# 1.   THERMODYNAMICS

**MAIN TOPIC:  Review the laws and application of Thermodynamics (TD) of macroscopic systems – to then be contrasted with the more microscopic Statistical Mechanical (SM) approach. The framework of TD underlies and predates that of equilibrium SM.**

## 1(a)   Basic Ideas of Thermodynamics

In thermodynamics (TD) one attempts to understand the properties of macroscopic objects such as a litre of gas, a wafer of Si, a bar magnet, or a melting block of ice etc. One needs to adopt a rather general approach here, and be creative in imagining different sorts of system to which one wants to apply TD ideas. Other examples: a piece of wood, or a piece of glass; a galaxy; a star; the earth; a lake; a fire; a person sleeping in a chair; a bacterium; a virus.

In TD, one is only interested in the macroscopic variables associated with the system – TD makes no reference to the *microscopic degrees of freedom.* In fact TD was developed in the 1800's at a time when very few scientists thought seriously about the possibility of microscopic objects like atoms. In contrast in statistical mechanics (SM) one uses knowledge of the microscopic constituents (and the interactions between them) and applies the laws of physics and statistics to derive macroscopic quantities and relationships between them.

One can approach TD both empirically, or using a more deductive approach.

**Empirical Approach**: It is presupposed that thermodynamical systems are either in thermal equilibrium, or close to it. What this means in practice is not always easy to say. One way is to ask whether some macroscopic system is changing at all in the timescale of interest. If it is not, then we can argue that it may well be in thermal equilibrium.
  **Examples**: an iceberg viewed over timescales of minutes or hours; a cup of warm tea over timescales of a few seconds; or a large lake over a period of a day or so.

However a moment's thought shows that this condition, while necessary, is certainly not sufficient. Thus, a system may be in a **steady state** without being in equilibrium.
   **Example 1**: a smoothly flowing calm stream or river (it looks the same from one minute to another, but one is not even looking at the same body of water at the 2 times)
   **Example 2**: a star over periods of, in some cases, many millions of years; it looks more or less identical, and yet huge amounts of energy have been emitted during this time.

It is clear that we will need eventually to adopt a more sophisticated approach to the idea of thermal equilibrium – this will come once we have more experience of what we are dealing with.

In any case, the empirical approach consists in defining various quantities which are supposed to describe the behavior of macroscopic bodies under slow changes. These macroscopic quantities are classified into 2 kinds, viz.,

*Intensive quantities*: these are variables such as temperature T, pressure p and density ρ. They are, by definition, independent of the system size.

*Extensive quantities*: these are variables such as mass M, internal energy U, volume V, magnetization M, and entropy S. They scale with the system size.

Historical Note: If the subject of thermodynamics, and the arguments in it, sometimes seem a bit ad hoc, then it may be useful to bear in mind that this reflects the historical development of the subject. What we now call the "science of thermodynamics" was originally a set of ideas and analyses carried out by engineers, chemists and some physicists (although the distinction between these subjects was not so well-defined back then). Key early figures were Sadi Carnot (1796-1832), who first analyzed heat cycles, Rudolf Clausius (1822-1888), and William Thompson (ie., Lord Kelvin, 1824-1907). However the first empirical work on gases and other simple systems came much earlier, and was done by Otto von Guericke (1602-1686), Robert Boyle (1627-1691), and Robert Hooke (1635-1703).

   If it seems odd to you that the way thermodynamics is formulated and even taught still bears the imprint of these early workers, then you should perhaps note 2 things:
  (i)   Most of the people that need to use thermodynamics are are still engineers, chemists, and others who are not physicists and who want to apply the results to practical problems
  (ii)  The same is true of all the different parts of physics. Thus, quantum mechanics is still taught in a way which reflects the philosophy and analyses of the "Copenhagen school" (Bohr, Heisenberg, etc.) and, with its anthropocentric emphasis on measurements, makes little intuitive sense. We shall see that in statistical mechanics, the vast majority of textbooks are still mired in the study of simple model systems, and have not caught up with the developments of the last 60-70 years across all of physics. This is the main reason I am not using a textbook for this course.

## Deductive Approach: A more theoretical approach to TD is to begin with a set of **laws** or **axioms** from which one derives relationships between the macroscopic variables of the system. These are the "Laws of Thermodynamics", usually expressed as follows:

Zeroth Law of thermodynamics: If two systems are each in thermal equilibrium with a third system, they are in thermal equilibrium with each other.

   The importance of the zeroth law is that it allows the definition of temperature in a non-circular way without reference to entropy (which comes from the other laws). The idea is that temperature is defined as that property of the 3 systems above which they all

have in common. Note that the zeroth law presupposes some operational definition of thermal equilibrium. Below we will elaborate on the notion of temperature and how it is measured.

First Law of thermodynamics: When energy passes between systems, in the form of work or heat, or possibly in the form of a transfer of matter, then the internal energy of the systems changes in accord with the law of conservation of total energy. Thus, the total energy of an isolated system is constant; energy can be transformed from one form to another, but not created or destroyed. Energy is an extensive quantity.

   The first law requires an understanding of what we mean by the different forms of energy. The internal energy is discussed below in more detail; it comprises both internal kinetic and potential energy contributions. One can also do work on the system from outside – this involves either potential energy transfer to or from the system (eg., by applying pressure, or by adding gravitational potential energy) or else heat transfer or heat generation. We elaborate on ideas of heat below. Note that energy can also be transferred in and out of a system in the form of matter, if we allow matter transfer as well.

Second Law of Thermodynamics:  The sum of the entropies of the interacting thermodynamic systems increases. Here we introduce a new extensive quantity, the entropy S. The entropy is introduced for several reasons. It is related to heat transfer, by the key relationship $dQ = T\, dS$. And since heat transfer in thermodynamics is related to irreversibility, changes in entropy are related to irreversibility in macroscopic processes.

   Irreversibility arises, eg., in chemical reactions, in the generation of heat by friction or viscous processes, and in the transfer of heat by conduction or radiation. A key observation is that when two bodies at different temperatures come into thermal contact, then heat always flows from the hotter body to the colder one, until they eventually reach shared thermodynamic equilibrium. The final entropy is always greater than or equal to the sum of the entropies of the initially isolated systems. Equality occurs when the process is considered to be completely reversible. From a macroscopic thermodynamic point of view, this happens if and only if all of the intensive variables of the 2 systems are equal - the final system then also has the same values for theses variables.

   In reality no physical process is ever exactly reversible – entropy always increases.

Third Law of thermodynamics: The entropy of a system approaches a constant value as the temperature T approaches absolute zero.

   Conventionally the zero-T entropy is often taken to be zero. However this is not correct, for 2 reasons. First, as one discovers in SM that zero entropy at T=0 only occurs of the system has a unique ground state (as defined in quantum mechanics), and this is not always so. Second, TD is often applied to systems that are only in thermodynamic equilibrium '*for all practical purposes*' (FAPP). Examples here include disordered systems (like glasses, or indeed almost any real physical system at low T). In such systems, thermal relaxation and heat transfer processes become extremely long, so that the system can exist in one of many different states at very low T, with no communication between these – over very long time periods it can then be treated, FAPP,

as though it is very close to T=0, but with a large number of possible T=0 states available.

# 1(b)  Some Key Quantities in Thermodynamics

Let us now recall in more detail a number of the key concepts and relations in TD. We will simply go through a number of key ideas and results, which many of you may be familiar with from previous courses. The general discussion here will be somewhat phenomenological – it will often resort to thought experiments in which different thermodynamic processes are involved, and is thus very closely related to the empirical view of TD. This is of course very much how the subject originally developed in the 19$^{th}$ century – and this approach has influenced the subject ever since.

   In the next section (section 1(c)) we will adopt a quite different (and more modern) approach, in which we define a set of "thermodynamic potentials" and use these to derive all the key quantities. This approach is due originally to Gibbs.

**Temperature *T***    Consider 2 systems A and B which are each in *thermal equilibrium*. We know from the zeroth law that if these 2 systems are also in mutual equilibrium if, when they are brought in thermal contact, there is no net heat transfer from one to the other. They then must have the same temperature (by our previous definition of temperature as that which equilibrium bodies have in common).

     But how do we then attach some sort of numerical value to this temperature? Commonly one differentiates between *empirical temperature*, and *absolute temperature*.

     ***Empirical Temperature*** $\theta$ is measured by using some system whose physical properties change in some easily measureable way with temperature. Many such systems can be used for this – eg., a column of  mercury marked so  that $\theta = 0$ at the melting point of water and $\theta = 100$ at the boiling point of water (this defines the Celsius temperature scale).

     ***Absolute Temperature*** T is defined so that its value represents the actual thermal energy in the system – the definition of absolute temperature T can then only be done using statistical mechanical arguments. The simplest way to do this is to define a temperature based on the pressure and of a fixed volume of gas of very low density – one uses the ideal gas law, according to which

$$pV = nRT \qquad\qquad\qquad\qquad (1)$$

where n is the number of kmoles and R=8300 Jkmole$^{-1}$ K$^{-1}$. This scale is independent of the gas type provided the gas is ideal – this means that the effect of interactions between gas molecules must be negligible (which is why we make the gas of very low density). For real gases this approximates the Kelvin or absolute temperature scale where 0 is

absolute zero and water melts at θ=273K.  Note that for ideal gases, T is simply proportional to the kinetic energy per particle of the gas.

Note that we have not derived (1); in fact, we can only say that it is valid **experimentally**, for sufficiently dilute gases. To properly define absolute temperature we need to know more SM theory. We will then see that there a various ways to do it, some more fundamental than others.

**Internal Energy _U_**    For every object there exists a *state quantity U*, called the internal energy.. A *state quantity* is a function of *state variables* (extensive or intensive) which define the system (e.g . p, V  for a gas) .  *U* can change in different ways, depending the system and how it is coupled to the environment around it. In an *isolated system* we have:

$$\Delta U = W \tag{2}$$

where *W* is the *work done on the object*  e.g. by gradual compression of a gas (see Figure below).

For a reversible process

$$\delta W = -pdV , \quad W = -\int_{V1}^{V2} pdV \tag{3}$$
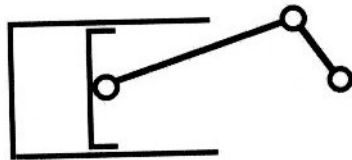


In a *closed system* - where the mass of the body is fixed -  heat may be still however be exchanged with the environment. One then writes that

$$\Delta U = Q + W \tag{4}$$

where Q is the amount of heat entering the system through the walls. The first law of TD is then basically stating energy conservation.  Note *W* and *Q* are not state functions, since they are not functions of state variables.  In differential form **the first law of TD** is:

$$dU = \delta Q - pdV \tag{5}$$
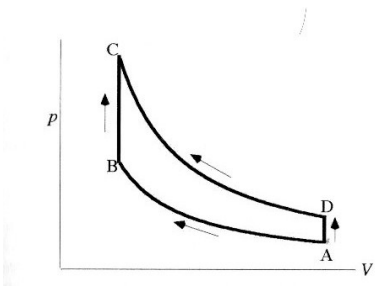
To see that $W$ and $Q$ are not state variables, note that one can move the system between two points A to C, each defined by specific values of state variables, via different paths. This is shown in the Figure, and one should compare paths through either D or B. The passage via different paths involves different amounts of work and heat transfer, but the total energy at the end is of course the same.

**Enthalpy $H$**     We define the enthalpy of a thermodynamic system according to

$$H \equiv U + pV \qquad (6)$$

so that

$$dH = dU + pdV + Vdp = \delta Q + Vdp \qquad (7)$$

The enthalpy is a state function and is useful for analyzing any process which can be carried out at constant pressure (e.g. heating a volume of gas at constant pressure). Suppose, eg., one boils a volume of water (eg., 1 litre) under constant pressure: Then the amount of heat needed to do this is

$$\delta Q = \Delta U + p\Delta V = \Delta H , \qquad (8)$$

where $\Delta U$ is the latent heat of the water at boiling point (ie., the energy required to transform it from liquid to gas at the boiling temperature), and $\Delta V$ is the change in volume brought about by the transformation under heating.

## Reversible Processes

A *reversible process* is a cyclical process in which a system is *returned to its original state* without any net heat transfer to the environment. (As already noted, this means that there is no change in total *entropy S*).

**Example 1**: Consider an isolated system, in equilibrium, initially at volume $V_1$, which is then allowed to expand slowly against a piston to occupy a volume $V_2 = V_1 + V_0$.
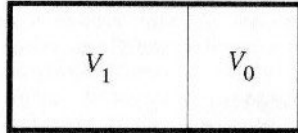
If the piston is frictionless the gas does work on the piston and the internal energy decreases. However we can do that same amount of work on the system, increase $U$ and return the gas to its original state. Thus this process is reversible.

To understand this properly, compare this process with one in which we suppose that the piston is massless, and offers no resistance, so that the gas freely expands to $V_2$. We can then compress the gas back to $V_1$. However this is not a reversible process – why not?

**Example 2**: Consider now a completely reversible process in which we allow energy $dU$ to move between 2 systems $\Sigma_1$ and $\Sigma_2$, while keeping the combined systems isolated.
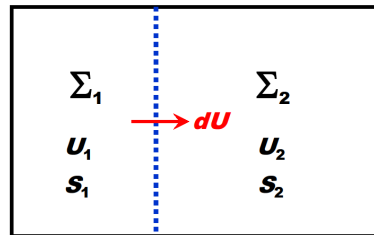


We assume that the 2 systems are in mutual equilibrium, and therefore at the same temperature T. One way to do this might be to very slowly move a partition between the 2 systems. The entropy of each will change, but there sum will remain constant – likewise the total energy will be conserved, ie., $dU = dU_1 + dU_2 = 0$, even though the energy of each system will change. Notice also that no heat flows between the systems, and the total entropy $S = S_1 + S_2$ does not change.

However, there is no requirement that the pressures be the same in the 2 systems – equilibrium only requires that their temperatures be the same. Suppose we now allow the partition to move – it will then do so, under the influence of the pressure difference between the 2 containers – and work $dW = dU$ will be done by one gas on the other, so that $dU_1 = - dU_2$.

Now, we have for the changes in entropy of the 2 systems that

$$
\begin{aligned}
dS \quad &= \quad (dS_1/dU_1)\, dU_1 \; + (dS_2/dU_2)\, dU_2 \\
&= \quad [(dS_1/dU_1) - (dS_2/dU_2)]\; dU \quad = \quad 0 \tag{9}
\end{aligned}
$$

where we use $dU = dU_1 = - dU_2$. Now, equation (9) is true for any pair of systems which have the one common property that the temperature T is the same for both – it is clear that for it to be obeyed for any such pair, we require $dS_1/dU_1 = dS_2/dU_2$, ie., any 2 bodies

in thermal equilibrium have the same value of dS/dU. We will therefore **DEFINE** the absolute temperature T such that

$$dU \ = \ T \ dS \qquad \qquad \text{(reversible)} \qquad \qquad (10)$$

ie., we define the absolute temperature by the equation

$$T \ = \ dU/dS \qquad \qquad (11)$$

which connects it to the entropy, in way which we did not do above (recall that eqtn (1) is fundamentally an experimental result – whereas (11) is a definition). Later on we shall show that (1) actually follows from the definition (9), using statistical mechanical arguments.


**Relationship Between Entropy and Heat:**  We can say more, again in the context of reversible thought experiments. Recall from the first law of TD. For a reversible process, we have $dU = \delta Q - pdV$ from eqtn. (5) above.

Let us now consider a fluid or a gas – we would like to express this same result in terms of differentials of the state functions $dV$ and $dS$.

We know that any macroscopic observable (in particular, $U$ or $S$) is a function of the state variables. That function depends on details of the system, and is embodied in the "equation of state". The equation of state is a relationship between state variables – the simplest example is the equation $pV = Nk_BT$ for an ideal gas.

Typically, for a gas or a fluid, we choose as state variables $p$ and $V$, since they are readily measured. Then $U(p,V)$ and $S(p,V)$ can be determined. However one can also write $U(S,V)$ as a function of $S$ and $V$ such that:

$$dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV$$

$$= TdS - pdV \ ; \qquad \qquad (12)$$

where we have used the identity $T \equiv \left( \dfrac{\partial U}{\partial S} \right)_V$ from above, and the fact that

$$p = -\left( \frac{\partial U}{\partial V} \right)_S \qquad \text{(isentropic process)} \qquad \qquad (13)$$

This latter relationship follows from the fact that $dU = -pdV$ for a reversible process in an isolated system (e.g slow compression of an isolated volume of gas); this process is of course isentropic.

Comparing eqtns. (5) and (12), we immediately see that for a reversible process one has

$$dS = \frac{\delta Q}{T} \qquad\qquad (14)$$

This is actually the original definition of entropy in Thermodynamics, introduced by Clausius in 1854

## **Irreversibility and Entropy**

As noted already above, no realistic physical process is ever truly reversible, although one can come close. One should note that the relations $\delta W = -pdV$ and $dS = \delta Q / T$ only hold necessarily for *reversible* processes.

In spite of this, a remarkable thing about the science of TD, which was used by early workers in the field, is that one can in some cases one can replace or model an irreversible process by some equivalent reversible process. For example, suppose a small amount of heat $\delta Q$ flows from a hot object at temperature $T_1$ to a colder object at temperature $T_2$ with no change is their respective volumes. This is an irreversible process.

Nevertheless the increase in entropy of system 2 is still $dS = dQ/T_2$, since one can replace system 1 at the higher temperature $T_1$ with a third object at the same temperature $T_2$ as system 2. The increase in entropy of system 2 does not depend on where the heat is coming from, so replacing system 1 by system 3 is an equivalent thought experiment as far as the change in entropy of system 2 is concerned. Since a small amount of heat can flow between objects at the same temperature with no net change in entropy this is allowed to be a reversible process and thus $dS = dQ/T_2$ is still valid. A similar argument holds for the loss in entropy associated with the heat leaving system 1. In that case the decrease in entropy is $dS = dQ/T_1$.

In the same way, we should note that even though the relation $\delta W = -pdV$ is only strictly valid for reversible processes, the relation $dU = TdS -pdV$ in eqtn. (12) can be used also for irreversible processes. This is because it is written in terms of state functions.

Suppose we then consider a reversible process whereby a volume of ideal gas expands isothermally by an amount $dV$, and at the same time does a small amount of work.

The work done, if acting on a piston, is just $\delta W = -pdV$. Then $dU = 0$, since the internal energy only depends on $T$ for an ideal gas (recall that $U = \frac{3}{2}Nk_BT$) so the gas must absorb an amount $dQ$ of heat from the surroundings ($\delta Q = pdV$). Then from eqtn. (14) the change in entropy $dS = \frac{\delta Q}{T}$. Now let us instead assume that the gas expands by leaking into the slightly larger volume, but now the temperature $T$ is held constant (this is of course an irreversible process). The temperature is unchanged, so as before $dU = 0$. However this time no work is done, and no heat is transferred. Eqtn. (14) is now invalid, since in this case $\frac{\delta Q}{T} = 0 \neq dS$. On the other hand eqtn. (12) is still valid, and can be used to calculate the change in entropy. Applying (12) to this process, we have

$$dS = \frac{pdV}{T} \tag{15}$$

Note there is no work being done.

Now let us look at finite changes in entropy brought about by irreversible processes. Let us consider the change in entropy of a system at temperature $T$ and *fixed volume V*. This is given for an infinitesimal change by (14), ie., we have $dS = dQ/T$ again.

Then for finite amounts of heat, where the temperature changes from $T_i$ to $T_f$, one can compute the total change in entropy by just integrating (14), so that:

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT \tag{16}$$

The total amount of entropy in some system at absolute temperature $T$ can then be determined by taking $T_i = 0$  $T_f = T$. If we assume that the system is simple, so that the third law of TD states that S=0 at T=0, then we get

$$S_{tot}(V,T) = \int_0^T \frac{C_V}{T} dT \tag{17}$$

For non-simple systems, where the $T = 0$ entropy is non-zero, we must add a constant to this. Notice that, unlike the heat $,Q$ the entropy $S$ is a state function.

Now the second law of TD states that the entropy of an isolated system always increases, because of irreversibility. A simple but typical example involves a completely isolated system which consists of two sub-systems $\Sigma_1$ and $\Sigma_2$, which are brought into thermal contact in such a way that an infinitesimal amount of heat $\delta Q$ flows from $\Sigma_1$ to $\Sigma_2$, with no change in their respective volumes (note this is different from the "Example 2" given above - before eqtn. (9) - where no heat was transferred, only energy). In this case the total (infinitesimal) change is entropy of the combined system is

$$dS = \frac{\delta Q}{T_2} - \frac{\delta Q}{T_1} \qquad = 0 \qquad (\text{if } T_1 = T_2)$$
$$> 0 \qquad (\text{if } T_1 > T_2) \qquad\qquad (18)$$

in accordance with our previous discussion – this is just the 2nd Law, in infinitesimal form.

**Heat Capacities $C_V$ and $C_p$**    The *Heat capacity* of some system is the amount of *energy* (not heat) required to raise the temperature of the system by some unit measure, for a unit volume of the system. It can be defined at constant volume or more typically at constant pressure, according to:

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V \qquad C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p \qquad\qquad (19)$$

Thus a large heat capacity implies a large change in energy for a small change in temperature. To see how this relates to the change when heart is added to the system, let us imagine that we supply an infinitesimal amount of heat to the system, at constant $V$. Then the change in energy $U$, and the resultant heat capacity at constant $V$, are given by

$$dU = \delta Q - pdV$$
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\delta Q}{\partial T}\right)_V \qquad\qquad (20)$$

In a similar way, the change in enthalpy $H$, and the heat capacity at constant $p$, are given by

$$dH = \delta Q + Vdp$$
$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\delta Q}{\partial T}\right)_p \qquad\qquad (21)$$

If one measures empirically the heat capacities, most of the thermodynamic variables or state functions are also determined. For example, we have:

$$U(V,T) = \int_0^T C_V dT \tag{22}$$

$$H(p,T) = \int_0^T C_p dT \tag{23}$$

and we can determine other state functions from these.

This concludes out 'phenomenological' analysis of TD. I have continued it up to a certain point, but although it gives a lot of physical feeling for the processes one is dealing with, it lacks generality. Let us not turn to a more deductive and more general approach.

# 1(c)  Thermodynamic Potentials

We now go over to a more deductive approach. This is often much easier to understand for people who want to use TD, but who are not yet terribly familiar with the often rather complicated empirical basis for many of the key concepts.
    In the introduction above (in section 1(a) I dicussed the deductive approach by referring to the laws of TD. However when using TD, this is not terribly useful. What is more useful is to appreciate that one can start from a limited set of quantities, which are sometimes called "thermodynamic potentials" (other names include "functions of state", or 'free energies', or also just the specific names for each particular one of these).
    The general idea involves starting from the internal energy U, and then deciding which particular changes in the state of the system can influence U. We then incorporate the corresponding terms into the definition of U, and look to see how changes in U are reflected in the underlying state variables.

## Thermodynamic Potentials for Gases

Let us note that in all of the above section (section 1(b)), which to some extent follows the historical development of the subject, we were actually assuming that the quantities involved in determining the TD state of the system were just the 4 quantities $(T,S)$ and $(p,V)$. Our formulation of the $1^{st}$ law was given in terms of these quantities and changes in them. The very common focus on these variables to introduce TD properties is for historical reasons – all the initial analyses of TD were done for gases.
    Now notice that we for any one of the two pairs of these quantities, we can imagine holding one constant while we infinitesimally vary the other. This then gives us 4 possible changes, viz., $(dS, dV)$,  or $(dS, dP)$, or  $(dT, dV)$, or $(dT, dP)$. The first of these

involves changing both of the extensive variables, the last involves changing both of the intensive variables, and the 2d and 3$^{rd}$ involve changing one of each.

We also started off by defining the change d$U$ by d$U = T$d$S - p$d$V$. We now see that by performing simple Legendre transforms on U, we can define 3 other functions, with the result that we have the following 4 "thermodynamic potential" functions:

| | | |
|---|---|---|
| Internal energy: | $U$ | |
| Enthalpy: | $H$ = | $U + pV$ |
| Helmholtz Free Energy: | $F$ = | $U - TS$ |
| Gibbs Free Energy: | $G$ = | $U - TS + pV$ |

(24)

with the consequent differentials given by

| | | |
|---|---|---|
| Internal energy: | d$U$ = | $T$d$S$ - $p$d$V$ |
| Enthalpy: | d$H$ = | $T$d$S + V$d$p$ |
| Helmholtz Free Energy: | d$F$ = | $-S$d$T - p$d$V$ |
| Gibbs Free Energy: | d$G$ = | $-S$d$T + V$d$p$ |

(25)

We notice immediately several important features of these results, arising purely from their mathematical form:

(i)  We exhaust all 4 combinations here, but notice the arbitrariness in starting from U as defined by the infinitesimal d$U$ in (24) above. We could equally have started with any one of the four potentials, and derived the other three by adding or subtracting terms involving the same pairs of variables. We start from $U$ and d$U$ in the forms give above for purely historical reasons – note that this choice involves the one combination in which both of the infinitesimal variations (d$S$ and d$V$) happen to be extensive.

(ii)  With these 4 different potentials we can immediately define 8 different first derivatives, simply by varying one or other of the 4 potentials with respect to one or other of the 2 variables it depends on. Consider, for example, the Helmholtz free energy F (often just called the "free energy"). From (25), we can differentiate this with respect to either $T$ or $V$ to get

$$p = -\left(\frac{\partial F}{\partial V}\right)_T \qquad\qquad S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad\qquad (26)$$

which allows us to define one of the state variables in terms of derivatives of F with respect to its conjugate. Thus suppose some TD potential $\Phi$ has a derivative that depends on derivatives d$x_j$ and d$Y_k$, then we define 2 derivatives like those in (26) by holding the conjugate variables $Y_j$ and $x_k$ constant.

(iii)  We can also define what are typically called "Maxwell relations", by further differentiating a pair of relations like (26) with the conjugate variable to the one already used; in other words, we look at quantities like d$^2\Phi$/d$x_j$ d$Y_k$. Thus, for example, starting from the 2 relations in (26) we can also write

$$\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 F}{\partial V \partial T}, \qquad \left(\frac{\partial p}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T \partial V} \qquad (27)$$

However, if we assume that the free energy $F$ is an analytic function of its two variables T and V, then these two derivatives must be the same, ie., it doesn't depend which order we take them in – so we immediately find that:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad (28)$$

And we see how this will work for any such pair of derivatives, provided that we can assume that $d^2\Phi/dx_j\, dY_k = d^2\Phi/dY_k\, dx_j$. This assumption of analyticity will work unless we are at a phase transition point. Maxwell relations are useful in the real world - if we can relate partial derivatives of state functions in this way, one may be easier to calculate or measure than the other. Thus they are particular important for experiments.

(iv) If we also know that some state function happens to be a constant, then we can use the triple product rule. As an example, suppose the entropy $S(U, V)$, considered as a function of the energy U and the volume V, is a constant under a slow change in volume, even if the energy varies - this would be a reversible isentropic process is a constant. Then we can write

$$\left(\frac{\partial S}{\partial V}\right)_U = -\left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_S \qquad (29)$$

And results like this turn out to be useful as well.

## General Thermodynamic Potentials

The definitions given above are obviously specifically tied to the idea that there are only 4 state variables, viz., $T, S, p$, and $V$. However, most systems at equilibrium will need many state variables to describe their TD properties. We can try defining the infinitesimal changes associated with them by looking at the amount of work required to make an infinitesimal change in the energy of the system, ie., we write

$$dQ = dU - \Sigma_j\, x_j\, Y_j \qquad (30)$$

where the set $\{ x_j \}$ comprises all the relevant intensive variables, and the set $\{ Y_j \}$ their conjugate extensive variables. The way this equation is set up makes it clear that it is simply a generalization of the 1st law of TD, as written in eqtns. (5) and (12) above

(where it is assumed that there is only one set of state variables apart from T and S, viz., p and V).

So what other sorts of state variables can we have in the set $\{ x_j, Y_j \}$? As just noted, a complex system may have a great many of these active at once, making the thermodynamic analysis quite complex.

Here are some common examples, listed by conjugate pair:

| Work done by force | infinitesimal dW | term in TD potential |
|---|---|---|
| Volume change (pressure) | $dW = -p\,dV$ | $-pV$ |
| Length change (tension) | $dW = f\,dL$ | $fL$ |
| Areal change (surface tension) | $dW = \gamma\,dA$ | $\gamma A$ |
| Strain (stress) | $dW = \sigma_{ij}\,d\varepsilon^{ij}$ | $\sigma_{ij}\,\varepsilon^{ij}$ |
| Electric polarization (E field) | $dW = \mathbf{E}.\,d\mathbf{p}$ | $\mathbf{E}.\mathbf{p}$ |
| Magnetization (B field) | $dW = \mathbf{B}.\,d\mathbf{M}$ | $\mathbf{B}.\mathbf{M}$ |
| Particle number (chemical potential) | $dW = \mu\,dN$ | $\mu N$ |
| Rotation (angular momentum) | $dW = \mathbf{\Omega}.\,d\mathbf{L}$ | $\mathbf{\Omega}.\mathbf{L}$ |

There are many more, some of which we will encounter in these notes. Note the different sign of $-pdV$ (the infinitesimal work done on the system by an external pressure acting inwards) from that of $f\,dL$ and $\gamma\,dA$ (work done on the systemby forces pulling outwards on the system). This difference is purely a matter of convention.

Clearly, if only two pairs of TD variables are active (ie., $(T,S)$ plus one other pair), then the analysis goes through in the same way as for gases above, with the new pair substituting for the pair $(p,V)$ discussed above; and we can define precise analogues to the enthalpy, and the Helmholtz and Gibbs free energies, for such cases.

Consider as an example the case where hydrostatic changes (involving stresses, etc., which change the volume, area, etc.) do not play a role, but where an applied magnetic field induction $\mathbf{B}$ can cause changes in the magnetization $\mathbf{M}$. Then the analogues of the equations in (25) above are just

| | | |
|---|---|---|
| Internal energy: | $dU = T dS - \mathbf{B}.\,d\mathbf{M}$ | |
| Enthalpy: | $dH = T dS + \mathbf{M}.\,d\mathbf{B}$ | |
| Helmholtz Free Energy: | $dF = -S dT - \mathbf{B}.\,d\mathbf{M}$ | |
| Gibbs Free Energy: | $dG = -S dT + \mathbf{M}.\,d\mathbf{B}$ | (31) |

with the parallel set of TD potentials in exact analogy with (23).

The case where only 2 sets of TD potentials plays a role is of course anomalous. More generally we will have at least three. Then the number of different combinations of derivatives becomes very large - hence the complexity of real thermodynamics

Clearly we cannot go through all possible examples. But it is useful at this point to say a little more about the Helmholtz free energy $F$. We will do this for the specific case of 'gas-like' systems, for which the results (24)-(29) apply.

**Free Energy F   (Helmholtz Free Energy)**   The Helmholtz free energy $F$, as we saw in (24) above, is given in terms of the energy $U$ by

$$F = U - TS \qquad\qquad (32)$$

and as we also saw, an infinitesimal change in F gives, for a simple 'gas-like system,

$$dF = dU - TdS - SdT = TdS - pdV - TdS - SdT$$

so that we get

$$dF = -SdT - pdV \qquad\qquad (33)$$

From this we observe that a change in $F$ gives the maximum work for an isothermal process, in the same way that a change in $U$ gives the maximum work for an isentropic process.

As we will discuss in more detail when we come to discuss the canonical distribution in SM, the free energy $F$ typically refers to a system in contact with a heat bath at some temperature $T$. We can then show, for the gas-like systems we are discussing, that a system with constant volume in thermal equilibrium with a heat bath will tend to *minimize* its free energy; more generally, $F$ will be at minimum for a system at constant $V$ and $T$.

To see this, suppose we have two gases separated by a piston both in contact with a heat bath at temperature $T$ (see diagram):
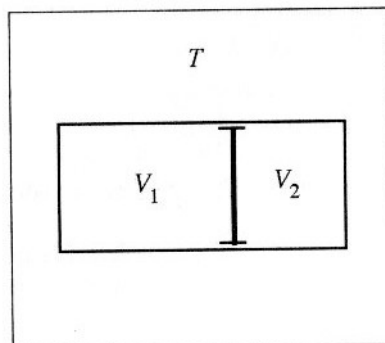


Consider now a small displacement of the piston such that $V_1 \rightarrow V_1 + dV$. Then $V_2 \rightarrow V_2 - dV$, and the change in free energy $F$ is just

$$dF = dF_1 + dF_2 = -p_1 dV_1 - p_2 dV_2 \tag{34}$$

The pressures must be equal to balance the force and $dV_1 = dV = -dV_2$ so that

$$dF = 0 \tag{35}$$

Thus the free energy is at a minimum is equilibrium for a system at constant temperature.

If on the other hand we were dealing with a closed system with some source of heat and an insulating piston, as shown in the diagram immediately below, then $U$ would be a minimum in equilibrium since we then have

$$dU = -p_1 dV_1 - p_2 dV_2 = 0 \tag{36}$$
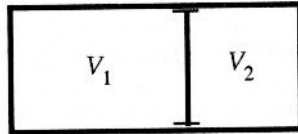


From these considerations we establish, using TD arguments, that:

*When the system is in contact with a heat bath there is a balance between lowering the internal energy and increasing entropy.*

We see that at higher $T$ entropy becomes more important, because the "$TS$" term in F wins; but when $T \to 0$, the "$U$" term wins.

One can also easily obtain $S$ and $U$ from $F$. Using the result (26) for S, ie., $S = -\left(\dfrac{\partial F}{\partial T}\right)_V$

we have

$$\boxed{\begin{aligned} U &= F + TS \\ &= F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left(\frac{\partial (F/T)}{\partial T}\right)_V = \left(\frac{\partial (\beta F)}{\partial \beta}\right)_V \end{aligned}} \tag{37}$$

where $\beta \equiv 1/kT$. This gives one way to determine the internal energy from measurements of the Helmholtz free energy, we shall also use it later extensively in SM as a purely theoretical relation.

One can use similar arguments to look at the enthalpy H and the Gibbs free energy, or free enthalpy $G$. Thus the Gibbs free energy is, as noted above,

$$G \;=\; H - TS$$
$$\quad = \; U - TS \;+ pV$$
$$\quad = \; F + pV \tag{38}$$

so that in an analogous way as that argued above for the Helmholtz free energy, a system at constant pressure in contact with a heat bath will tend to minimize its free enthalpy – more generally, free enthalpy is minimized in systems with constant $T$ and $p$ .

## Particle Exchange and the Chemical Potential

If we also allow matter to be exchanged with the heat bath (in, eg., the form of particles) then we need to define further state variables (in this case, as we saw in the table after eqtn. (30), the total particle number N, and the chemical potential μ).

To see how this works, we will consider a total system comprised of 2 sub-systems $\Sigma_a$ and $\Sigma_b$ which are each in thermal equilibrium with a heat bath $\Sigma_0$ at temperature $T$ and are also separated from each other by a permeable membrane, so that particles can diffuse back and forth between them.  Let us assume that there are $N_a$ and $N_b$ particles, in $\Sigma_a$ and $\Sigma_b$ respectively.  Then the situation is as shown in the figure – particles can pass freely between the two systems, and also from the bath into either of the 2 sub-systems, so that the numbers $N_a$ and $N_b$ are not constant, but fluctuate in time. We will assume that the is an energy associated with the transfer of a particle into either of the sub-systems – we thus define two chemical potentials $\mu_A$ and $\mu_B$, which denote these two energies. In general these two do not have to be the same.

We see that we have now generalized the idea of a *reservoir* to one of a bath that can exchange both heat and particles with the system, without any changes in its own $T$ and $\mu$ . The reservoir is now characterized by its own temperature and by a chemical potential  (or indeed potentials, if there is more than one kind of particle).
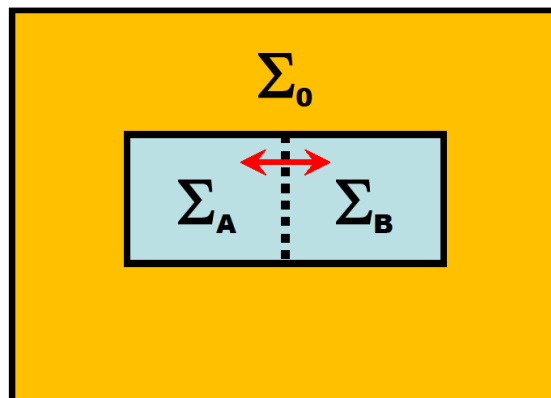
We can set up the thermodynamic theory for this situation most simply by writing again the infinitesimal change in U wrought by changes in extensive variables. One way to do this would be by simply taking our previous result (in (12) or (25)) for d$U$, and adding to it the term coming from a change in the particle number – we thus write

$$dU = TdS - pdV + \mu dN \qquad\qquad (39)$$

If we use this we now have 3 pairs of thermodynamic variables in play, viz., $(T,S)$, $(p,V)$, and $(\mu, N)$. This may be more than we want – for example, we may have a situation where changes in $p$ and $V$ can be neglected, in which case we would just use the reduced result

$$dU = TdS + \mu\, dN \qquad\qquad (40)$$

**<u>Thermodynamic Potentials</u>**: Let us for the time being stick with our initial result in (39), allowing all the terms in the energy infinitesimal d$U$. We can of course, starting from (39), write down the new results for the enthalpy, and the Helmholtz and Gibbs free energies. One way we can do this is to simply define these exactly as in (24), without any reference to the chemical potential $\mu$ or to $N$; then, using (39), we immediately get differentials given by

| | | |
|---|---|---|
| Internal energy: | $dU$ = | $TdS - pdV + \mu dN$ |
| Enthalpy: | $dH$ = | $TdS + Vdp + \mu dN$ |
| Helmholtz Free Energy: | $dF$ = | $-SdT - pdV + \mu dN$ |
| Gibbs Free Energy: | $dG$ = | $-SdT + Vdp + \mu dN \qquad (41)$ |

However, we can also make another choice for our definition of the thermodynamic potential functions, more in keeping with (39) , which is to include all of the different terms in the different thermodynamic potentials; this also gives us a larger freedom to vary these.

We can therefore also define the following set of thermodynamic functions:

| | | |
|---|---|---|
| Internal energy: | $U$ | |
| Generalized Enthalpy: | $\Phi$ = | $U + pV - \mu N$ |
| Helmholtz Free Energy: | $F$ = | $U - TS$ |
| Grand canonical potential: | $\Omega$ = | $U - TS + pV - \mu N \qquad (42)$ |

with the consequent differentials given by (again, starting from (39)):

| | | |
|---|---|---|
| Internal energy: | $dU$ = | $TdS - pdV + \mu dN$ |
| Enthalpy: | $d\Phi$ = | $TdS + Vdp - Nd\mu$ |
| Helmholtz Free Energy: | $dF$ = | $-SdT - pdV + \mu dN$ |
| Gibbs Free Energy: | $d\Omega$ = | $-SdT + Vdp - Nd\mu \qquad (43)$ |

Notice that we can now define thermodynamic derivatives with respect to variation of $\mu$ as well as with respect to $N$, using these definitions.

Perhaps the best way to understand how to use this formalism, and to see how these different thermodynamic potentials can arise in practice, is by looking at examples – we will do this in the main part of the course.

**Equilibrium for a single system**:  Let us first consider the situation where we only have one sub-system instead of two, able to exchange energy and particles with the surrounding bath. In this case we can assert that the entropy of this system must be a function of 3 extensive variables, ie., we have

$$S \;=\; S(U,V,N) \tag{44}$$

Since $S$ is assumed to be an analytic function of the state variables $U, V$ *and* $N$ we must have

$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN \tag{45}$$

which must be zero at equilibrium. Applying the triple product rule above while keeping $N$ constant, we can then write

$$\left(\frac{\partial S}{\partial V}\right)_{U,N} = -\left(\frac{\partial U}{\partial V}\right)_{S,N}\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{p}{T} \tag{46}$$

since

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = 1/T \qquad \text{and} \qquad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -p \tag{47}$$

Inserting these into eqtn. (45), we immediately get

$$dS = \frac{dU}{T} + p\frac{dV}{T} - \mu\frac{dN}{T} \tag{48}$$

We can immediately solve for $dU$ here, to get

$$dU \;=\; TdS - pdV + \mu dN \tag{49}$$

which is just what we originally wrote down in (40) and (41);  we have thus derived this relation simply by making the assumption in (44) that the entropy is a function of the 3 extensive variables *U, V,* and *N,* and then assuming thermal equilibrium.
   By differentiating with respect to *N,* holding V and S constant, we also get the isoentropic (adiabatic) relation

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{50}$$

which is nothing but a generalization of the first law of TD, this time to include the transfer of particles between system and bath. Note that both $S$ and $U$ are seen here to be functions of the three extensive variables $U$, $V$, and $N$.

Since it is difficult to hold S constant when $N$ changes, it is more practically useful to express $\mu$ in terms of a change in $F$. We get (41) and/or (43) by assuming as usual that $F = U - TS$, which then implies as before that $dF = dU - TdS - SdT$. Then using (41), (43), or (49) for $dU$ we obtain d$F$ in the form given in (41) and (43), ie., we find that $dF = -SdT - pdV + \mu dN$. From this is immediately follows that

$$\boxed{\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}} \tag{51}$$

which is a key equation in the practical use of this method. Note that $F = F(T,V,N)$ is a function of two extensive variables $V$ and $N$, one intensive variable $T$.

We can also express $\mu$ in terms of the change in free enthalpy $G$ caused by adding a particle. This is also useful, since it is easier to perform the particle addition while holding $p$ and $T$ constant rather than $V$ and $T$. Since $G \equiv F + pV = U - TS + pV$ it follows that $dG = dF + pdV + Vdp = -SdT + Vdp + \mu dN$, as in (41) (note that we are in (41) varying d$N$ rather than d$\mu$, so we use (41) instead of (43)). We thus have another definition of $\mu$, as

$$\boxed{\mu = \left(\frac{\partial G}{\partial N}\right)_{T,p}} \tag{52}$$

Notice here that $G(T,p,N)$ is a function of only one extensive variable, ie. $N$; both $T$ and $p$ are intensive variables. One might then guess that it should be possible to write G entirely as a function proportional to $N$, ie., that $G = aN + b$. This is true - in fact we can demonstrate the very remarkable and simple relation that

$$G = \mu N \tag{53}$$

This can be seen as follows. Let the size of the system (and number of particles) increase by $\lambda$, all the while keeping $p$ and $T$ constant. Since $G$ is extensive it must increase by the same factor, so we have

$$\lambda G = G(T, p, \lambda N) \tag{54}$$

The derivative of (54), taken holding p, T, and $N$ constant, then gives

$$G = \left( \frac{\partial G}{\partial (\lambda N)} \right)_{T,p,N} N \tag{55}$$

ie., the constant of proportionality is the quantity in brackets – we extract it by putting $\lambda = 1$, to get

$$G = \left( \frac{\partial G}{\partial N} \right)_{T,p} N = \mu N \tag{56}$$

which demonstrates (53).

**Mutual Equilibrium State for 2 sub-systems**: Now let us go back to the figure we had before, showing 2 different sub-systems coupled to a bath, with all three of these systems exchanging energy and particles. What will now determine the final steady state, for our pair of sub-systems? The equilibration will occur of course via thermal and diffusive transport between the 2 sub-systems in the figure, as well as with the bath.

To simplify the analysis, let us assume that we allow the 2 sub-systems to exchange energy with the bath, but no particles (however, particles are still exchanged between the 2 sub-systems). Complete equilibrium (thermal and diffusive) at the bath temperature $T$ will then be reached once the total entropy $S_{tot} \equiv S_0 + S_a + S_b$ is maximized, subject to the two conditions

$$U_{tot} = U_0 + U_a + U_b \quad = \quad \text{const} \tag{57}$$

$$N_{tot} = N_a + N_b \quad\quad = \quad \text{const} \tag{58}$$

Let us now cut off the connection to the bath, leaving the 2 sub-systems at temperature $T$. To determine the equilibrium conditions, we can imagine varying about them. Consider a small number of particles $dN$ and a small amount of energy $dU$, both going from $\Sigma_a$ to $\Sigma_b$. We accordingly define $dU = -dU_a = dU_b$, and $dN = -dN_a = dN_b$. Then we have a variation in total entropy given by

$$dS_{tot} = \left[ \left( \frac{\partial S_b}{\partial N_b} \right)_U - \left( \frac{\partial S_a}{\partial N_a} \right)_U \right] dN + \left[ \left( \frac{\partial S_b}{\partial U_b} \right)_N - \left( \frac{\partial S_a}{\partial U_a} \right)_N \right] dU \tag{59}$$

Since $\Sigma_a$ and $\Sigma_b$ are assumed to be already in *thermal equilibrium,* then the 2nd term in big square brackets is zero already. The condition for *diffusive equilibrium* is then:

$$\left( \frac{\partial S_b}{\partial N_b} \right)_U = \left( \frac{\partial S_a}{\partial N_a} \right)_U \tag{60}$$

However this is nothing but the condition that the chemical potentials for the two systems *are the same*, since we have from either (41) or (43) that:

$$\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V\ldots} \tag{61}$$

where we hold all state variables constant except for $N$. This is an important conclusion – the 2 sub-systems cannot reach mutual equilibrium until their chemical potentials $\mu_a$ and $\mu_b$ are the same. The chemical potentials are not fixed quantities – just like other intensive thermodynamic variables, like $p$ and $T$, they can vary according to the conditions.

What now of the equilibrium with the bath? It is obvious that if we repeat this argument, now allowing particle exchange with the bath as well as between the 2 sub-systems, then equilibrium will only be reached once *all three* chemical potentials are the same, ie., once we have $\mu_0 = \mu_a = \mu_b$, where $\mu_0$ is the bath chemical potential. Since the bath is considered to be so large that its thermodynamic properties do not change, this means simply that all the intensive properties ($T_a$, $T_b$, $p_a$, $p_b$, and $\mu_a$, $\mu_b$) all relax to equal the values possessed by the bath. Since the zero of the potential is arbitrary, one often simple fixes $\mu_0 = 0$ to begin with.

How do the two sub-systems relax to these equilibrium values? Let us suppose that $\Sigma_a$ and $\Sigma_b$ are *not* initially in diffusive equilibrium – this means that they must have different chemical potentials. Let's assume, to be specific, that $\mu_a > \mu_b$. Suppose we now transfer $dN$ particles from $\Sigma_a$ to $\Sigma_b$, where d$N$ can be positive or negative. Then the change in total free energy $F = F_a + F_b$ will be:

$$dF = \left(\frac{\partial F_a}{\partial N_a}\right)_{T,V} dN_a + \left(\frac{\partial F_b}{\partial N_b}\right)_{T,V} dN_b \tag{62}$$

Now, since $dN_b = -dN_a = dN$ it immediately follows that

$$dF = (\mu_b - \mu_a)dN \tag{63}$$

Since $F$ must be at a minimum in equilibrium, the change $dF$ caused by $dN$ particles moving from $a$ to $b$ must be negative unless we have already reached equilibrium. Thus in eqtt (63), $dN$ must be a positive number. In other words particles move from higher chemical potential to lower chemical potential. We should have expected this – the definition of chemical potential tells us that it denotes the energy required to add a single particle to the system, so the energy of the pair of sub-systems combined is lowered if we

transfer particles from the sub-system with the higher chemical potential to the one with the lower one.

# APPENDIX:   Some Worked Examples in Thermodynamics

It is useful to some simple problems worked out in thermodynamics. Again, the following is just scratching the surface of what is a very large topic. The following are chosen to illustrate some of the key ideas and identities.

## Example 1: Specific Heats for an Ideal Gas

We consider the ideal gas, for which we have the usual relation $pV = Nk_BT$. We would like to find out expressions for the specific heats $C_p(T)$ and $C_V(T)$ for this system, and for the relation between them. Recall that we have

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\delta Q}{\partial T}\right)_V \qquad\qquad C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\delta Q}{\partial T}\right)_p$$

(A.1)

for these quantities, where as before $H = U + pV$.

Before beginning, let's note that any **equation of state** for the simple one-species gas is an equation relating the three thermodynamic variables $p$, $V$, and $T$. The ideal gas relation is just the simplest possible equation of state, and it fixes one of these variables in terms of the other two. If we then ask how to parametrize the 4$^{th}$ thermodynamic variable, ie., $S$, for the system, we see that in general $S$ can be written as $S = S(p,V,T)$, a function of the three other variables. However, since one of $p,V$, and $T$ is fixed in terms of the other three by the eqtn.  of state, we can write either $S = S(T,V)$, or $S = S(p,T)$, or $S = S(p,V)$.

There are a number of different ways to analyze the specific heat of the system. Let's start with one that stresses the use of the Maxwell relations. Let's make the choice of writing $S = S(T,V)$, as described above. Then we can write

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$$

(A.2)

For an infinitesimal change in S(T,V).  Since we are after the specific heats, which are given by T X (partial derivatives of S with respect to T), then we start by calculating these derivatives. First we have that

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{\partial}{\partial T}\left[\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV\right]_p$$

$$= \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \qquad \text{(A.3)}$$

Subtracting off the derivative at constant V, and then multiplying by T to get the specific heats, we just get

$$C_p - C_V = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \qquad \text{(A.4)}$$

for the difference in specific heats. Note here that all we have dfound is the difference – we do not yet know what each one is, nor do we even know how they depend on temperature.

Now for an ideal gas, the 2$^{nd}$ term on the right hand side of (A.4) is in a form that is very useful to us, because it is written in terms of variables in the equation of state; we have from $pV = NkT$ that

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{NkT}{V}\right)_V = \frac{Nk}{V} \qquad \text{(A.5)}$$

The 1$^{st}$ term is not in a convenient form sicne we do not know how S depends on V at constant T. However we can easily rewrite it using a Maxwell relation, viz., using

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \text{(A.6)}$$

so that

$$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p \qquad \text{(A.7)}$$

and since

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{Nk}{p} \qquad \text{(A.8)}$$

for a free gas, we immeidately get our final result, viz., that

$$\boxed{C_p - C_V = Nk \qquad (ideal\ gas)} \qquad \text{(A.9)}$$

Note that this result does not tell us what $C_p(T)$ and $C_V(T)$ are individually. We will discover when we do statistical mechanics that they are temperature-independent constants, proportinal to $Nk$.

## Example 2: <u>Adiabatic Expansion for an Ideal Gas</u>

It is of considerable interest to discover how p and V vary when adiabatically change the temperature T of an ideal gas. Alternatively, we can ask how T changes when p and V change in such a way that the change is adiabatic. This can happen with any mass of gas if there insufficient time for much heat to pass in our out of the gas. A classic example deals with large volumes of air in the atmosphere which rise or fall either because their density does not match that of surrounding gas, or because they are moving over mountains, etc. There are alos many astrophysical examples. In all these cases, the amount of heat exchange wth the environment, during the timescale of the change, is much smaller than the heat content of the mass of gas.

By definition, in an adiabatic change

$$dQ \; = \; TdS = 0 \qquad (adiabatic)$$

(A.10)

Let's start from the equation of state, and rewrite it in differential form as

$$d(pV) \; = \; pdV + Vdp \; = \; Nk\,dT \; = \; (C_p - C_V)dT$$

(A.11)

and write the first law in the form

$$C_V\,dT \; = \; -pdV$$

(A.12)

so the total differential d($pV$) takes the form

$$\gamma\,pdV + Vdp \; = \; 0$$

(A.13)

where we define

$$\gamma = C_p/C_V$$

(A.14)

But now it is mmediately obvious that we can integrate the differential form in (A.13), to get the desired result:

$$\boxed{pV^\gamma \; = \; const \qquad (ideal\ gas)}$$

(A.15)

This result is of key importance. We will find the temperature-independent ratio γ using statistical mechanics methods.


## Example 3: <u>Isothermal Expansion for an Ideal Gas</u>

An obvious question one can ask is how all of this is affected by departures from ideal gas behaviour. To answer this is it helpful to have a simple generalization of the ideal gas law that is analytically tractable. Such an equation was provided by van der Waals in 1873, in his PhD dissertation. His equation of state is

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

(A. 16)

in which the correction to the pressure comes from interactions between the atoms or molecules, and the correction to the volume comes from the finite volume occupied by these species. Note that $b$ is always positive (atoms and molecules can't have negative volume), but the sign of $a$ can be negative if attractive interactions dominate. The correction to the pressure is clearly a low-density approximation – it is proportional to $\rho^2$, ie., to the density squared, ie, comes from pairwise interactions between atoms/molecules. For denser gases we expect higher order corrections proportional to $\rho^3$, $\rho^4$, etc.

There are lots of basic questions that one can ask about this model, but here is a really simple one:

Q: suppose we expand or compress the van der Waals gas isothermally (keeping $T$ = const). How then does the free energy change? Note that this question is less relevant to large volume gases in the atmosphere or in outer space, where it would involve extremely slow expansion or contraction, because of the time required for heat to be transferred in or out of the gas so as to keep $T$ = const. It is more relevant to much smaller volumes of gas, but we note that we require a surrounding heat bath to keep the temperature constant.

A: Suppose we change the volume from V1 to V2. Then since dT = 0, the change in free energy is just that coming from the volume change, and we have

$$\delta F \ = \ - \int_{V_1}^{V_2} p dV$$

(A.17)

The pressure, from the equation of state, is

$$p \ = \ \frac{NkT}{V - b} - \frac{a}{V^2}$$

(A.18)

and so we just integrate (A.17) to get

$$\delta F \ = \ - \int_{V_1}^{V_2} dV \left[ \frac{NkT}{V - b} - \frac{a}{V^2} \right]$$

$$= \ -NkT \ln \left( \frac{V_2 - b}{V_1 - b} \right) + a \left( \frac{V_2 - V_1}{V_1 V_2} \right)$$

(A.19)

which is an interesting result, very simply derived. Notice how much further it simplifies if we go to the ideal gas limit with $a = b = 0$.