

Thermodynamic potentials

A number of thermodynamic quantities have been defined—useful under differing conditions of fixed pressure, volume, temperature, particle number, etc. These are the enthalpy, the Helmholtz free energy, and the Gibbs free energy. Together with the internal energy, these are referred to as thermodynamic potentials (TP).

The total energy required to create a system of particles at sea level air pressure would include the expansive work done in displacing the air.

We define the *enthalpy* to be

$$H = U + PV$$

The enthalpy is useful when a change takes place in a system while pressure is constant .

We now shall introduce the other two thermodynamic potentials: the **Helmholtz free energy** F and **Gibbs free energy** G . Depending on the type of a process, one of these four thermodynamic potentials provides the most convenient description. All four functions have units of energy.

Let's say the system is in contact with a heat bath, so that the temperature is constant. The pressure may not be constant. To create the system, some of its total energy can be taken from the environment in the form of heat. So the total work required to create the system is not all of U , but less than U . Define the *Helmholtz Free Energy* of the system as $F = U - TS$

Any change in a system at constant temperature will entail a change in F ,

$$dF = dU - TdS = dQ + dW - TdS$$

where W is all the work done on the system.

Now, if the system is at constant pressure as well as constant temperature, then the extra work needed to create the system is the *Gibbs Free Energy*:

$$G = U - TS + PV$$

If we envision infinitesimal changes in thermodynamic variables, we can derive thermodynamic identities for the thermodynamic potentials. All the thermodynamic properties of a system can be found by taking partial derivatives of the TP. For each TP, a set of so-called “natural variables” exists

We have already, the thermodynamic identity for internal energy

$$dU = TdS - PdV + \mu dN$$

Now, consider the enthalpy, H :

$$dH = dU + PdV + VdP = TdS + VdP + \mu dN$$

Now, we consider the free energy F :

$$dF = dU - TdS - SdT = -SdT - PdV + \mu dN$$

and the Gibbs energy

$$dG = dU - TdS - SdT + PdV + VdP = -SdT + VdP + \mu dN$$

Potential	Variables
$U(S, V, N)$	S, V, N
$H(S, P, N)$	S, P, N
$F(T, V, N)$	V, T, N
$G(T, P, N)$	P, T, N

When considering different types of processes, we will be interested in two questions:

- (i) what determines the *stability* of a system and how the system evolves towards an equilibrium;
- (ii) how much work can be extracted from a system.

Isolated Systems, independent variables S and V

Advantages of U : it is conserved for an *isolated* system (it also has a simple physical meaning – the sum of all the kin. and pot. energies of all the particles).

In particular, for an isolated system $\delta Q=0$, and $dU = \delta W$.

Earlier, by considering the total differential of S as a function of variables U , V , and N , we arrived at the thermodynamic identity for *quasistatic* processes :

$$dU = TdS - PdV + \mu dN$$

The combination of parameters on the right side is equal to the *exact differential* of U . This implies that the *natural variables* of U are S , V , N :

$$U = U(S, V, N)$$

Considering S , V , and N as independent variables

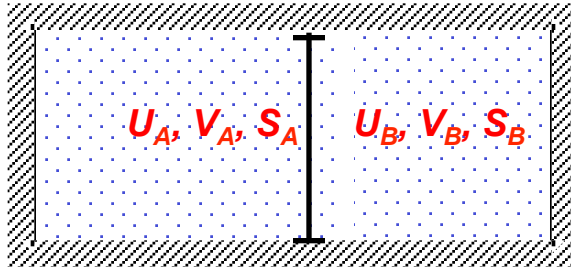
$$dU(S, V, N) = \left(\frac{\partial U}{\partial S} \right)_{V, N} dS + \left(\frac{\partial U}{\partial V} \right)_{S, N} dV + \left(\frac{\partial U}{\partial N} \right)_{S, V} dN$$

This yields:

$$\left(\frac{\partial U}{\partial S} \right)_{V, N} = T \quad \left(\frac{\partial U}{\partial V} \right)_{S, N} = -P \quad \left(\frac{\partial U}{\partial N} \right)_{S, V} = \mu$$

Again, this shows that among several macroscopic variables that characterize the system (P , V , T , μ , N , etc.), only three are independent, the other variables can be found by taking partial derivatives of the TP with respect to its natural variables.

Equilibrium in Isolated Systems



For a thermally isolated system $\delta Q = 0$. If the volume is fixed, then no work gets done ($\delta W = 0$) and the internal energy is conserved, $U = \text{const}$.

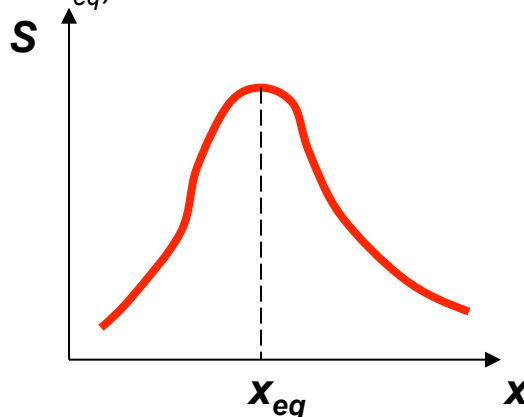
While this constraint is always in place, the system might be out of equilibrium (e.g., we move a piston that separates two sub-systems, see Figure). If the system is initially out of equilibrium, then some *spontaneous processes will drive the system towards equilibrium*. In a state of stable equilibrium no further spontaneous processes (other than ever-present random fluctuations) can take place. The equilibrium state corresponds to the maximum multiplicity and maximum entropy. All microstates in equilibrium are equally accessible (the system is in one of these microstates with equal probability).

$$(S)_{\text{eq}} = \max$$

This implies that in any of these spontaneous processes, the entropy tends to increase, and the change of entropy satisfies the condition

$$dS \geq 0$$

Suppose that the system is characterized by a parameter x which is free to vary (e.g., the system might consist of ice and water, and x is the relative concentration of ice). By spontaneous processes, the system will approach the stable equilibrium ($x = x_{\text{eq}}$) where S attains its absolute maximum.



Enthalpy (independent variables S and P)

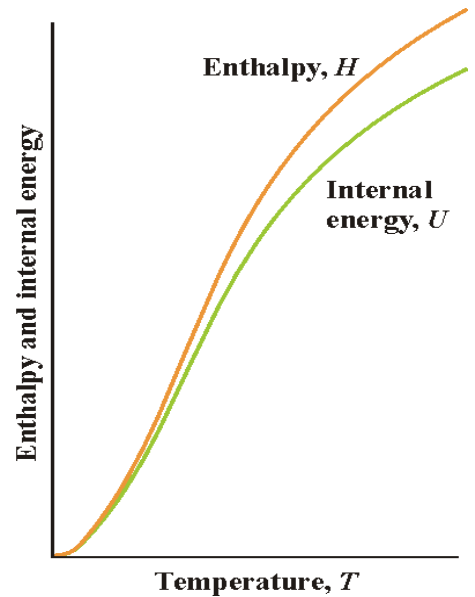
The volume V is not the most convenient independent variable. In the lab, it is usually much easier to control P than it is to control V . To change the natural variables, we can use the following trick:

Legendre transformation

$$U(S, V) \rightarrow U(S, P) + PV$$

$$dH(S, P, N) = T dS + V dP + \mu dN$$

H is also a thermodynamic potential, with its natural variables S , P , and N . It represents the internal energy of a system plus the work needed to make room for it at $P = \text{const}$.



$$dH(S, P, N) = \left(\frac{\partial H}{\partial S} \right)_{P, N} dS + \left(\frac{\partial H}{\partial P} \right)_{S, N} dP + \left(\frac{\partial H}{\partial N} \right)_{S, P} dN$$

$$\left(\frac{\partial H}{\partial S} \right)_{P, N} = T \quad \left(\frac{\partial H}{\partial P} \right)_{S, N} = V \quad \left(\frac{\partial H}{\partial N} \right)_{S, P} = \mu$$

In general, if we consider processes with “other” work (such as electrical work):

$$dH = TdS + VdP + \mu dN + \delta W_{\text{other}}$$

At this point, we have to consider a system which is not isolated: it is in a thermal contact with a thermal reservoir.

$$dH = TdS + VdP + \delta W_{\text{other}} = \delta Q + VdP + \delta W_{\text{other}}$$

Let us consider the $P = \text{const}$ processes with purely “expansion” work ($\delta W_{\text{other}} = 0$):

$$(dH)_{P, \delta W_{\text{other}}=0} = \delta Q$$

For such processes, the change of enthalpy is equal to the thermal energy (“heat”) received by a system.

$$C_P = \left(\frac{\partial Q}{\partial T} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P$$

For the processes with $P = \text{const}$ and $\delta W_{\text{other}} = 0$, the enthalpy plays the same part as the internal energy for the processes with $V = \text{const}$ and $\delta W_{\text{other}} = 0$.

Example: the evaporation of liquid from an open vessel is such a process, because no effective work is done. The heat of vaporization is the enthalpy difference between the vapor phase and the liquid phase.

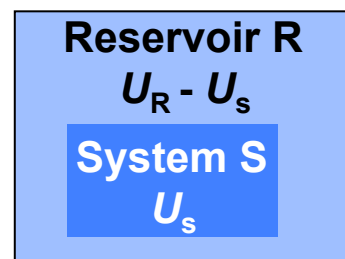
Systems in contact with a thermal reservoir

There are two complications:

1. the energy in the system is no longer fixed (it may flow between the system and reservoir);
2. in order to investigate the stability of an equilibrium, we need to consider the entropy of the combined system (= the system of interest+the reservoir) – according to the 2nd Law, this total entropy should be maximized.

What should be the system’s behavior in order to *maximize the total entropy*?

$$S_{\text{total}} = S_{\text{system}} + S_{\text{reservoir}}$$



For systems in thermal contact with a reservoir, we can replace the entropy with another, more-convenient-to-work-with function. This, of course, does not mean that we can get rid of entropy. We will be able to work with a different “energy-like” thermodynamic potential for which entropy is not one of the natural variables.