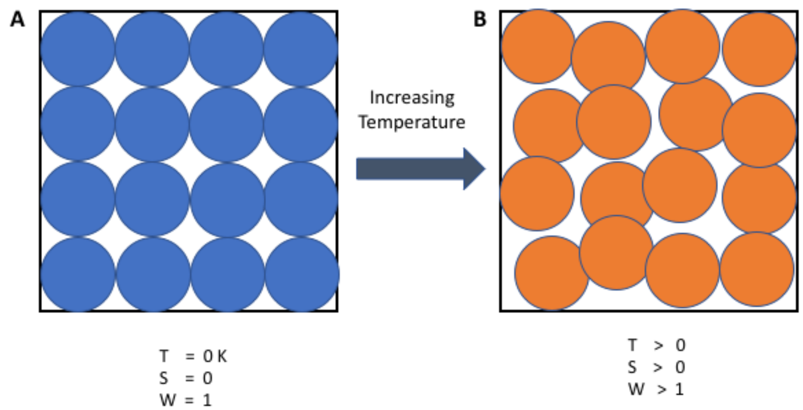
Lecture 18. *Third Law*

- More about Entropy
- Absolute value of entropy?
- How can we measure entropy?

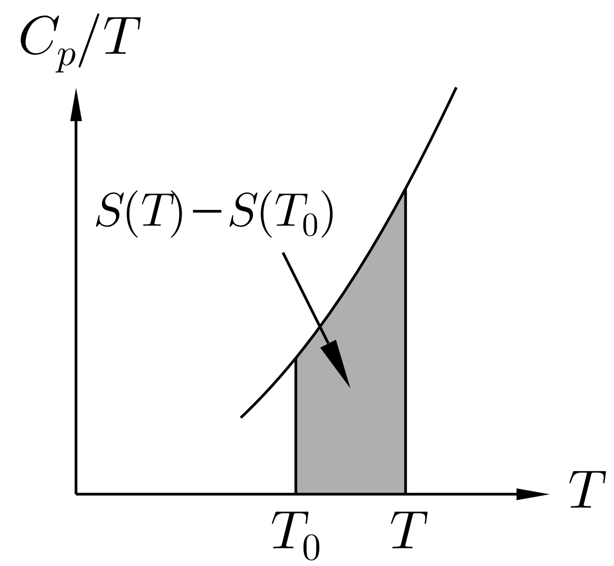


Wikipedia

Using heat capacity

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \quad \Rightarrow \quad S = \int \frac{C_p}{T}\mathrm{d}T$$

Definite integral: $S(T) = S(T_0) + \int_{T_0}^{T} \frac{C_p}{T}\mathrm{d}T$



We can only learn about change in entropy rather than entropy itself.

Third Law of Thermodynamics provides the reference entropy at T=0

Third Law (Nernst and Planck)

Change in enthalpy ΔH in a reaction and change in Gibbs function ΔG.

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

As T goes to zero, the change in Gibbs is the change in enthalpy.

This was confirmed experimentally. However, experiments shows that they approached each other asymptotically. Nernst postulated that $\Delta S \to 0$ when $T \to 0$.

Nernst's statement of the third law: Near absolute zero, all reactions in a system in internal equilibrium take place with no change in entropy.

Planck's statement of the third law: The entropy of all systems in internal equilibrium is the same at absolute zero, and may be taken to be zero.

Notes

Only true at internal equilibrium (for instance: not glass)

This is compatible with the statistical mechanics definition

Is the entropy really zero?

Imagine N spinless atoms in a perfect crystal. Their entropy should be zero. But if one considers the nucleus momentum's I and if it is $I > 0$ then, we have $2I + 1$ possible orientations for each nuclear spin. The entropy is thus not zero!

What is wrong? In an actual system, the components of the system must be able to exchange energy with each other. Nuclear spins do indeed feel a tiny but non-zero magnetic field due to the other momenta! We would need to go down a lot in T to get zero… or would we?

What about very weak interaction within the nucleus, etc?

We have many subsystems that are weakly coupled to each other.

Simon called those subsystems "**aspects**" and formulated the third law as:

Simon's statement of the third law

The contribution to the entropy of a system by each aspect of the system which is in internal thermodynamic equilibrium tends to zero as $T \to 0$

Consequences of the third law (1)

Heat capacities tend to zero as $T \to 0$

$$C = T\left(\frac{\partial S}{\partial T}\right) = \left(\frac{\partial S}{\partial \ln T}\right) \to 0$$

because as $T \to 0, \ln T \to -\infty$ and $S \to 0$. Hence $C \to 0$

This result disagrees with the classical prediction of $C = R/2$ per mole per degree of freedom.

Consequences of the third law (2)

Thermal expansion stops

since $S \to 0$ as $T \to 0$, we have for example that

$$\left(\frac{\partial S}{\partial p}\right)_T \to 0$$

as $T \to 0$, but by a Maxwell relation, this implies that

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \to 0$$

and hence the isobaric expansivity $\beta_p \to 0$

Consequences of the third law (3)

No gas remains ideal at T → 0

For an idea gas, we saw $C_p - C_V = R$ per mole.

However, as $T \to 0$, both C_p and C_V tend to zero, and this equation cannot be satisfied.

In addition, the expression for its entropy $\left(S = C_V \ln T + R \ln V + \text{ constant }\right)$ fails as well: As $T \to 0$, this equation yields $S \to -\infty$.

The ideal gas model does not work at low-T.

Of course, it is at low temperature that the weak interactions between gas molecules become more important.

Consequences of the third law (4)

Curie's Law breaks down

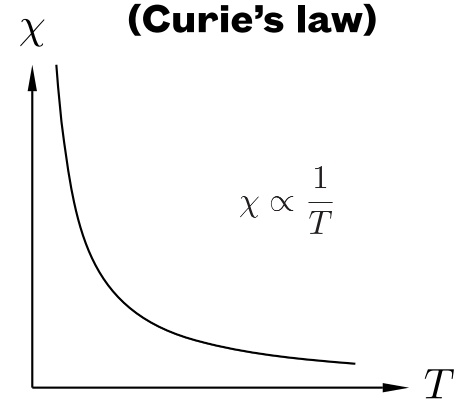
Curie's law: the susceptibility χ is proportional to $1/T$ and hence $\chi \to \infty$ as $T \to 0$. However, the third law implies that $(\partial S/\partial B)_T \to 0$ and hence

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial m}{\partial T}\right)_B = \frac{VB}{\mu_0}\left(\frac{\partial \chi}{\partial T}\right)_B$$

Must tend to zero but this disagrees with Curie's law

The issue is the independence between magnetic moments!

Magnetic susceptibility (Curie's law)



Susceptibility measures the infinitesimal response to infinitesimal applied field. When thermal fluctuations are removed at T=0, these become apparent.

The microscopic parts of a system can behave independently at high temperature, where the thermal energy $k_B T$ is much larger than any interaction energy.

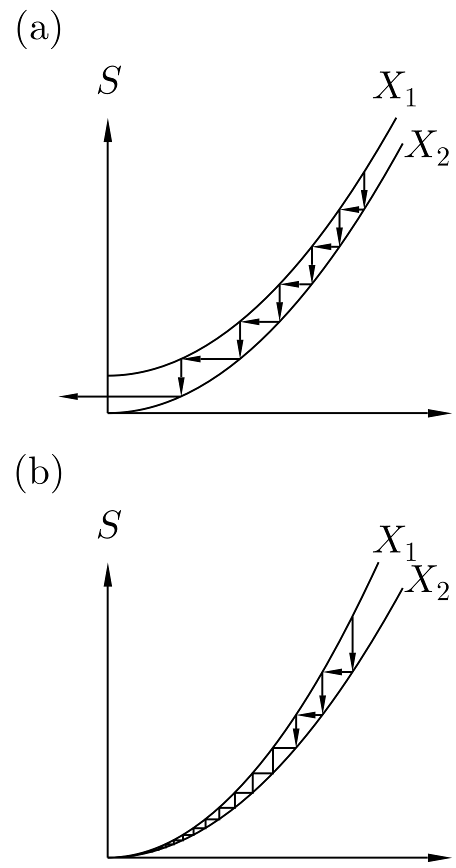
Consequences of the third law (5)

Unattainability of zero T

Cooling is produced by isothermal increases in X and adiabatic decreases in X.

If the third law did not hold, it would be possible to proceed according to Fig. A and cool all the way to absolute zero.

However, because of the third law, the situation is as in Fig. B and the number of steps needed to get to absolute zero becomes infinite.



X can be magnetic field

Carnot Engine

A Carnot engine operating between reservoirs has an efficiency $\eta = 1 - \left(T_\ell / T_\mathrm{h}\right)$

If $T_\ell \to 0$, the efficiency η tends to 1. If you operated this Carnot engine, you would then get perfect conversion of heat into work, **in violation of Kelvin's statement of the second law of thermodynamics.**

Is the unattainability of absolute zero (a version of the third law) is a simple consequence of the second law?

How can a Carnot engine operate between two reservoirs, one of which is at absolute zero. It is not clear how you can perform an isothermal process at absolute zero, because once a system is at absolute zero it is not possible to get it to change its thermodynamical state without warming it (heat capacity being zero!).

Thus the third law is a separate postulate which is independent of the second law.

The third law points to the fact that many of our "simple" thermodynamic models, such as the ideal gas equation and Curie's law of paramagnets, need substantial modification if they are to give correct predictions as $T \rightarrow 0$

Summary

- The third law of thermodynamics can be stated in various ways:
  - **Nernst**: Near absolute zero, all reactions in a system in internal equilibrium take place with no change in entropy.
  - **Planck**: The entropy of all systems in internal equilibrium is the same at absolute zero, and may be taken to be zero.
  - **Simon**: The contribution to the entropy of a system by each aspect of the system which is in internal thermodynamic equilibrium tends to zero as $T \to 0$
- Unattainability of $T = 0$:it is impossible to cool to $T = 0$ in finite number of steps.
- The third law implies that heat capacities and thermal expansivities tend to zero as $T \to 0$ Interactions between the constituents of a system become important as $T \to 0$, and this leads to the breakdown of the concept of an ideal gas and also the breakdown of Curie's law.