Third Law of Thermodynamics

- Thermodynamic entropy

$$\Delta S = S(T) - S(0) = \int_0^T \frac{C\,dT}{T}$$

- Statistical entropy

$$S = k_B \ln \Omega + S(0)$$

[Boltzmann, Gibbs]

Nernst heat theorem (1906)

In a chemical or physical transformation

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

Consequences:

(i) $C \to 0$ as $T \to 0$

(ii) $\Omega = 1$ at $T = 0$

Ground state is non-degenerate

Planck's statement (1911)

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

Simon's statement (1937)

The contribution to the entropy of a system by each aspect which is in internal thermodynamic equilibrium tends to zero at absolute zero.

"Aspect" $\equiv$ Degree of freedom

Experimental basis of Third Law

Equivalence of thermal and statistical entropies for gases

Thermal:

$$S(T) = \underbrace{\int_0^{T_m} \frac{C_s}{T} dT + \frac{L_m}{T_m}}_{\text{Solid}} + \underbrace{\int_{T_m}^{T_b} \frac{C_L}{T} dT + \frac{L_{vap}}{T_b}}_{\text{Liquid}} + \underbrace{\int_{T_b}^{T} \frac{C_{gas}}{T} dT}_{\text{gas}}$$

Statistical:

ideal gas of N identical particles at T

$$Z(N) = \frac{Z^N(1)}{N!} = \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2}$$

$$F = -k_B T \ln Z$$

$$S = -\left(\frac{\partial F}{\partial T} \right)_V$$

Calculated (statistical) and measured (calorimetric) entropies of gases.

Gas	Temperature (K)	Statistical ($J\,K^{-1}mol^{-1}$)	Calorimetric ($J\,K^{-1}mol^{-1}$)
Ar	87.3†	129.7	129.6
O_2	90.2†	170.9	170.9
N_2	77.3†	153.0	153.4
Cl_2	239.1†	216.5	216.6
HCl	188.0†	174.1	173.5
HD	298.1	144.3	144.7
CH_4	111.6†	153.8	153.4
C_2H_4	169.4†	198.9	198.9

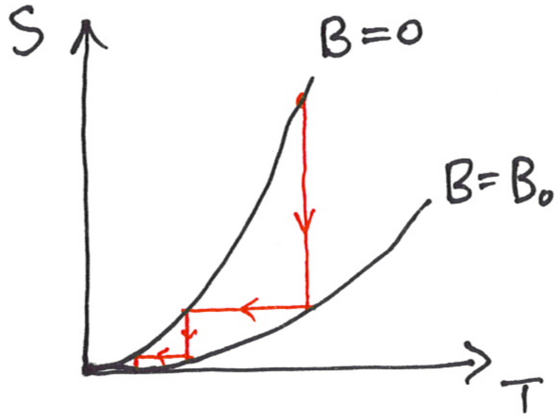
† boiling point

Data from J. Wilks, *The Third Law of Thermodynamics* (OUP, 1961).

Unattainability of absolute zero

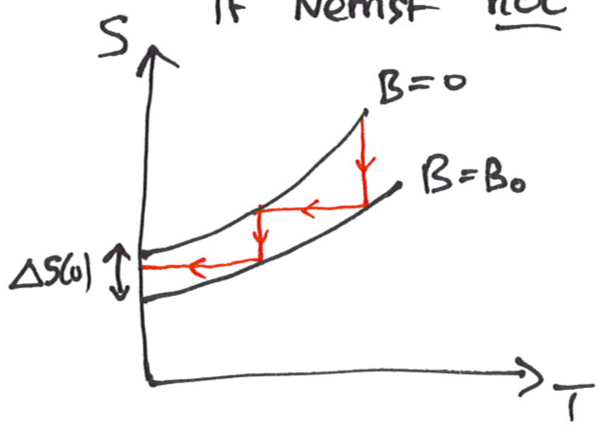
It is impossible to cool any substance to absolute zero in a finite number of steps

e.g. magnetic cooling



Never reaches T=0

If Nernst <u>not</u> true



<u>can</u> reach T = 0

NB. 3rd Law $\Rightarrow$ unattainability

BUT unattainability $\not\Rightarrow$ 3rd Law