## Third law of thermodynamics

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The third law concerns the behavior of systems (in internal equilibrium) as the temperature is lowered and made to approach the absolute zero. We will again refer to our pet system which is a hydrostatic system. It is an experimental fact that as the system<sup>1</sup> approaches absolute zero, the changes in Gibbs and Enthalpy in any isothermal process approaches the same,

$$\Delta G = \Delta H|_{T \to 0}$$

This can be explained theoretically noting first that, G = U - TS + PV = H - TS, so that

$$\Delta G = \Delta H - T\Delta S - S\Delta T,$$

and since for an isothermal process,  $\Delta T = 0$ ,

$$\Delta G = \Delta H - T \Delta S.$$

As  $T \to 0$ , it is now obvious that,

$$\lim_{T \to 0} \Delta G = \lim_{T \to 0} \Delta H.$$

So this is not surprising that experiments find this behavior. However experiments reveal not only do the change in Gibbs function and the enthalpy function approach each other, the slope of the changes in fact vanish, i.e.,

$$\lim_{T \to 0} \frac{\partial (\Delta G)}{\partial T} = \lim_{T \to 0} \frac{\partial (\Delta H)}{\partial T} = 0.$$

In particular for an isobaric process,

$$\lim_{T \to 0} \left( \frac{\partial (\Delta G)}{\partial T} \right)_P = \lim_{T \to 0} \left( \frac{\partial (\Delta H)}{\partial T} \right)_P = 0$$

Swapping the order of  $\Delta$  and  $\frac{\partial}{\partial T}$  we get,

$$\lim_{T \to 0} \Delta \left( \frac{\partial G}{\partial T} \right)_P = 0.$$

Next, we recall that,  $\left(\frac{\partial G}{\partial T}\right)_P = -S$  and obtain the result,

$$\lim_{T \to 0} \Delta S = 0,$$

## i.e. in the neighborhood of absolute zero, all processes in a system/substance in internal equilibrium occur with no change in entropy. This result is known as the Nernst Heat theorem (1907).

Planck, in 1911, however made an even stronger statement which do not follow from the preexisting thermodynamic relations, that not only is the entropy change in a process, but the *entropy* itself approaches zero as the system (throughout in internal equilibrium) is made to approach T = 0 K, i.e.,

$$\lim_{T \to 0} S = 0.$$

<sup>&</sup>lt;sup>1</sup>Most of these experiments concerned chemical reactions occurring at constant temperature and pressure.

This statement is known as the third law of thermodynamics, to wit: the entropy of every substance/system in internal equilibrium at absolute zero is itself zero.

The third law is an independent law which determines the integration constant we encounter while we obtain the expression for the entropy integrating the TdS equations. For example at constant volume, integrating the first TdS equations, one has

$$S(V,T) = \int_0^T \frac{C_V}{T} dT + S_0.$$

Then the third law fixes,  $S_0 = 0$ , or,

$$S(V,T) = \int_0^T \frac{C_V}{T} dT.$$

Similarly at constant pressure,

$$S(P,T) = \int_0^T \frac{C_P}{T} dT.$$

But both the expressions for S, be it at constant V or at constant P appear to diverge as  $T \to 0$ , unless  $C_P, C_V \to 0$  faster than T. So at absolute zero,

$$C_p, C_V \to 0.$$

 $C_P - C_V \propto T$ 

Now we already know that as a consequence of the second law we have a heat capacity equation,

$$C_P = C_V$$
, as  $T \to 0$ .

But the third law has a stronger implication that not only are these two equal but they vanish as  $T \to 0$ .

Similar behavior is exhibited by the other response function, thermal expansivity,  $\beta$ . Using the Maxwell relation,

$$\beta \propto \left(\frac{\partial V}{\partial T}\right)_P \propto -\left(\frac{\partial S}{\partial P}\right)_T$$

Now since at absolute zero, according to the Nernst heat theorem

$$\lim_{T \to 0} \left( \frac{\partial S}{\partial P} \right)_T = \lim_{T \to 0} \left( \frac{\partial S}{\partial V} \right)_T = 0,$$

one has

so,

$$\lim_{T \to 0} \beta = 0.$$

The third law also implies that it is impossible to reduce the temperature of a system to absolute zero in any finite number of operations, as we shall see shorty. This alternative version of the third law is better known as the Unattainability (of absolute zero) statement. The most efficient method to cool a system is to isolate it from its surroundings i.e. (adiabatic) and make it perform work purely at the expense of its internal energy. This decrease in internal energy will in turn lower its temperature. To this end consider a reversible adiabatic (isentropic) process by which the temperature as well some other state variable X, could be any extensive variable or intensive get changed. The entropy of the initial and final states, in consistency with the third law, are given by,

$$S_1(X_1, T_1) = \int_0^{T_1} \frac{C_X(X_1, T)}{T} dT, \quad S_2(X_2, T_2) = \int_0^{T_2} \frac{C_X(X_2, T)}{T} dT$$

Since the process is isentropic,

$$S_1(X_1, T_1) = S_2(X_2, T_2)$$



Figure 1: ST diagrams for a process displaying the equivalence of the Planck statement and the unattainability statement of the third law of thermodynamics

$$\int_{0}^{T_{1}} \frac{C_{X}(X_{1},T)}{T} dT = \int_{0}^{T_{2}} \frac{C_{X}(X_{2},T)}{T} dT$$

Now let's say the isentropic process can be taken all the way to  $T_2 = 0$  beginning with some finite  $T_1$ . Then the above equality becomes,

$$\int_{0}^{T_1} \frac{C_X(X_1, T)}{T} dT = 0.$$

However the integrand is manifestly positive for all T > 0 as  $C_X$  and T are both positive, and the hence statement cannot be true. Therefore no such isentropic process is possible which absolute zero is attained. This is a version of the unattainability statement of the third law.

A more instructive example which shows the equivalence of the Planck's statement and the uttainability statement of the third law using our pet systems, the hydrostatic system or the paramagnet is as follows. Let's consider a gas undergoing an isothermal compression in contact with a heat reservoir at temperature T during which the pressure increases, say from an initial value P to higher value P'. This is then followed by an reversible adiabatic (isentropic) expansion back to initial pressure P, causing the temperature to drop to T' below T (Check that this is what happens for instance when you have an ideal gas.). Thus this two step process will bring the gas at its original pressure while lowering it's temperature. In case of the paramagnet one first performs a reversible isothermal magnetization from an initial value M to a larger value M', followed by the reversible adiabatic demagnetization till the original magnetization M is restored. The adiabatic demagnetization stage causes cooling and is the standard technique to produce low temperatures in the lab using paramagnetic salt. Now if a *finite* number of such a sequence of two step cooling process allows one to lower the temperature of the system (gas or paramagnet) to absolute zero, then constant P lines should look like in the left S-T diagram in figure (1) above. However according to the third law of thermodynamics, the constant P lines must all converge to the S = 0 at T = 0 as the entropy of a system when lowered to T = 0 must go to zero regardless of the pressure (or magnetization). If all these isobars converge at S = 0 when T = 0, as in the S-T diagram on the right in figure (1), then the triangles representing the two step process (vertical downward isothermal compression followed by horizontal leftward adiabatic expansion) becomes smaller and smaller as one approaches T = 0, and it is clear it will take *infinite* such steps to reach T = 0. Thus, the Planck statement leads to the unattainability statement.