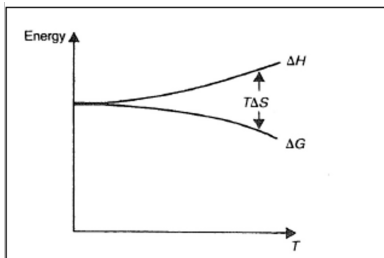


## Third Law Of Thermodynamics

- The Third Law defines the behaviour of entropy at absolute zero.

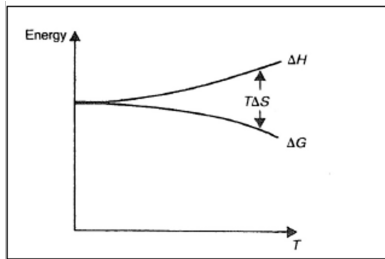
### The Nernst Heat Theorem

Any system undergoing a process between equilibrium states as a result of external influences, such as pressure, experiences a change in entropy. This change in entropy tends to zero as the temperature characterising the process tends to absolute zero.



- Nernst made experimental observations as summarised in the diagram.

## Third Law Of Thermodynamics



- noticed that for many chemical reactions, the change in enthalpy  $\Delta H$ , increased as  $T$  rose, while  $\Delta G$  was reduced. Asymptotically, (at zero  $T$ ) it appeared that they went to the same value, and with zero slope.
- $\Delta G = G_f - G_i = \Delta H - \Delta(TS) = H_f - H_i - T(S_f - S_i) = \Delta H - T \Delta S$
- Obviously  $\Delta H = \Delta G$  at  $T=0$ , but the curves only touch asymptotically if  $\Delta S \rightarrow 0$ .

- An alternative statement of the Third Law, attributed to Planck, refers to a perfect crystalline state.

### Planck

The entropy of all perfect crystals is the same at absolute zero, and may be taken to be zero.

- The key feature is that all perfect crystals would all have the same value of entropy at the absolute zero of the thermodynamic temperature  $T$ . That this value should be uniquely chosen is not just a matter of convenience. The choice  $S = 0$  at  $T = 0$  allows a strong link to be made between thermodynamics and statistical mechanics where the same assumption is made and supported by evidence from a very wide range of physics phenomena.

- All this leads naturally to a third statement of the Third Law.

### General

The contribution to the entropy from **each aspect** of a system which is in thermodynamic equilibrium disappears at absolute zero.

- It is usually helpful to be able to separate out the various contributions to entropy (which is an “extensive” variable – so various contributions can be added). For a crystal, contributions come from the arrangements of atoms (“configurational entropy”), from the orientations of atomic spins, or molecular units, from nuclear properties (“nuclear spin”) and from motion of all of these (eg lattice vibrations). Isenthalpic processes may involve entropy changes in individual components only the total is conserved.
- The validity of the Third Law, however it is stated, stems from its derivation from properties of substances in general and its successful use in describing the low temperature behaviour of a wide range of processes and parameters.

## Third Law - Consequences

- Vanishing Thermal expansion coefficient,  $\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = - \frac{1}{V} \left( \frac{\partial S}{\partial P} \right)_T$ . By the Nernst statement, as  $T$  approaches zero,  $\Delta S \rightarrow 0$ , and so  $\beta \rightarrow 0$ .
- Vanishing Heat capacity  $C_V = T \left( \frac{\partial S}{\partial T} \right)_V$ .
- Using  $\frac{d}{dT} \ln T = \frac{1}{T}$ , which implies  $d \ln T = \frac{dT}{T}$ , hence  $C_V = \left( \frac{\partial S}{\partial \ln T} \right)_V$ .
- As  $T \rightarrow 0$ ,  $\ln T \rightarrow -\infty$ . so for a given small change  $\Delta T$ ,  $\Delta S \rightarrow 0$  but  $\Delta(\ln T)$  may still be quite large.
- This means  $\frac{\Delta S}{\Delta \ln T} \rightarrow 0$ , and  $C_V \rightarrow 0$  as  $T \rightarrow 0$ . Same is true for  $C_P$
- Experimentally, for metals at low temperatures  $C_P = aT + bT^3$  where  $a$  and  $b$  are constants. The first term is associated with heat uptake by (or release from) the conduction electrons aspect, the second is associated with the lattice vibrations aspect.

Kinetic Theory of  
Gases

Thermodynamics

State Variables

Zeroth law of  
thermodynamics

Reversible and  
irreversible  
processes

First law of  
Thermodynamics

Second law of  
Thermodynamics

Entropy

Thermodynamic  
Potential

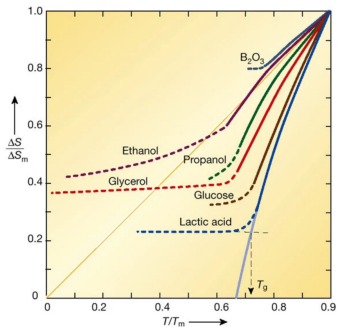
Third Law of  
Thermodynamics

Phase diagram

# Third Law Of Thermodynamics

## Another statement of the Third Law

It is impossible to reach absolute zero using a finite number of processes.



Data derived from specific heat measurements for various supercooled liquids - entropy cannot be reduced even if cooled to 0K !

## Third Law Of Thermodynamics

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Phase diagram

- **Kauzman's Paradox:** Glasses look as if their entropy cannot be reduced to zero even if they can be cooled to 0 K - Nature 410, 259-267, 2001. There are many ways to arrange the atoms to still be a glass. A glass does not have the long range order of a crystalline substance. Like a liquid – glass can flow (though extremely slowly) with structure gradually crystallising. So **glasses are not equilibrium systems!**