Lecture: 2 Thermodynamic equilibrium

1-Thermal equilibrium
If a system and all its internal parts A, B, C satisfy that $T_A = T_B = T_C = \ldots$ it is said that it is in thermal equilibrium.

2-Mechanical equilibrium
When all the forces in the system balance we say that the system is in mechanical equilibrium.

3-Chemical equilibrium
If a chemical reaction or a phase transition takes place inside of the system, the number of particles or molecules of different kind or their numbers present in the different phases can change. We have seen this occurring when we discussed the isotherms of CO₂.

Increasing the force F causes the CO₂(g) molecules to disappear and to become part of the liquid. When the force is changed and after a sufficient time, the number of molecules in the gas and liquid phase remain constant in time. If we look closely we see that there is a continuous exchange of molecules between the phases. But from a macroscopic point of view, the average number of molecules in the gas and liquid phases remains constant.

This situation is called "Chemical Equilibrium". We will give more detailed description of the chemical equilibrium later on in this curse. A system that is in mechanical, thermal and chemical equilibrium at the same time is said to be in thermodynamic equilibrium.

Functions of state

When a system is in thermodynamic equilibrium its properties do not depend on time. But if we change the pressure, for example, the system accommodates to the new value of the pressure by changing some other of its properties (perhaps the volume). These properties (p, T, V etc) are called thermodynamic variables or coordinates of the system. However, once the system is at equilibrium the thermodynamic variables adopt values that are the same regardless of how we prepared the system. For example, for a pure gas with no chemical reactions or phase changes, $T = f(p,V)$ where f is a function (equation of state). If p is adjusted first, and then the volume is adjusted, the temperature adopts a new value. If instead the same volume adjustment is done first, and then the pressure
adjustment, the same final temperature is obtained. Thus it is said that T is a function of state.

If in general we have a function of state $G = g(x, y)$ where $x, y$ could be $p$ and $V$ for instance. A small change in the function of state $G$ can be written as

$$dG = \left( \frac{\partial g}{\partial x} \right)_y dx + \left( \frac{\partial g}{\partial y} \right)_x dy$$

which we rewrite as

$$dG = A(x, y)dx + B(x, y)dy$$  \hspace{1cm} (1)

usually functions of state are smooth and continuous with well defined derivatives at any point $(x, y)$. For this type of functions we can calculate the second derivative,

$$\left( \frac{\partial}{\partial x} \left( \frac{\partial g}{\partial y} \right)_x \right) = \left( \frac{\partial}{\partial y} \left( \frac{\partial g}{\partial x} \right)_y \right)$$  \hspace{1cm} (2)

This last equation is only satisfied for certain functions that we call analytical. Eqn. 2 can be combined with Eqn 1 to get

$$\left( \frac{\partial B(x, y)}{\partial x} \right)_y = \left( \frac{\partial A(x, y)}{\partial y} \right)_x$$  \hspace{1cm} (3)

which has two consequences:

1) $dG = A(x, y)dx + B(x, y)dy$ can be integrated to give a function of state.
2) $dG$ is an exact differential which only depends on the difference in the function of state between two states but not on the path between them

$$dG = A(x, y)dx + B(x, y)dy$$ can be considered to be a dot product of

$$\vec{G} = \hat{i}A(x, y) + \hat{j}B(x, y)$$ and $d\vec{r} = \hat{i}dx + \hat{j}dy$. We now can calculate the line integral of $\vec{G} \cdot d\vec{r}$ as:

$$\oint \vec{G} \cdot d\vec{r} = \int ds \cdot \text{curl}(G)$$  \hspace{1cm} (4)

with our definition of the vector the curl only may have a $z$ component:

$$\left( \text{curl}(G) \right)_z = \left( \frac{\partial B(x, y)}{\partial x} \right)_y - \left( \frac{\partial A(x, y)}{\partial y} \right)_x = 0$$  \hspace{1cm} (5)

but Eqn. (5) is only equal to zero if the crossed derivatives (Eqn. (3)) are equal. Then it will be true that

$$\oint \vec{G} \cdot d\vec{r} = 0$$  \hspace{1cm} (6)

If we separate this integral over a closes curve into two portions or paths, we get
\[
\oint_{\text{path 1}} \mathbf{G} \cdot d\mathbf{r} + \oint_{\text{path 2}} \mathbf{G} \cdot d\mathbf{r} = 0
\]

which implies
\[
\oint_{\text{path 1}} \mathbf{G} \cdot d\mathbf{r} = \oint_{\text{path 2}} \mathbf{G} \cdot d\mathbf{r} = 0
\]

Figure 2

Conclusion:
We can choose different paths to go from state \( r_1 = (x_1, y_1) \) to state \( r_2 = (x_2, y_2) \)
\( g(x_1, y_1) \rightarrow g(x_2, y_2) \). And the change in \( G \) is independent of the path chosen, but it only
depends on \( r_1 = (x_1, y_1) \) and \( r_2 = (x_2, y_2) \). Then the function of state can always be
defined by integrating
\[
g(x, y) = \int_{r_1}^{r_2} \mathbf{G} \cdot d\mathbf{r}
\]
However, to have a unique value that only depends on \( r = (x, y) \) we must specify a
reference value \( r_1 = (x_1, y_1) \), and \( g(x, y) \) is now relative to \( g(x_1, y_1) \). Fortunately we are
going to be interested only in the differences between the value of the function \( G \).
For a small change in the value of \( G \)
\[
dG = g(x + dx, y + dy) - g(x, y) = \int_{r_1}^{r + dr} \mathbf{G} \cdot d\mathbf{r} - \int_{r_1}^{r} \mathbf{G} \cdot d\mathbf{r} = \int_{r_1}^{r + dr} \mathbf{G} \cdot d\mathbf{r}
\]  
(7)
\]
this means that \( dG \) only depends on \( r + dr \) and \( r \), and not on our choice of \( r_1 \) which
allows us to define a standard state without the risk of losing generality of the
conclusions that we arrive at. Extensive use of this is done in the field of thermochemistry
which we shall use as an example of application of thermodynamics next class.
Some thermodynamic functions do not satisfy these properties, (i.e. they are not
analytical, or they are not state functions). The differential form of such functions (in the
form given by Eqn. (1) will not be an exact differential in the sense that Eqn. (3) will not
be satisfied for them (the crossed second derivatives will not be equal).
The first law of thermodynamics

In mechanics the energy of a system is given by the Hamiltonian function, which is constant for a conservative system. If we include all the variables that describe the processes, all systems are conservative. It follows that the energy is always conserved. We consider a system “A” surrounded by the rest of the universe, and we say that the system has a certain amount of energy \( U \) in it. Then if energy is taken from the universe and put into the system, the total \( U_{\text{total}} = U_{\text{universe}} + U(A) \) is constant. A well known fact is that energy can be deposited in system A by doing work on it or by supplying heat. Either way we do this we arrive at system \( A' \) regardless of how do we deposit the energy in it. This is the statement of “the first law of thermodynamics”

\[
\Delta U = q + W
\]  

where \( q \) is the amount of heat transferred to the system and \( W \) is the work done on it. If we isolate a system such as 1 kg of water, so no heat can flow through the walls of the container.

If we perform mechanical work on this system initially at temperature \( T_1 \) by letting the weight of mass \( m \) get lower in the lab, such that the propellers stir the water causing it to heat up (the internal energy of the water increases. We could measure the final temperature \( T_2 \) after a certain amount of mechanical work has been done on the system

\[
W_{\text{mechanical}} = mgh
\]

If now repeat the experiment by keeping the weight \( m \) fixed, so no mechanical work is done, and we start at temperature \( T_1 \) again, but now we pass a current on the resistor that
act as a heater. The amount of electrical work done on the resistor is \( W_{\text{elec}} = I^2 Rt \) which it completely converted into heat at the system, we see that the final temperature \( T_2 \) can be reached after some time. Once the system has reached \( T_2 \) it is indistinguishable from the system at \( T_2 \) obtained by lowering the mass \( m \) through a difference in height of \( h \). We can also supply some mechanical work \( W \) and some heat \( q \) and produce the very same temperature change from \( T_1 \) to \( T_2 \). Which is exactly what the first law says (Eqn. (8)). We adopt the convention that \( W > 0 \) if the energy of the system increases. During a process the internal energy of the system increases if the process that caused the change can be produced by lowering a weight somewhere in the surrounding of the system and using this mechanical work to cause the change. If the system does work on the surroundings, then it will be equivalent to displace a mass against a force \( F \).

The total work done is
\[
W = -\int_{z_i}^{z_f} Fdz = -F \int_{z_i}^{z_f} dz = -F(Z_f - Z_i)
\]
if \( Z_f < Z_i \) then \( W > 0 \) we can always create an imaginary process that does the work on the system by lowering a weight \( h = Z_f - Z_i \) and \( F = mg \).

**Work of compression and expansion:**

The system is enclosed in a container that is covered by a frictionless piston of zero mass, and area \( A \) under an external pressure \( p_{\text{ext}} \).
The magnitude of the external force is \( F = p_{\text{ext}} A \). We shall assume that the motion of the piston is quasistatic so no turbulences in the system or the surroundings are generated during the process such that no heat spreading phenomena can occur without us knowing about them. If the system expands and rises the piston by \( dz \) the work done is

\[
-F \Delta z = -p_{\text{ext}} A \cdot dz = \delta W
\]

Note that it is the external pressure what matters and not the internal pressure what matters. But \( A \cdot dz = dV \) or \( \delta W = -p_{\text{ext}} dV \)

For a compression \( \delta W > 0 \) an for a expansion \( \delta W < 0 \)

In general work can be different from expansion-compression. But the general ideal is the same.
The system variables can be of two different types: I) the variables like the volume or the energy of the system depend on how big the system is. These variables are called *extensive*. II) The variables like the temperature or the internal pressure do not depend on the size of the system, and these are called *intensive variables*. By carefully looking at the equation of the work of expansion-compression we can see that it is the product of the form

\[ \text{Work} = (\text{change in an extensive variable}) \times (\text{intensive variable}) \]

This is the general form of any type of work;

the factor *(change in an extensive variable)* is called the generalized displacement

the factor *(intensive variable)* is called the generalized force.

<table>
<thead>
<tr>
<th>Type of work</th>
<th>Definition</th>
<th>Generalized force</th>
<th>Generalized displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expansion/compression</td>
<td>(-p_{ext}dV)</td>
<td>pressure</td>
<td>Volume</td>
</tr>
<tr>
<td>Surface expansion</td>
<td>(-\gamma d\sigma)</td>
<td>Surface tension</td>
<td>Surface area</td>
</tr>
<tr>
<td>Electrical</td>
<td>(-\phi dq)</td>
<td>Electric potential</td>
<td>charge</td>
</tr>
</tbody>
</table>

Expansion against a constant pressure
In this case the system does work against a constant force so that we can take it out of the integral:

\[ W = \int_{v_i}^{v_f} -FdV = \int_{v_i}^{v_f} -p_{ext}dV = p_{ext}\int_{v_i}^{v_f} dV = -p_{ext}(V_f - V_i) \]

We can represent this in a p-V diagram and the shaded area represents the magnitude of the work done:

![Figure 5](image)

**Reversible expansions:**
To achieve a reversible process we must be able to revert its direction by applying an infinitesimal change in the force that drives the process. For an expansion this can be done by a small change in the external pressure so that it can became smaller or larger
than the internal pressure by the application of such infinitesimal change. But this is to say that the external pressure only differs by an infinitesimal amount from the internal pressure. Therefore they must be essentially identical at all times! This means that the system is at equilibrium during the process. This is not a trivial statement because a process is what occurs spontaneously to take a system from whatever state to an equilibrium state. For an expansion/compression work, if we do it reversibly then

\[ W = \int_{V_i}^{V_f} -p_{\text{ext}}\,dV = -\int_{V_i}^{V_f} p\,dV \]

Now in order to calculate the amount of work we need to know the value of p at all times. Since the pressure depends on the volume of the system, we can use the equation of state:

\[ W = -\int_{V_i}^{V_f} p(V)\,dV \]

If we have an ideal gas in the cylinder enclosed by the piston in Figure 3 and we let the gas expand reversibly, the system will do an amount of work

\[ W = -\int_{V_i}^{V_f} nRT\,dV = -nRT\ln\frac{V_f}{V_i} \]

assuming that the temperature and n are constant, we obtain the work of reversible expansion/compression, which is negative if the gas expands and positive if we compress it. Also note that if the system expands at a higher temperature the amount of work it does on the surroundings is higher. As before, we can represent this in a p-V diagram and the shaded area represents the magnitude of the work done:

![Figure 5. Reversible expansion. The grey shaded rectangle represents the work done during the corresponding irreversible process.](image)

If we were to compress the gas from Vf to Vi, we need to do less work than we would need if we were to do this irreversibly. The difference equals the difference in the grey shaded rectangle and the area under the isotherm T. During a reversible expansion the gas does more work (area under the isotherm T for work done against a variable pressure)
than during the corresponding irreversible expansion (lower rectangle area, expansion against pf).

In general the first law of thermodynamics can include other forms of work;
\[ \Delta U = q + \sum W_i = q + W_{\text{exp-comp}} + W_{\text{elec}} + W_{\text{magnt}} + \ldots \]

The corresponding terms depend on the system that we are trying to describe. Note that the first law does not say what would happen, or in which direction a process will occur. Despite of its mundane simplicity, a great deal can be done with it. Before we move on to the second law of thermodynamics, we will discuss an important application of thermodynamics; calorimetry.