Measurement of entropy

- entropy – property of a thermodynamic system. quantifies the number of microstates Ω (microscopic configurations) which are consistant with the macroscopic properties of the system (volume, temp, pressure) $[S] = JK^{-1}$

  $S = k_B \ln \Omega$ k_B – boltzmann constant

  for ideal gas $\Omega \propto N$ N – number of molecules

- measured in 2 ways: calorimetric procedure and theoretically
- calorimetric measurement of entropy
  ↳ we start by measuring its heat capacity C at different temperatures then using the below equation

  molar heat capacity C_m

$$S_m(T) = S_m(0) + \int_0^{T_f} \frac{C_{p,m}(s,T')}{T'}dT' + \frac{\Delta H_{fus}}{T_f}$$

heating solid to melting point

entropy of fusion solid → liquid

$$+ \int_{T_f}^{T_b} \frac{C_{p,m}(l,T')}{T'}dT' + \frac{\Delta H_{vap}}{T_b}$$

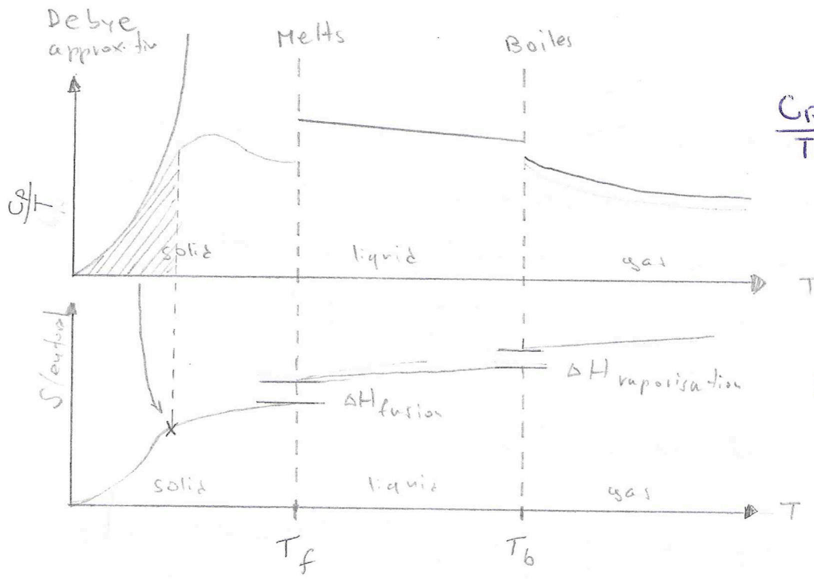
heating liquid to boiling point

entropy of vaporisation liquid → gas

$$+ \int_{T_b}^{T} \frac{C_{p,m}(g,T')}{T'}dT'$$

heating gas to desired T

- T' is the variable of integration not to be confused with T the desired temp
- $C_{p,m}$ is the experimentally determined heat capacity at different T'
- normally we fit a polynomial to the obtained results and then integrate the polynomial analytically
- standard molar entropy $S_m^{\ominus}(T) = \frac{S^{\ominus}(T)}{n}$
- it is difficult to determine heat capacity near $T = 0$ kelvin but theoretically we can assume capacity of non-metallic solid C is proportional to T^3 $C \propto T^3$ this is called the Debye extrapolation (Debye T^3 law) $C = \underbrace{k}_{\text{constant}} T^3$

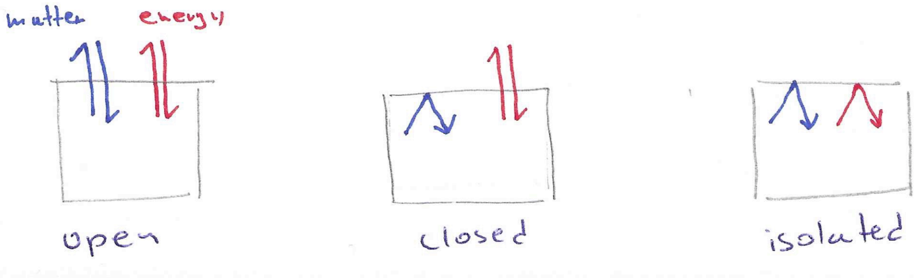


$\frac{C_p}{T}$ over T

S over T

the area on $\frac{C_p}{T}$ graph against T up to a certain point is the entropy of the substance at the point T

- 0^{th} law of thermodynamics
  - ↳ defines thermal equilibrium + basis of definition of temp
  - ↳ if system 1 and 2 are both in thermal equilibrium with system 3 then systems 1 and 2 are also in thermal equilibrium with eachother
- 1^{st} law of Thermodynamics
  - ↳ heat and work are equivalent ways of changing the internal energy of a system
  - ↳ if heat is put into a system its internal energy has to ↑ so E conserved
- 2^{nd} law of Thermodynamics
  - ↳ heat doesnt flow spontaniously from a cold body to a hotter body (down ΔT)
  - ↳ no process is possible in which the only result is absorption of heat and its complete conversion to work.
- 3^{rd} law of Thermodynamics
  - ↳ as systems temperature $T \rightarrow 0$ approaches absolute 0K the entropy approaches a constant value typically close to 0
  - ↳ entropy of perfect crystal lattice at T = 0 kelvin $S = 0$
  - ↳ exception are non-crystaline solids - glass
- Nernst heat theorem - entropy of regular array of molecules at T=0 is always $0\,JK^{-1}$



(think of it as rather the is voting to exchange the E of matter with)