Lecture-9

Contents

- Measurement of Entropies
  - Calorimetric Measurement of Entropy
  - Calculating the entropy at low temperatures

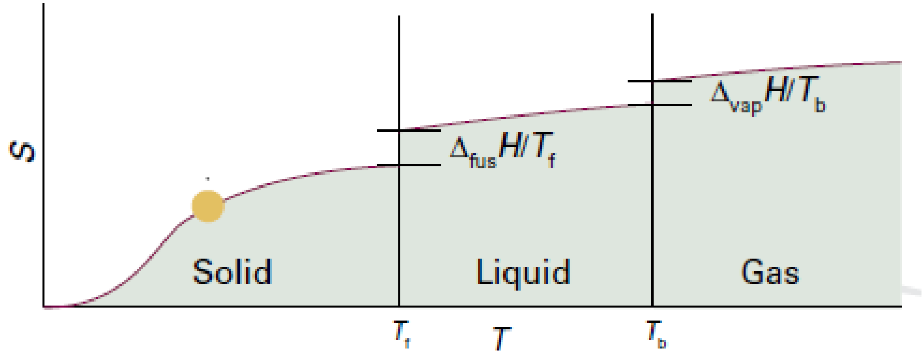
Measurement of Entropy

Entropy of a substance can be determined in two ways:

1. **Calorimetric measurement:** By measuring the heat required to raise the temperature of a sample from $T = 0$ to the temperature of interest.
2. **Statistical Analysis:** Calculated parameters or spectroscopic data are used to calculate the entropy by using Boltzmann's statistical definition.

Calorimetric Measurement of Entropy

Two equations are used in calorimetric measurement of entropy:



1. Entropy and temperature

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_p(T)}{T} \mathrm{d}T$$

2. Entropy of phase transition

$$\Delta S(T_{trs}) = \frac{\Delta_{trs}H(T_{trs})}{T_{trs}}$$

Entropy is equal to the corresponding temperature, plus the entropy of each phase transition

The entropy of a system at a temperature *T* is related to its entropy at *T* = 0 and its heat capacity C_p at different temperatures.

If a substance melts at T_f and boils at T_b, then its molar entropy at a particular temperature T above its boiling temperature is given by

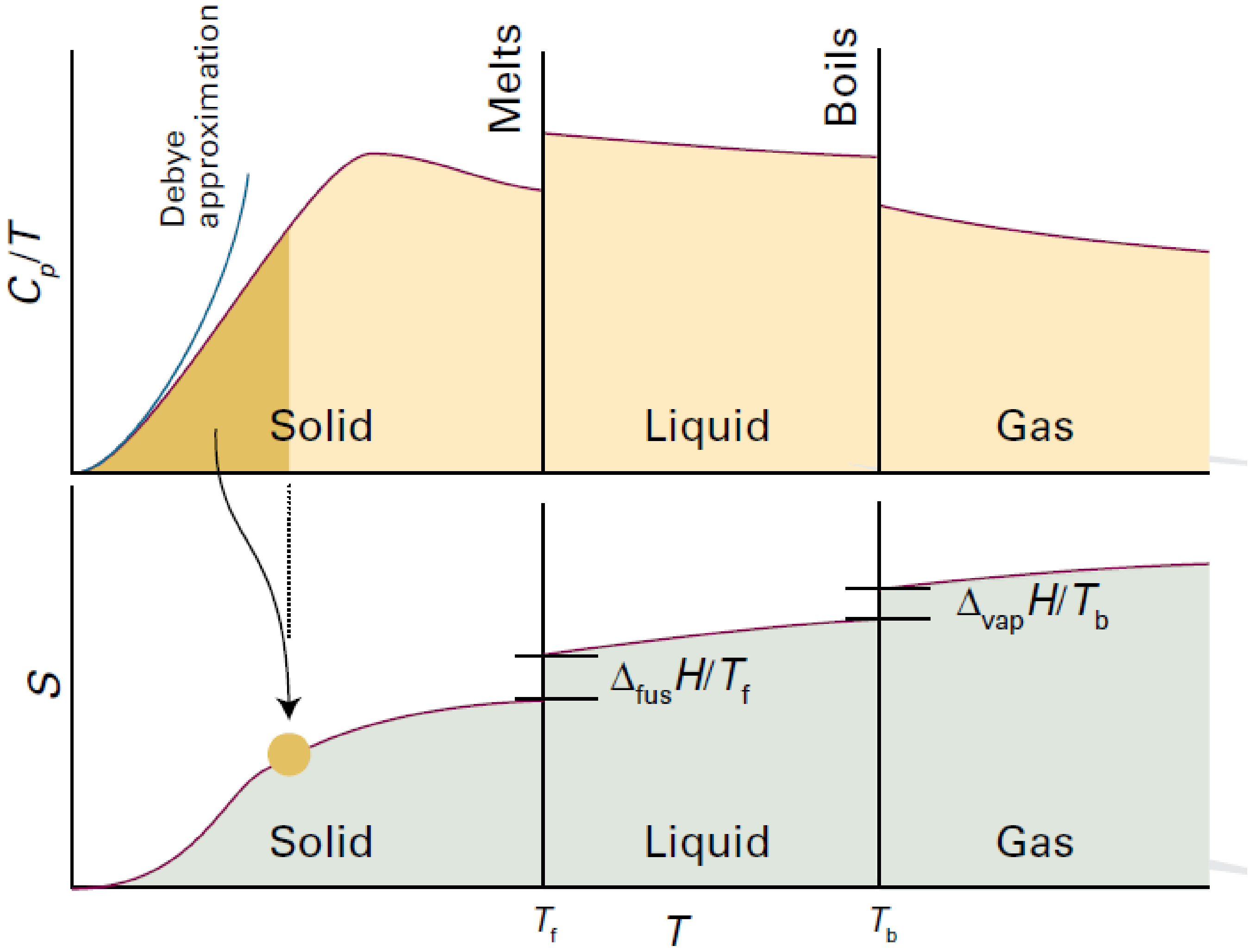
$$S_{\mathrm{m}}(T) = S_{\mathrm{m}}(0) + \overbrace{\int_0^{T_{\mathrm{f}}} \frac{C_{p,\mathrm{m}}(\mathrm{s},T')}{T'}\,\mathrm{d}T'}^{\text{Heat solid to its melting point}} + \overbrace{\frac{\Delta_{\mathrm{fus}}H}{T_{\mathrm{f}}}}^{\text{Entropy of fusion}}$$

The variable of integration has been changed to *T′* to avoid confusion with the temperature of interest, *T*.

$S_m(0)$ = residual molar entropy

$$+ \overbrace{\int_{T_{\mathrm{f}}}^{T_{\mathrm{b}}} \frac{C_{p,\mathrm{m}}(\mathrm{l},T')}{T'}\,\mathrm{d}T'}^{\text{Heat liquid to its boiling point}} + \overbrace{\frac{\Delta_{\mathrm{vap}}H}{T_{\mathrm{b}}}}^{\text{Entropy of vaporization}} + \overbrace{\int_{T_{\mathrm{b}}}^{T} \frac{C_{p,\mathrm{m}}(\mathrm{g},T')}{T'}\,\mathrm{d}T'}^{\text{Heat vapour to the final temperature}}$$

- All the properties required, except $S_\mathrm{m}(0)$, can be measured calorimetrically.
- The integrals can be evaluated either graphically or by fitting a polynomial to the data and integrating the polynomial analytically.
- The area under the curve of $C_{p,\mathrm{m}}(T)/T$ against T is the integral required. Provided all measurements are made at 1 bar on a pure material, the final value is the **standard entropy** and division by the amount of substance, n, gives the **standard molar entropy**.
- Because $\mathrm{d}T/T = \mathrm{d}\ln T$, an alternative procedure is to evaluate the area under a plot of $C_{p,\mathrm{m}}(T)$ against $\ln T$.



The variation of C_p/T with the temperature for a sample is used to evaluate the entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition encountered between $T = 0$ and the temperature of interest.

Calculating the entropy at low temperatures

- It is difficult to determine entropy near $T = 0$.
- There are good theoretical grounds for assuming that the heat capacity of a non-metallic solid is proportional to T^3 (the Debye T^3 law).
- In this method, C_p is measured down to as low a temperature as possible and a curve of the form aT^3 is fitted to the data.
- The fit determines the value of *a*, and the expression $C_{p,m}(\mathrm{T}) = aT^3$ is then assumed to be valid down to $T = 0$.

The molar constant-pressure heat capacity of a certain non-metallic solid at 4.2 K is 0.43 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$. What is its molar entropy at that temperature?

Answer

Because the temperature is so low, you can assume that the heat capacity varies with temperature according to $C_{p,\mathrm{m}}(T) = aT^3$.

The integration required is

$$S_\mathrm{m}(T) = S_\mathrm{m}(0) + \int_0^T \frac{aT'^{\,3}}{T'}\,\mathrm{d}T' = S_\mathrm{m}(0) + a\overbrace{\int_0^T T'^{\,2}\,\mathrm{d}T'}$$

$$= S_\mathrm{m}(0) + \tfrac{1}{3}aT^3 = S_\mathrm{m}(0) + \tfrac{1}{3}C_{p,\mathrm{m}}(T)$$

From which it follows that

$$S_\mathrm{m}(4.2\,\mathrm{K}) = S_\mathrm{m}(0) + 0.14\,\mathrm{J\,K^{-1}\,mol^{-1}}$$