Principle of minimum Energy
The second law of thermodynamics asserts that there exists a function $S$ of the energy of the system $S(U, V, N)$ that is a monotonic increasing function of the internal energy $U$. This function reaches an extremum (maximum) at equilibrium. This would be if we use $dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN$ as our fundamental relation. From this we clearly see that $dS = 0$ for constant internal energy once we reach the equilibrium. To see this consider the figure:

At constant U equilibrium is achieved when $S$ is a maximum with respect to another variable $X_j$. If we start with a system for which the variable $X_j$ is not at the value corresponding to equilibrium, the system constrained to be at constant $U$ will evolve, and $S$ will increase and $X_j$ will vary during this process. The process stops when $S$ achieved a maximum:

$$\left(\frac{dS}{dX_j}\right)_U = 0 \quad \text{Equilibrium.}$$

Near the equilibrium point we have $$\left(\frac{dS}{dX_j}\right)_U < 0$$

Another way of looking at this is by taking the fundamental relation $dU = TdS - pdV + \mu dN$. In this case, we constrain the system to have a constant entropy. This is represented in the following figure:
At constant entropy, equilibrium is achieved when $U$ is a minimum with respect to other (unconstrained) variables $X_j$. Let alone, the system at constant entropy will evolve towards minimizing the energy by adjusting $X_j$.

**The use of thermodynamic potentials**

We have seen how we can use the entropy to find the equilibrium condition. All the thermodynamic potentials contain the same information about the system, and therefore we should be able to predict the equilibrium conditions with any of them. The choice of the potential to use depends on the system and on what are the variables that we can control.

Using the Free energy (Helmholtz Potential)
We know that a system will evolve to an equilibrium situation in which $S$ is a maximum, and $dS = 0$ at equilibrium.

$F$ can be used to find the equilibrium condition:
Let's consider a system at constant $T$:

The system plus the reservoir are considered to be isolated from the rest of the universe. For the system plus the reservoir it must always be:

$$dS_{total} = dS_{system} + dS_{bath} \geq 0 \quad \text{(the equal sign is at equilibrium)}$$

The system and the bath are in thermal contact and heat can be exchanged between them. In addition, the volume of the system is not fixed. This means that the system can do work on the bath.

If $\delta q_{system}$ is the heat exchanged from the system to the bath. $\delta W_{system}$ is the work done by the system the first law for this case is

$$dU_{system} = \delta q_{system} + \delta W_{system}$$

$$dU_{bath} = \delta q_{bath} + \delta W_{bath}$$

Because the entire thing is isolated,

$$\delta W_{system} = -\delta W_{bath}$$

$$\delta q_{system} = -\delta q_{bath}$$

From the second law we have

$$TdS = \delta q_{\text{rev}} \geq \delta q_{\text{irrev}}$$

$$\delta W_{\text{rev}} \leq \delta W_{\text{irrev}}$$

then

$$dU_{system} - TdS_{system} = \delta W_{system}^{(\text{rev})} \leq \delta W_{system}^{(\text{irrev})}$$

At constant Temperature we can write this in the form:

$$d(U_{system} - TS_{system}) = dF_{system} = \delta W_{system}^{(\text{rev})} \leq \delta W_{system}^{(\text{irrev})}$$
It follows that the change in F is the work reversibly done by or on the system under constant temperature.(isothermal reversible work). As we can see this reversible work is more negative than the corresponding irreversible work. (if the system does work on the bath, it does more work reversibly than when it does it irreversibly. Conversely, if the bath does work on the system, the work is smaller (less of a positive work) when done reversibly. This means that we obtain the maximum useful work if we carry out the process reversibly. In this case the equal sign of \( dS_{\text{total}} = dS_{\text{system}} + dS_{\text{bath}} \geq 0 \) holds, from which we get:
\[
dS_{\text{total}} = 0 = dS_{\text{system}} + dS_{\text{bath}}
\]
\[
dS_{\text{bath}} = -dS_{\text{system}} = -\frac{\delta q_{\text{system}} \text{(rev)}}{T} = -\frac{1}{T}(dU_{\text{system}} - \delta W_{\text{system}} \text{(rev)})
\]
\[
TdS_{\text{total}} = TdS_{\text{system}} + TdS_{\text{bath}} = 0
\]
Now we replace (*) for \( dS_{\text{bath}} \) in the last expression,
\[
TdS_{\text{total}} = TdS_{\text{system}} - dU_{\text{system}} + \delta W_{\text{system}} \text{(rev)} = 0
\]
\[
TdS_{\text{total}} = -dF_{\text{system}} + \delta W_{\text{system}} \text{(rev)} = 0 \quad \text{(Isothermal, reversible)}
\]
or if \( \delta W_{\text{system}} = 0 \) then \( dF_{\text{system}} \leq 0 \)
\[
dF_{\text{system}} = d(U - TS) = dU - TdS \leq 0 \quad \text{Therefore F reaches a minimum at equilibrium}
\]
A system that is isothermal with a bath, and that can only exchange heat but NO WORK will try to minimize its free energy F. Any isothermal process that increases the internal never occur spontaneously. Irreversible isothermal process happens spontaneously until \( dF = 0 \) (F reaches a minimum)

**Using the Enthalpy: Joule Thompson Effect**

In laboratory processes we are mostly using a constant pressure and constant temperature, so that the Gibbs potential is the best choice. However there is one important situation

![Diagram](image)

In which the process occurs at constant Enthalpy. As strange as this may sound, it is the
basic principle behind industrial cooling. Consider the last figure above, where a gas is forced through a porous plug or obstruction in the pipe. The cylinder and the pistons are a box volume $V_i$ gas is forced through at an initial pressure and temperature $P_i$, $T_i$. The cylinder and the pistons are insulating. Upon passing through the porous membrane, real gases usually cool down. So $T_f < T_i$, however the temperature change depends on the initial pressure.

To understand why this happens, we start by calculating the internal energy before and after the gas goes through:

$$U_f = U_i + p_f V_i - p_f V_f$$

from here we get by rearranging

$$U_f + p_f V_f = U_i + p_i V_i$$

Therefore this process is Iso-Enthalpic. It occurs at constant enthalpy.

We now calculate the temperature change by first writing the temperature change as a derivative:

$$dT = \left( \frac{dT}{dp} \right)_{H,N} dp$$

At this stage, we would not be able to go any further, because we do not know what to do with the derivative at constant Enthalpy. What we do next is quite standard, although it might appear quite snazzy at this stage. The derivative manipulations will be discussed shortly. Now lets finish this derivation:

We first write the derivative as:

$$dT = \left( \frac{dT}{dp} \right)_{H,N} dp = \left( \frac{\partial H}{\partial p} \right)_{T,N} dp$$

since both $N$ and $H$ are constant.

Next, we recognize the derivatives. The one in the numerator can be written in terms of the fundamental relation for the enthalpy: $dH = TdS + VdP + \mu dN$ from which we see that

$$\left( \frac{\partial H}{\partial p} \right)_{T,N} = T \left( \frac{dS}{\partial p} \right)_{T,N} + V \left( \frac{dP}{\partial p} \right)_{T,N} + \mu \left( \frac{dN}{\partial p} \right)_{T,N}$$

because $N$ is constant the last term vanishes.

The second term equals $V$:

The derivative in the denominator can also be connected to some known quantity:

$$\left( \frac{\partial H}{\partial T} \right)_{p,N} = NC_p$$

With these replacements we get:
\[ dT = \left( \frac{dT}{dp} \right)_{H,N} dp = -T \frac{dS}{\partial p} \frac{1}{NC_p} dp. \]

How can we replace \( \frac{dS}{\partial p} \) by something recognizable?

We do this by writing the Gibbs potential which is a state function, and therefore its second derivatives satisfy the relation

\[
\left( \frac{dS}{\partial p} \right)_{T,N} = -\left( \frac{dV}{\partial T} \right)_{P,N}
\]

We finally note that \(-\left( \frac{dV}{\partial T} \right)_{P,N} = -\alpha V\) the isobaric expansion coefficient.

Then

\[
dT = -T \frac{dS}{\partial p} \frac{1}{NC_p} dp = -\alpha VT + V \frac{dV}{NC_p} dp = \frac{V}{NC_p} (\alpha T - 1) dp
\]

Since in our experiment P on the side we are pushing the piston is larger that the pressure on toe other side, \(dp < 0\). For this experiment, the gas will cool down only if \((\alpha T - 1) > 0\) so that \(dT < 0\) this implies that \(T_{\text{inversion}} > \frac{1}{\alpha}\). If the gas starts at a temperature equal or lower than \(T_{\text{inversion}}\) it cools down. Else it gets hotter.


The last figure shows some isenthalps. The maxima of the isenthalps is connected by the inversion curve.