Free energy

Here we derive expressions for the Helmholtz and Gibbs free energies from the Clausius inequality:

$$\Delta S \geq 0 \tag{1}$$

which we obtained for a non-reversible Carnot engine.

Clausius inequality

Alternatively, we could have also looked at any other process and compare the reversible and irreversible pathways connecting states A and B to get the Clausius inequality. Because energy is a state function, the energy of the system does not depend on the path (note that we don't specify what happens with the environment!):

$$(\Delta U_{A\to B})^{\text{rev}} = (\Delta U_{A\to B})^{\text{irrev}} \tag{2}$$

For both the reversible and irreversible process we have that the energy of the system can only change if either heat Q is transferred into it (positive heat) or out of it (negative heat), or if work is done by it (negative work) or on it (positive work):

$$dU = dQ + dW \tag{3}$$

For the reversible process, we have furthermore that

$$dU = TdS + dW^{\text{rev}} \tag{4}$$

with $dS = \frac{dQ}{T}$. Because U is a state function, the change in system's energy is the same for both paths

$$dQ^{\text{irrev}} + dW^{\text{irrev}} = TdS + dW^{\text{rev}} \tag{5}$$

This equality also implies that in order to compute the change in a state function, we can always choose the path that is most convenient! We also know that the irreversible work is always less than the reversible work $(-dW^{\text{irrev}}) < (-dW^{\text{rev}})$. The sign is negative, because this is the work we can get *out* of the system. Remember we did a numerical example for reversible versus irreversible expansion of one mole of ideal gas to show that reversible expansion work is indeed larger. This thus implies that for an irreversible process we could have changed more heat into work, but did not. We can thus consider the difference between the irreversible and reversible works as the dissipation work done *by* the system (or 'lost' work)

$$(-dW^{\text{diss}}) = (-dW^{\text{rev}}) - (-dW^{\text{irrev}}) \tag{6}$$

Because, the entropy is also a state function, the entropy change of the *system* (dS) is the same for both reversible and irreversible processes. So we take it to the left hand side of equation 5:

$$dS = \frac{1}{T} dQ^{\text{irrev}} + \frac{1}{T} \left[(-dW^{\text{rev}}) - (-dW^{\text{irrev}}) \right] \tag{7}$$

Because $(-dW^{\text{irrev}}) < (-dW^{\text{rev}})$, this means that the second term on the right hand side of the equation is larger than zero, so that

$$dS > \frac{dQ^{\text{irrev}}}{T} \tag{8}$$

In other words, there is less heat up taken from the environment in the irreversible process. Therefore, the change in entropy of the *environment* $(\Delta S_0 = -\frac{Q^{\text{irrev}}}{T})$ is smaller than the change in entropy of the *system* (ΔS). We subscript everything associated with the environment with a 0 here. The *total* entropy of system *plus* environment increases

$$\Delta S^{\text{tot}} = \Delta S - \frac{Q^{\text{irrev}}}{T} = \Delta S + \Delta S_0 > 0 \tag{9}$$

This is the Clausius inequality.

From here on, the derivation follows chapter 4 in the book of Mandl, "Statistical Physics". In words, the Clausius inequality states that for a process to occur *spontaneously* in an *isolated* system, the entropy of that system must increase. The equality ($\Delta S^{\text{tot}} = 0$) is obtained if the process occurs reversibly. Then, we get maximum work, and thus convert the maximum amount of heat into work.

The goal is to obtain an expression for determining the direction of spontaneous change only in terms of the system that we are interested in (*e.g.* chemical substance) *and* the constraints on that system imposed by the environment (*e.g.*, temperature, pressure or volume). We consider that system *plus* its (very large) environment isolated. The environment can even be the total universe *minus* the system. The details don't matter; it is only essential that there is no exchange of heat or work between the system *plus* environment on the one hand and the rest of the universe on the other hand, *i. e.*, $\Delta U^{\text{tot}} = 0$ for all processes.

If the system's energy is changed by heat (Q) flowing into the system from the environment (or out from the system into the environment) and the environment is so large that heat exchange with system does not affect its temperature (T_0), the change in entropy of the environment is

$$\Delta S_0 = -\frac{Q}{T_0} \tag{10}$$

where the minus sign indicates that we look at the heat from the perspective of the system. The change in entropy of the system *plus* environment can now be written solely in terms of the heat exchange of the system (Q) and the the entropy change of the system (ΔS):

$$\Delta S^{\text{tot}} = \Delta S - \frac{Q}{T_0} \geq 0 \tag{11}$$

Although the heat exchange (Q) can change the state of the system, and hence also its entropy (S is a state function!), the change of the entropy in the system ΔS is in principle independent of $\frac{Q}{T_0}$ here. For example, the heat flowing into the system from the environment can be used to break gas molecules apart (every gas approaches an ideal gas at sufficiently low pressure) without raising the temperature. In this case U remains the same, but the entropy of the system (S) doubles (why that is will be explained in the next lectures).

Maximum useful work

The effect of the pressure (P_0) of the environment on the system is that for any change of the system that involves changes in the system's volume (ΔV), expansion (or compression) work is done:

$$W = -P_0 \Delta V \tag{12}$$

This is also 'lost' work in that it cannot be used for anything other than for the expansion or compression of the system against the pressure (P_0) of the environment. Yet, we often want to use work for something else, like generating electric current, or mechanical motion. That we call useful work: $(-W_{\text{u}})$. It has a negative sign here, because we want to take that work out of the system. If, in addition to the unavoidable expansion/compression work ($-P_0\Delta V$) such useful work (which depends on the path along which we change in the system) is done as well, the total work done by the system is

$$W^{\text{tot}} = -P_0 \Delta V - (-W_{\text{u}}) \tag{13}$$

(note $- \times - = +$) The total work W^{tot} changes the energy of the system by

$$\Delta U = Q - P_0 \Delta V - (-W_{\text{u}}) \tag{14}$$

If we isolate Q, which is the heat exchange between the system and environment during the change

$$Q = \Delta U + P_0 \Delta V + (-W_{\text{u}}) \tag{15}$$

and insert this expression for Q into equation 11 we get for the entropy change of the system *plus* environment

$$\Delta S^{\text{tot}} = \Delta S - \frac{1}{T_0} \left[\Delta U + P_0 \Delta V + (-W_{\text{u}})\right] \geq 0 \tag{16}$$

multiplying on both sides by T_0, the temperature of the environment:

$$T_0 \Delta S^{\text{tot}} = T_0 \Delta S - \Delta U - P_0 \Delta V - (-W_{\text{u}}) \geq 0 \tag{17}$$

After some reshuffling this rearranges into

$$-\left[\Delta U + P_0 \Delta V - T_0 \Delta S\right] \geq (-W_{\text{u}}) \tag{18}$$

Thus, the total useful work the system can perform is

$$(-W_{\text{u}}) \leq -\left[\Delta U + P_0 \Delta V - T_0 \Delta S\right] \tag{19}$$

Remember a negative work on the system, means a positive work for us, which is what we want obviously! Again, the maximum work is obtained, if the process of extracting the work is done reversibly, in which case $\Delta S^{\text{tot}} = 0$ and

$$(-W_{\text{u}}) = -\left[\Delta U + P_0 \Delta V - T_0 \Delta S\right] \tag{20}$$

We normally consider systems at a constant temperature that are also kept at constant volume (achieved by fixing the boundaries of the system) or at constant pressure. If the process occurs in a system at constant temperature (T_0) and constant volume ($\Delta V = 0$), the maximum useful work that can be obtained from a process occurring in the system is determined by the change in *Helmholtz free energy* (ΔA):

$$(-W_{\mathrm{u}}) \leq -\left[\Delta U - T_0 \Delta S\right] = -\Delta A \tag{21}$$

Because U and S are state functions, also the Helmholtz free energy ($A = U - T_0 S$) is a state function that depends only on the constraints (temperature, volume) imposed on the system. Note that in case the process is a chemical reaction, also the extent of the reaction, or the concentrations of the substances, is a constraint that determines the state of the sytem, and hence the Helmholtz free energy. Unlike pressure and temperature, however, we we cannot always easily control the extent of a reaction. We will talk about this in the following lectures.

From equation 17, we also see that $-\Delta A - (-W_{\mathrm{u}})$ is equal to $T_0 \Delta S^{\mathrm{tot}}$, the change in entropy of the system *plus* environment! In other words, at constant volume and temperature, the heat exchange between the system and environment can not only be used to change the energy of the system (ΔU) but also to let the system perform useful work ($-W_{\mathrm{u}}$):

$$Q = \Delta U + (-W_{\mathrm{u}}) \tag{22}$$

The entropy of the environment thus changes by

$$\Delta S_0 = -\frac{Q}{T_0} = \frac{1}{T_0}\left[-\Delta U - (-W_{\mathrm{u}})\right] \tag{23}$$

If no useful work is done, less heat is extracted and only used to change the energy of the system and $Q = \Delta U$.

Any process that decreases A while doing irreversibly useful work (or no useful work at all, which is extremely irreversible) increases S^{tot} and can thus occur spontaneously (Clausius inequality). If the useful work is extracted reversibly, all of the ΔA can be transformed into that work. In this case $\Delta S^{\text{tot}} = 0$, which is how we defined reversibility.

If the pressure is kept constant, while the volume is allowed to vary, a part of the total work is needed to do the unavoidable expansion or compression and is therefore no longer available to do useful work. The maximum useful work that the system can do at constant pressure and temperature is determined by the change in Gibbs free energy

$$(-W_{\text{u}}) \leq -\left[\Delta U + P_0 \Delta V - T_0 \Delta S\right] = -\Delta G \tag{24}$$

As before, a process is spontaneous if $\Delta G \leq 0$ and the equilibrium, at which there is no net change anymore, is reached when $\Delta G = 0$.