is equivalent to knowing the single function \( S(U, V, n) \), and all thermodynamic information for the system. Defining functions of the variables \( U, V \) and \( n \) is denoted as the entropy representation, as knowing...
only the entropy as a function of $S(U,V,n)$ suffices to define all thermodynamic properties.

An alternative presentation would be the energy representation. If the function $U(S,V,n)$ is known for all values of $S$, $V$, $n$, one can calculate the partial derivatives

$$T(S,V,n) = \left(\frac{\partial U}{\partial S}\right)_{V,n} ; \; P(S,V,n) = -\left(\frac{\partial U}{\partial V}\right)_{S,n} ; \; \mu_i(S,V,n) = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n}$$

and, knowing the partial derivatives for one particular set of variables $S$, $V$, $n$, $U$ at that point is also determined, from the fact that $U$ is first-order homogenous. The single function $U(S,V,n)$ contains all thermodynamic information. Alternative one would need to know all of the partial derivatives as then the function can be reconstructed. Let me emphasize that knowing for example $T(S,V,n)$ by itself would not yield all thermodynamic information, and neither would the knowledge of, for example, $U(T,V,n)$.

The above representations of thermodynamics are a first illustration of the use of so-called ‘natural variables’. While knowledge of $U(S,V,n)$ is paramount to having all thermodynamic information, knowledge of for example $U(T,V,n)$ would not suffice. The latter would be analogous to knowing only one of the partial derivative functions, e.g. $T(S,V,n)$, instead of $(2+r)$. Let me note that the expression

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \sum_i \left(\frac{\partial U}{\partial n_i}\right)_{T,V,n} dn_i$$

is perfectly legitimate, and would provide information on changes in $dU$ over small ranges of $T$, $V$, $n$. However, the knowledge of the partial derivatives for all values of $T$, $V$, $n$, still would not allow me to reconstruct $U$ itself, and there would be numerous types of thermodynamic data I would not have access to. The first-order homogeneity property is key in this respect.

It is of interest to start from the equation for $U$

$$U = TS - PV + \sum_i \mu_i n_i$$

and analyse how it would change under changes in all of the quantities:

$$dU = TdS + SdT - PdV - VdP + \sum_i \mu_i dn_i + \sum_i n_i d\mu_i$$

substituting

$$TdS = dU + PdV - \sum_i \mu_i dn_i$$

we find

$$SdT - VdP + \sum_i n_i d\mu_i = 0$$

This is an important relation between changes in the intensive parameters, and is called the Gibbs-Duhem equation. An analogous relation between all intensive variables would hold for any thermodynamic system: the intensive variables are not all independent. The
Gibbs-Duhem relation is important to understanding other formal aspects of thermodynamics.

I think it is good to point out here, that the above assertions are not so easy to proof mathematically. The material is often stated (and usually less explicitly than I did) without proof. The most typical treatment of thermodynamics would give you a set of prescriptions, that (apparently) work, and that we are all supposed to adhere to, otherwise things might not work anymore. The purpose of these notes is to try to convince you that there are reasons why things work, and that the choice of variables is indeed delicate (and somewhat mysterious) in thermodynamics. The mathematics is relatively straightforward if we know entropy is a concave and first-order homogeneous function. Then one can carry out a number of well-defined transformations and obtain other functions with well-defined properties and mathematically equivalent prescriptions. This will be discussed in the subsequent section. I (and others) have postulated that entropy has these convenient mathematical properties. I am not at all sure that the physical quantity entropy necessarily must have these properties. Probably not all of them, and counter examples are sometimes considered in the available textbooks (Callen and PMB). I am not aware of a more general mathematical formulation of thermodynamics that would cover all possible scenarios. It might also get mathematically complicated. Let us continue.

**Maximum Entropy principle vs. Minimum Energy principle.**

In chapter 5 of Callen (available on the chem450 website) it is discussed in full detail that the

**Maximum entropy principle:**

*The equilibrium value of any unconstrained parameter is such as to **maximize** the entropy for a given value of the total energy.*

Is equivalent to a

**Minimum energy principle:**

*The equilibrium value of any unconstrained parameter is such as to **minimize** the energy for a given value of the total entropy.*

The principle is easily verified for the example of lifting the internal constraints that were discussed before. For example if we have a system consisting of two subsystems characterized by $S,V,n,T,P,\mu_i,i=1,2$ and the total change in $U$ is the sum over the two subsystem energies, $dU = dU_1 + dU_2$, where we note that now the total energy is allowed to change, while the subsystem entropies are considered adjustable variables, but preserving the total entropy. The minimum energy principle says the energy can only decrease or stay equal upon removing a constraint.

i) Analysis temperature: If we change the wall from adiabatic to ‘reversibly diathermal’, heat can flow reversibly between the subsystems, changing the internal entropies of the subsystems, but preserving total entropy

$$dS_2 = -dS_1$$

Hence
Hence heat/entropy flows until $U$ reaches its extremum (minimum), which is when the temperatures are equal. Moreover, when the temperatures are not equal, e.g. $T_1 > T_2$, we would find $dS_i < 0$ as energy cannot increase upon removing a constraint. The subsystem at the higher temperature loses entropy, or, heat flows from hot to cold. All as it should be. It will be clear that the minimum energy principle is not easy to apply in practice as it requires preserving total entropy, which is a difficult experimental constraint.

This leads to our next topic, as much of thermodynamics is concerned with using different experimental situations in which certainly variables are easily controlled, e.g. pressure or temperature. We still want to predict changes in equilibrium states as constraints are removed, or if the control variables are changed from one setting to another. From a mathematical perspective we need to be able to transform variables, while preserving all of the information contained in functions like $S(U,V,n)$, or $U(S,V,n)$.

**Legendre Transformations.**

As just noted, in thermodynamics it is desirable to change variables without losing information. In this context the concavity of the entropy is important and (equivalently) the convexity of the internal energy. In a Legendre transformation one can change a function such that a partial derivative of the original function becomes a variable for the new function. The procedure is invertible (with no loss of information) if the function is either convex or concave in the transformed variable. Upon Legendre transformations (as we use them in thermodynamics), a convex function turns into a concave function and conversely (where the change of convexity vs. concavity is restricted to the variables involved in the transformation). The idea of Legendre transformations is well described in the literature, and I will post notes on the web that explain this important topic. Below I will discuss Legendre transformation of the energy, $U$, which leads to other so-called thermodynamic potentials. The thermodynamic potentials are concave in intensive variables and convex in external variables (like the energy). Minimizing these thermodynamic potentials under suitable constraints provides new principles of equilibrium. Alternatively, one can use Legendre transformations of the entropy, and this gives rise to various so-called Massieu functions which obey a maximizing principle to define new equilibrium states (in analogy to entropy). I will here list important examples with the most pertinent discussion.

Let us start from

$$U(S,V,n) = TS - PV + \sum_i \mu_i n_i$$

$$dU = TdS - PdV + \sum_i \mu_i \ dn_i$$

and obtain the various thermodynamic potentials:

i) Helmholtz free energy $A$:

Defining
\[ A = U - TS; \quad dA = dU - SdT -TdS \]

we find
\[ dA = -SdT - PdV + \sum_i \mu_idn_i \]

where the new variables are T, V, n, where we note that T was the partial derivative of U, with respect to S.

\[ A(T,V,n) = U - TS = -PV + \sum_i \mu_i n_i \]

we can also write
\[ dA = -PdV -VdP + \sum_i \mu_idn_i + \sum_i n_id\mu_i \]

and subtracting the Gibbs-Duhem relation we get back to the previous expression for \( dA \) in terms of \( dT, dV, dn \). If one would know the function \( A(T,V,n) \) for all values of \( T, V, n \) one would have all thermodynamic information. Equivalently to knowing \( A(T,V,n) \) would be to know
\[ P(T,V,n), \mu_i(T,V,n) \]

The Helmholtz free energy is minimized for systems in contact with a heat reservoir such that the system remains at constant temperature. Hence instead of constant \( S \) (in the minimum energy principle), we now have constant \( T \), far more friendly in practice. In the analysis of the internal constraint problem, both subsystems would be at the temperature of the reservoir and we can create a moveable wall (equilibrate pressure), or a permeable wall (equilibrate chemical potential). Energy can float freely from and into the reservoir, and there is no constraint on total energy of the total system (excluding the reservoir). One can also adjust the temperature of the reservoir, and the subsystems would equilibrate by minimizing their Helmholtz free energy.

ii) Enthalpy
Defining
\[ H = U + PV; \quad dH = dU + PdV +VdP \]

we find
\[ dH = TdS +VdP + \sum_i \mu_idn_i \]

where the new variables are S, P, n, and we note that P was the original partial derivative of \( U \) with respect to \( V \), and P has turned into a variable now, rather than \( V \).

\[ H(S,P,n) = U + PV = TS +\sum_i \mu_i n_i \]

we can also write
\[ dH = TdS + SdT + \sum_i \mu_idn_i + \sum_i n_id\mu_i \]

and subtracting the Gibbs-Duhem relation we get back to the earlier expression for \( dH \) in terms of \( dS, dP, dn \). If one would know the function \( H(S,P,n) \) for all values of \( S, P, n \) one would have all thermodynamic information. Equivalently to knowing \( H(S,P,n) \) would be to know
\[ T(S,P,n), \mu_i(S,P,n) \]
The enthalpy is minimized for systems in contact with a pressure reservoir such that the system remains at constant pressure. The constant pressure condition removes the possibility to control the total volume of the system (or subsystems). The wall between the subsystems can be made ‘reversibly diathermal’, allowing the flow of entropy, and leading to equilibration of temperature, or it can be made permeable to chemical species leading to equilibration of temperature and chemical potential. In addition the pressure of the reservoir can be changed, leading to new equilibrium conditions for the subsystems, still described by minimization of enthalpy.

iii) Gibbs free energy
Defining
\[ G = A + PV = U - TS + PV; \quad dG = dA + PdV + VdP \]
we find
\[ dG = -SdT + VdP + \sum \mu_i dn_i \]
where the new variables are \( T, P, n \)
\[ G(T, P, n) = A + PV = \sum \mu_i n_i \]
we can also write
\[ dG = \sum \mu_i dn_i + \sum n_i d\mu_i \]
and subtracting the Gibbs-Duhem relation we get back to the previous expression for \( dG \) in terms of \( dT, dP, dn \). If one would know the function \( G(T, P, n) \) for all values of \( S, P, n \) one would have all thermodynamic information. Equivalent to knowing \( G(T, P, n) \) would be to know
\[ \mu_i(T, P, n) \]
The Gibbs free energy is minimized for systems in contact with a temperature and pressure reservoir such that the system remains at constant temperature and pressure. The wall between the subsystems can only be made permeable for specific chemical species, leading to equilibration of chemical potential. In addition changes can be induced by regulating temperature and pressure of the reservoir.

iv) Grand canonical function \( Z \)
Defining
\[ Z = U - TS - \sum \mu_i n_i; \quad dZ = dU - SdT - TdS - \sum \mu_i dn_i - \sum n_i d\mu_i \]
we find
\[ dZ = -SdT - PdV + \sum n_i d\mu_i \]
where the new variables are \( T, V, \mu_i \),
\[ Z(T, V, \mu_i) = U - TS - \sum \mu_i n_i = -PV \]
we can also write
\[ dZ = -PdV - VdP \]
and subtracting the Gibbs-Duhem relation we get back to the previous expression for \( dZ \) in terms of \( dT, dV, d\mu \). If one would know the function \( Z(T,V,\mu) \) for all values of \( T, V, \mu \), one would have all thermodynamic information. Equivalently to knowing \( Z(T,V,\mu) \) would be to know \( P(T,V,\mu) \).

This less familiar potential would be minimized for systems in contact with a thermal reservoir and reservoirs of particles kept at particular chemical potentials. The volume would still be an internal constraint and releasing this constraint would lead to equilibration of pressure in the subsystems.

It will be clear from this discussion that the selection of the proper variables and thermodynamic potentials can be quite important for the convenient solution of problems in both thermodynamics and statistical mechanics. I should also emphasize that the use of different types of thermodynamic potentials allows us to disregard the reservoir and focus on the system of interest. If the reservoir would be included in the discussion it is just another subsystem and the maximum entropy or minimal total energy would be the guiding equilibrium principles. However, the properties of the environment are often quite ill-defined and it is necessary to take them out of the equation, hence the necessity to use different variables and thermodynamic potentials. The transformation of variables and associated functions is an integral part of thermodynamic theory. If the wrong choice of variables is made problems can become impossibly hard to solve (for discussion see Callen, chapter 5 and 6).

There is one more item to cover in our fundamental (or elementary) discussion of thermodynamics and it concerns more tricks with variables.

**Transformations using Partial derivatives.**

In thermodynamics any partial derivative can be expressed in terms of other partial derivatives that might be more easily measured. If we restrict ourselves to one component systems, in particular the expansion coefficients

\[
\alpha(T,P) = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left( \frac{\partial^2 \mu}{\partial T \partial P} \right)_T
\]

\[
\kappa(T,P) = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left( \frac{\partial^2 \mu}{\partial P^2} \right)_T
\]

and the constant pressure molar heat capacity

\[
C_p(P,T) = \left( \frac{\partial H}{\partial T} \right)_P = -T \left( \frac{\partial^2 \mu}{\partial T^2} \right)_P
\]

are widely used, which can be viewed as the three independent second derivatives of the Gibbs free energy. For all three of these quantities extensive data tables exist, and there exists a standard procedure to obtain any kind of partial derivative in thermodynamics (for one component systems) in terms of these derivatives. I find the procedure described in the book by Myron Tribus (chapter 9 for one-component systems and chapter 13 for...
multicomponent systems, involving partial molar quantities) particularly instructive (and intriguing), and copied notes will be provided on the web site. The procedure described by Callen is also useful (and perhaps more straightforward albeit more laborious). All of these procedures are based on fundamental relations concerning partial derivatives of implicit functions (related to changing variables), and the so-called Maxwell relations. They are covered in the reading material on the web site, and I will (or might) provide further discussion in class.