

The 3rd Law



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Nernst (1864 –1941)

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Chapter 6: The Third Law

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

Postulated by Nernst

The entropy of all systems in internal equilibrium is the same at absolute zero and may be taken as zero.

Re-formulated more generally by Planck in 1911

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Experimental determination of entropy

- The heat capacity relates to the entropy changes, e.g. at constant pressure:

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p \Rightarrow \left(\frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T}$$

so if C_p is measured at a certain pressure as a function of temperature we can integrate numerically to get the entropy at that pressure as a function of temperature:

$$S(T) = S(T=0) + \int_0^T \left(\frac{\partial S}{\partial T} \right)_p dT = S(0) + \int_0^T \frac{C_p}{T} dT$$

but this requires the value of the entropy at absolute zero.

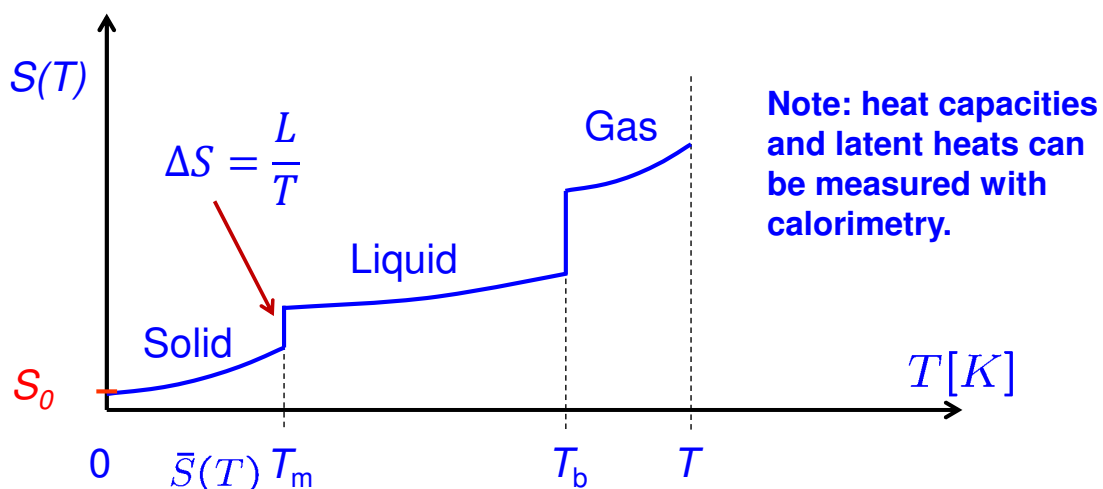
- As a substance is heated from absolute zero it will also go through one or more phase transitions. As the substance crosses one of these phase transitions, with a latent heat L , the entropy will increase by:

$$\Delta S = \frac{L}{T}$$

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A typical S - T diagram

- At a phase transition, the entropy change relates to the latent heat:



- The only quantity we do not know is S_0 , and this is given by the 3rd law..

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Origin of 3rd Law: Work of Nernst

- As with the other laws of thermodynamics, the 3rd law started as an empirical law based on experimental observation, but its 'proof'/ an understanding of why it works relies on statistical thermodynamics.
- Nernst proposed the law on the basis of data on chemical thermodynamics and his own measurements of electrochemical cells – recall that $-dG$ gives the maximum amount of non 'pV' work (in this case electrical work in the external circuit as measured by the cell voltage) that can be done for changes occurring at constant T and P .
- Nernst looked at the relation between ΔH and ΔG for chemical reactions as the temperature was reduced.

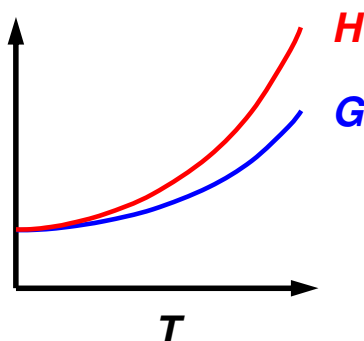
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Origin of 3rd Law: Work of Nernst

- By definition: $G = H - TS$
and at constant T $\Delta G = \Delta H - T\Delta S$

So one expects ΔG to tend to be equal to (*i.e.* approach) ΔH as T goes to zero.

- Nernst however found that not only was this was true, but that they approached each other asymptotically, *i.e.* that ΔS approached zero as T approached absolute zero.



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Origin of 3rd Law: Planck's generalisation

- Planck generalised Nernst's statement that changes in entropy for systems in internal equilibrium at 0K must be zero to the fact that all systems in equilibrium with each other at 0K must have the same entropy and that this could therefore be assigned a value of zero.
- Every configuration of a system will have a different energy (unless they are related by some symmetry). At some level all particles interact, which implies some potential energy differences for different structures. The significance of an energy difference in determining the most likely configuration increases as the temperature drops (as seen in the Boltzmann factor, $\exp(-E/k_B T)$) – and as absolute zero is approached, if the system is in equilibrium, i.e. still capable of moving from microstate to microstate, it will drop into the ground energy state with $\Omega=1$. Entropy is a measure (via the log) of the number of microstates of the system and for non identical, independent systems needs to be extensive. If all the components are in their respective ground states, there is only one microstate for the whole collection, but if we add a constant to $S = -\sum_i p_i \log p_i = -1 \cdot \log 1 = 0$, it would cease to be extensive.
- Remember we are dealing with quantum states. Classically, different orientations of the system would be considered different states, but quantum mechanically there is just one, non rotating, rotational ground state. Similarly there is one ground translation state defined according to the wavefunction boundary conditions.
- States with a symmetry relation other than rotation, for example optical isomers will have the same energy, but may be considered as different substances, (they have different structures) with a zero latent heat phase transition between them. 364

3rd Law: an example

- Consider a binary alloy – at high temperatures (e.g. if nothing else, in gas phase), whatever the energetics, two components will mix since the importance of energy differences between the mixed/unmixed state reduces as temperature increases.
- If the components have a lower total energy when unmixed, then as 0K is approached they will separate out into 2 crystals each of a pure component, with some optimal macroscopic form and value of the ratio of the area of the interface between them to the area of free surfaces.
- If the lower energy state is a mixed one – then there will be some optimum minimum energy geometry.
- Either way – its clear there is only one ground state structurally as well as energetically. BUT in practice this will not be achieved because they cannot achieve equilibrium at low temperatures because atomic rearrangements require an activation energy – so they end up frozen in some higher entropy non-equilibrium state. 365

Consequences of the Third Law

- All heat capacities C_x go to 0 as $T \rightarrow 0$

$$C_x = T \left(\frac{\partial S}{\partial T} \right)_x$$

Experimentally S is observed to go smoothly to zero (no infinite gradient) and given T is also going to zero, C_x also goes to zero.

- At low enough temperatures only the first excited state, (energy ε) has any significant probability of occupation other than the ground state giving a system energy (Overhead 284) as $T \rightarrow 0$ of:

$$U = \frac{\varepsilon}{1 + e^{\varepsilon/kT}}$$

and a heat capacity $\left(\frac{\partial U}{\partial T} \right)_x$ as $T \rightarrow 0$:
$$= \frac{\varepsilon e^{\varepsilon/kT}}{kT^2(1 + e^{\varepsilon/kT})^2} \rightarrow \frac{\varepsilon e^{-\varepsilon/kT}}{kT^2} \rightarrow 0$$

- In contrast, classical equipartition of energy \Rightarrow energy = $\frac{1}{2} kT$ per degree of freedom $\Rightarrow U \propto T$ right down to $T = 0$ and hence

$$C_x = (\partial U / \partial T)_x \text{ remains finite.} \quad 366$$

Consequences of the Third Law

- Via Maxwell relations, we can relate entropy changes also to other physical quantities.

- e.g. Isobaric thermal expansion coefficient

$$\beta_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = -\frac{1}{V} \left(\frac{\partial S}{\partial p} \right)_T \rightarrow 0 \quad \text{as } T \rightarrow 0$$

- or, consider Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \rightarrow 0 \quad \text{as } T \rightarrow 0$$

- This has been tested for ^4He , and ^3He for which, at the appropriate pressure, solid and liquid coexist right down to $T = 0$. This implies that if two phases can co-exist at 0K, then the latent heat for the transition between them must be zero.

The unattainability of absolute zero

- It can be shown that a consequence of the entropy of all systems in thermal equilibrium dropping to zero is that absolute zero can never be obtained and indeed the third law can be formulated in terms of this:

It is impossible by any procedure, no matter how idealized, to reduce the temperature of any system to zero temperature in a finite number of finite operations.

How can you cool something?

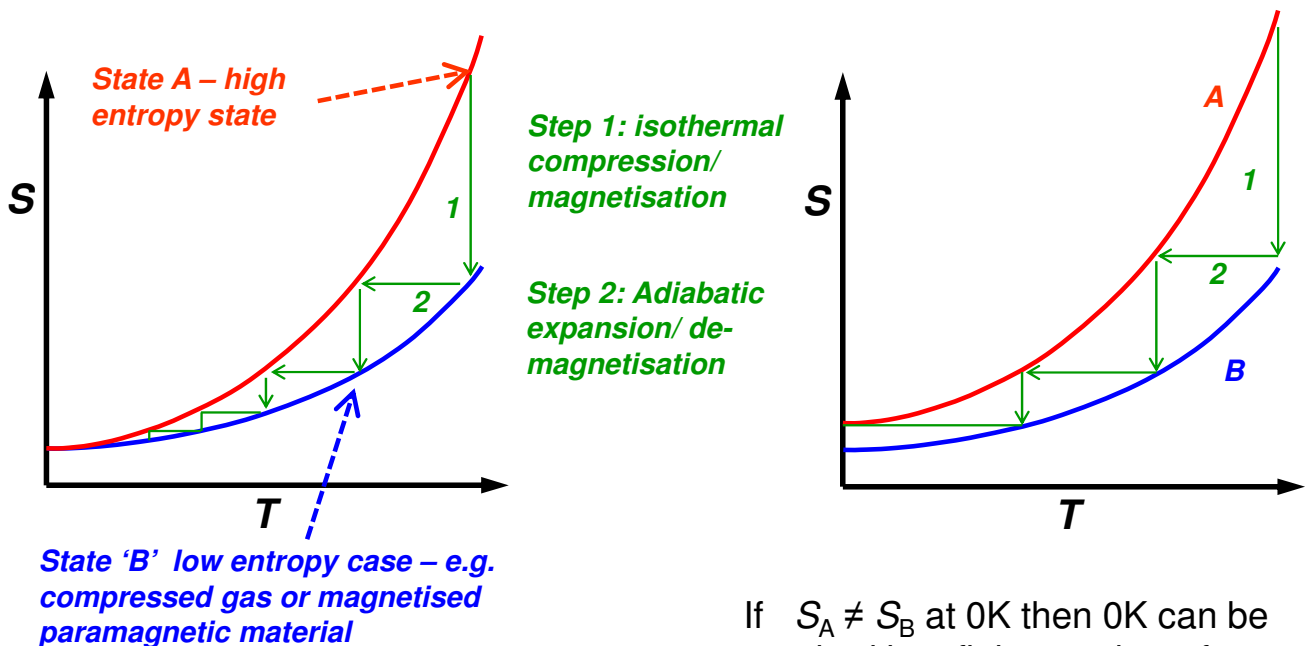
- All reversible processes can be broken down into a series of Carnot cycles, so without loss of generality we can just considering cooling steps that are related to Carnot cycles.
- To cool a substance at pressure P_A from temperature T_1 you just need two steps of the Carnot cycle. (1) Keep it in contact with a thermal reservoir at T_1 and compress it (i.e. do work on it so that heat flows out and its entropy drops) isothermally to a higher pressure P_B , and then disconnect it from the reservoir and allow it to expand adiabatically (i.e. at constant entropy) which will cause it to cool.
- At this point we already have the attainability of absolute zero scuppered : take the example of an ideal gas expansion, to reach zero temperature you would need an infinite expansion of the gas. More generally, in an adiabatic change the system does work against an external constraint, losing heat energy and cooling in the process, but the entropy stays the same. If the entropy is always zero at absolute zero, it must be positive for positive temperatures (heat capacity is always positive) – so starting at a non zero temperature means starting at finite entropy – which is unchanged in an adiabatic process, which therefore cannot reach absolute zero.

Multistage Cooling??

- Take a large quantity of 'Carnot cycle medium'
- Compress it isothermally- giving out heat and pushing it to a low entropy at constant temperature.
- Expand it adiabatically – it cools at constant entropy.
- Split into two parts –one large (gives you a reservoir at this lower temperature) and one small.
- Isothermally compress the smaller part, using the larger part as a reservoir to sink the heat.
- Adiabatically cool the smaller part – etc
- Note this can be generalised to any system on which you can do work at constant temperature/relax adiabatically – e.g. adiabatic demagnetisation – but as can be seen from the figure on the next overhead – if all entropies go to the same (zero) value you need an infinite number of steps.

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Multistage Cooling



If $S_A \neq S_B$ at 0K then 0K can be reached in a finite number of steps.

Actual case: 3rd law dictates both systems have same entropy at 0K, hence infinite number of steps needed to attain 0K.

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Chapter 6 - Summary

- Third Law: "**As $T \rightarrow 0$, the entropy goes to zero**"
- Empirically derived but has clear statistical/quantum basis: the system drops into a unique ground state as temperature drops to zero.
- Heat capacities $C_x \rightarrow 0$ as $T \rightarrow 0$, etc.
- Unattainability of Absolute Zero.