

Lecture 15

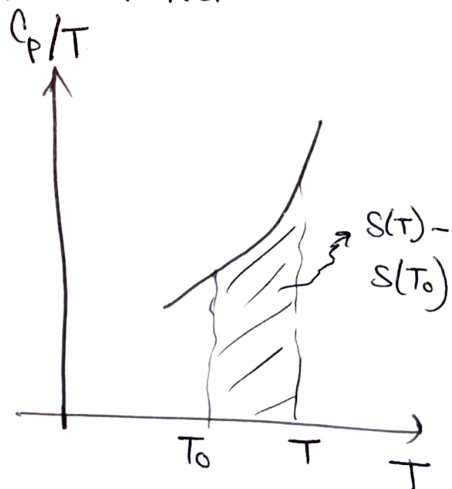
We have shown that the entropy of an isolated system always either remains the same or increases with time. But what value of entropy does a system take, and how can we measure it?

One way to measure the entropy of a system is to measure the heat capacity. We have shown,

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

$$\therefore S = \int \frac{C_P}{T} dT \Rightarrow S(T) = S(T_0) + \int_{T_0}^T \frac{C_P}{T} dT$$

So, we can only calculate the change in entropy and not its absolute value. The third law of thermodynamics gives us some additional information. It provides us with an absolute value of entropy at a particular temperature, that is absolute zero.



The third law of thermodynamics

Walter H. Nernst came up with the first statement

of third law of thermodynamics after examining the data on chemical ~~reactions~~ thermodynamics and doing experiments with electrochemical cells. The essential conclusion he came into concerned the change in enthalpy ΔH and Gibbs free energy in a reaction. We know,

$$G = H - TS \Rightarrow \Delta G = \Delta H - T\Delta S$$

So, as $T \rightarrow 0$, $\Delta G \rightarrow \Delta H$. Experimental data showed that this was true, but ΔG and ΔH not only came together ~~but~~ close together on cooling, but they approached each other asymptotically. On the basis of the data, Nernst also postulated that, $\Delta S \rightarrow 0$ as $T \rightarrow 0$. His statement of third law is,

"Near absolute zero, all reactions in a system in internal equilibrium take place with no change in entropy."

Max Planck's statement was -

"The entropy of all system in internal equilibrium is the same at absolute zero, and may be taken to be zero." Internal equilibrium means all parts of a system is in equilibrium with each other.

Nernst's postulate was due to the fact that, only $T \rightarrow 0$ is not enough for $\Delta G \rightarrow \Delta H$, since they are almost equal as $T \rightarrow 0$, the ΔS must also be such that, $\Delta S \rightarrow 0$, so that $\Delta G \rightarrow \Delta H$ for sure.

Now, the Max Planck's postulate, - ~~that for a p~~ was actually given for perfect crystals. It makes sense intuitively. For perfect crystals, as $T \rightarrow 0$, all the vibrations and motion ceases to zero. So, at $T=0$, there must be only one state possible, and so, $S = k_B \ln 1 = 0$.

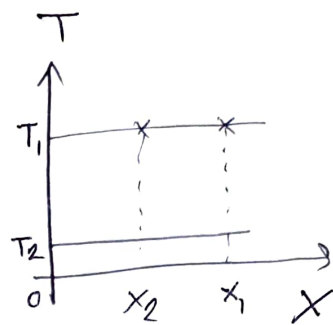
Now, if you have defined entropy to be 0 at $T=0$ (or you can define for other objects that at $T=0$ entropy has a value of say, S_0), then we can always find entropy of a state when the system warms to that state.

$$\therefore S(T) - S_0 = \int_0^T \frac{C dT}{T}$$

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This can be called the absolute entropy.

To be more precise, think about the graph of T vs X where X is some thermodynamic variable. At a constant temperature, T_1 , you take your system from X_1 to X_2 , and you measure the entropy change $\Delta S(T)$, which has some non-zero finite value. We repeat this experiment at a lower temperature T_2 , and then at $T \rightarrow 0$. It is observed that, as $T \rightarrow 0$, $\Delta S(T) \rightarrow 0$, for any X_1 and X_2 . This is the statement of ~~the~~ third law of thermodynamics. Going one step further, since the entropy becomes a constant, one can take that constant to be zero.

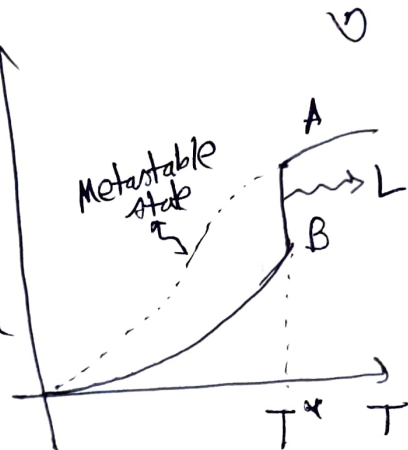


$$\therefore \lim_{T \rightarrow 0} S(X, T) \equiv 0$$

The extension of taking $S=0$ as $T=0$, is experimentally checked for ~~the~~ metastable phases of a substance. Certain materials can exist in a number of similar crystalline structures (called allotropes). Of course, at a given temperature, only one of these structure is stable. Let us imagine that, as high temperature equilibrium phase A is ~~at~~ cooled down, it makes a transition at temperature T^* to phase B, releasing latent heat L .

Under rapid cooling, the transition is avoided, and phase A persists in the metastable equilibrium.

The entropies in these two phases can be calculated using heat capacities $C_A(T)$ and $C_B(T)$. Now, if we want to find the entropy at a bit higher temperature above T^* ,



then,

$$\text{For A: } S_A(T^* + \epsilon) = S_A(0) + \int_0^{T^*} \frac{C_A(T')}{T'} dT'$$

$$\text{For B: } S_B(T^* + \epsilon) = S_B(0) + \int_0^{T^*} \frac{C_B(T')}{T'} dT' + \frac{L}{T^*}$$

Since entropy is a state function,

$$S(T^* + \epsilon) = S_B(T^* + \epsilon) \Rightarrow S_A(0) + \int_0^{T^*} \frac{C_A(T')}{T'} dT' = S_B(0) + \int_0^{T^*} \frac{C_B(T')}{T'} dT' + \frac{L}{T^*} \quad \text{--- (1)}$$

Using equation (1) and finding the integrals along with measurements one can verify

that, $S_A(0) = S_B(0) = 0$.

Consequences of the third law

1. Heat capacities tend to zero as $T \rightarrow 0$:

$$S(T_0, x) - S(0, x) = \int_0^{T_0} \frac{C_x(T')}{T'} dT'$$

As $T_0 \rightarrow 0$, the integral will diverge unless $C_x(T_0) \rightarrow 0$.

From another perspective, $C_x = T \left(\frac{\partial S}{\partial T} \right)_x = \left(\frac{\partial S}{\partial \ln T} \right)_x$

Now, as $T \rightarrow 0$, $\ln T \rightarrow -\infty$ and $S \rightarrow 0$ and hence, $C_v \rightarrow 0$.

2. Since $S(T=0, x) = 0$ for all coordinates x ,

$$\lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial x} \right)_T = 0.$$

3. Thermal expansivity vanish as $T \rightarrow 0$:

$$\beta_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

But, $\left(\frac{\partial S}{\partial p} \right)_T \rightarrow 0$ as $T \rightarrow 0$. Then again, one of the Maxwell's relations states, $\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p$

$$\therefore \beta_p \rightarrow 0 \text{ as } T \rightarrow 0$$

4. No gases remain ideal as $T \rightarrow 0$:

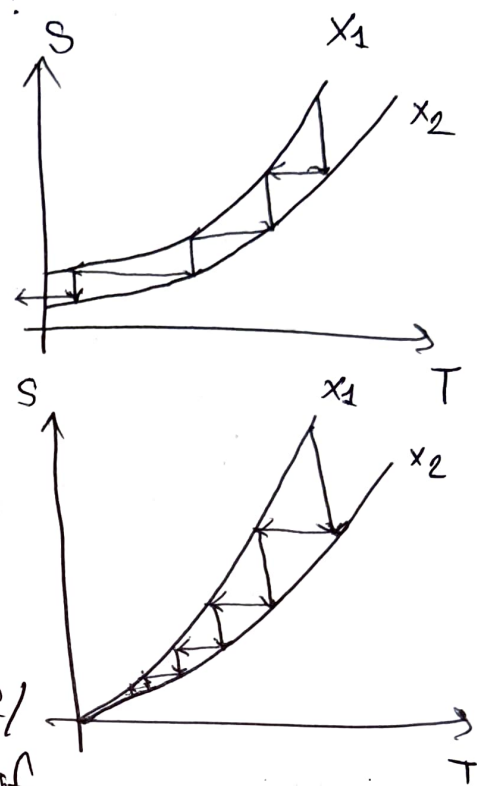
For ideal gases, we ~~have~~ have seen that

$C_p - C_v = R$ and $C_v = \frac{3}{2} R$ per mole. However, as $T \rightarrow 0$, C_p and C_v both goes to zero, and so ~~if~~ these are not satisfied near absolute zero. Furthermore, for ideal gas we found that, $S = C_v \ln T + R \ln V + \text{constant}$. Now, as $T \rightarrow 0$, $\ln T \rightarrow -\infty$, that implies ~~so~~ $S \rightarrow -\infty$ as $T \rightarrow 0$. So, the idea of ideal gas is not so good in $T \rightarrow 0$ region.

5. It is impossible to cool any system to absolute zero in a finite number of steps:

Consider the plots of the figure here, which is S vs T . This is plotted for different values of a parameter x (which may be magnetic field). ~~Collar~~ Colling is produced

by isothermal increase in the parameter x followed by an adiabatic/isentropic decrease in the value of



x . Say, x is the magnetization in a material. At some time, the spin orientation is, say, $\uparrow\downarrow\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\uparrow$ with a random distribution. ~~If now~~ The spin down \downarrow orientation has a lower energy than higher spin up \uparrow orientation. If the magnetic field is increased, the sample becomes $\downarrow\downarrow\downarrow\uparrow\downarrow\downarrow\uparrow\downarrow\uparrow$ by giving away some energy to the surroundings. Since, the spin distribution will be less random, it will contribute to the lowering of the entropy. Now, we isolate the system from the surrounding and gradually let the applied field to be zero. The process is obviously

adiabatic/isentropic, and called adiabatic demagnetization. Since the process is adiabatic, there is no change in entropy of the material. However, since there is no magnetic field to align against, the spins assume their original higher entropy random alignment. This is counterbalanced by the decrease of entropy of the molecules that carry the electrons. However, returning to higher energy spin state means ^{need for} increase in energy, and temperature of the system must decrease, because there is nothing to take energy from other than internal energy. The same process is repeated to get to lower and lower temperature. However, due to third law, the entropy must be the same for both states as $T \rightarrow 0$. According to the second graph you can never really go to zero using the process in finite steps. If $S \rightarrow 0$ as $T \rightarrow 0$, then, from the first figure, you could go to zero in finite steps.

So, it is impossible to lower the temperature to absolute zero in finite number of steps.

Remarks:

Consider a Carnot engine operating between T_c and T_H . The efficiency is, $\eta = 1 - \frac{T_c}{T_H}$. If $T_c \rightarrow 0$, $\eta \rightarrow 1$. So, $T_c = 0$ is a clear violation of Kelvin's statement. So, is third law just another consequence of second law? It might seem so, but it's not this simple. Can you produce an isothermal expansion at $T_c = 0$? Think about this, why or why not.