Statistical Molecular Thermodynamics

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Video 7.3

Standard Entropy

Third-Law Entropy Values

$$S(T) = \int_0^T \frac{C_P(T')dT'}{T'}$$

Valid in so far as the third law stipulates that $S(0) = 0$

For this to be true, there must be no phase transition between 0 and T. For phase transitions (e.g., melting):

$$\Delta_{trs}S = \frac{q_{rev}}{T_{trs}}$$

For a phase transition that takes place at fixed P

$$\Rightarrow \quad \Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$$

$$S(T) = \int_0^{T_{fus}} \frac{C_P^s(T)dT}{T} + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{C_P^l(T)dT}{T} + \frac{\Delta_{vap}H}{T_{vap}} + \int_{T_{vap}}^{T} \frac{C_P^g(T')dT'}{T'}$$

Low Temperature Behavior of C_P

For nonmetallic solids the Debye T^3 law is observed:

$$\overline{C}_P(T) = \frac{12\pi^4}{5} R \left(\frac{T}{\Theta_D} \right)^3 \qquad 0 < T \leq T_{low}$$

The "Debye temperature"

Debye derived this relationship through consideration of quantized phonon energy levels in solids

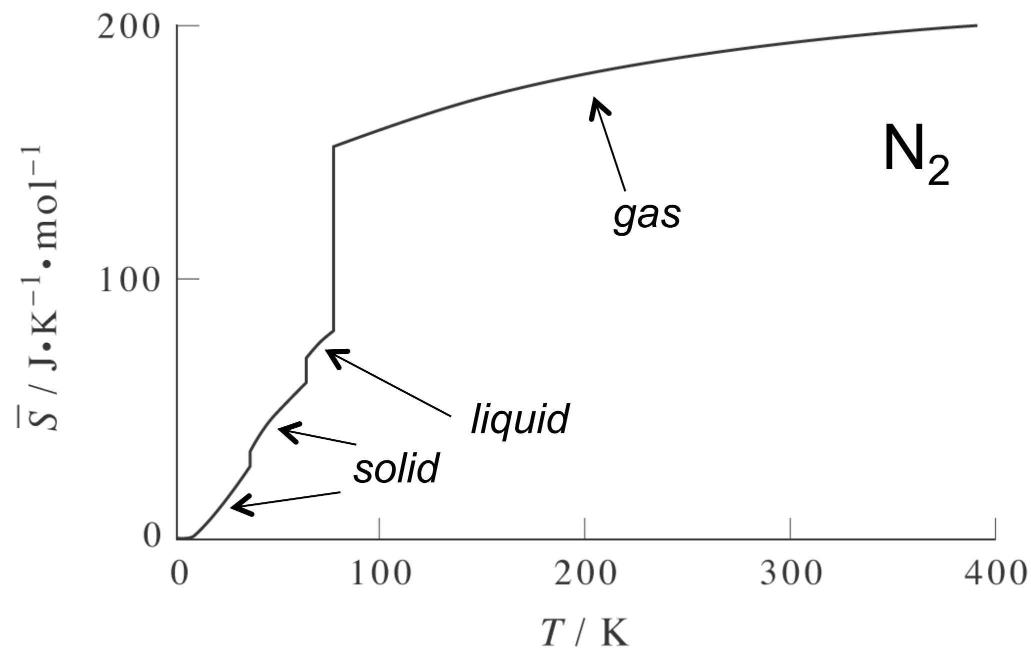
The lowest temperature contribution to entropy is thus:

$$\overline{S}(T) = \int_0^T \frac{\overline{C}_P(T')dT'}{T'} = \frac{12\pi^4 R}{5\Theta_D{}^3} \int_0^T T'^2 dT' = \frac{12\pi^4 RT^3}{5\Theta_D{}^3 3} = \frac{\overline{C}_P(T)}{3}$$

very convenient as it obviates need to measure $C_P(T)$ all the way down to $0\ K$

Calorimetric Entropy Determination

Process	S, J•K^{-1}•mol^{-1}
0.00 – 10.00 K	2.05
10.00 – 35.61 K	25.79
solid-solid phase transition	6.43
35.61 – 63.15 K	23.41
solid-liquid phase transition	11.20
63.15 – 77.36 K	11.46
liquid-gas phase transition	72.00
77.36 – 298.15 K	39.25
non-ideality	0.02
Total:	191.61



Values of entropies for gases given in the literature are *standard entropies*. These are by convention corrected for the non-ideality of real gases at 1 bar.