STATISTICAL MOLECULAR THERMODYNAMICS

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Video 7.4

Entropy from the Partition Function

ENTROPY AND THE PARTITION FUNCTION

Recalling:

$$S = k_{\mathrm{B}} \ln Q + k_{\mathrm{B}} T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

From the definition of *Q* we may write instead:

$$S = k_{\mathrm{B}} \ln \sum_j e^{-E_j / k_{\mathrm{B}} T} + \frac{1}{T} \frac{\sum_j E_j e^{-E_j / k_{\mathrm{B}} T}}{\sum_j e^{-E_j / k_{\mathrm{B}} T}}$$

How does *S* behave as the temperature goes to zero?

Is the statistical thermodynamic definition of entropy consistent with the Third Law of Thermodynamics?

THE LOW T PARTITION FUNCTION

$$Q = \sum_j e^{-E_j / k_\mathrm{B} T}$$

Working with levels, instead of states, we have:

$$\begin{aligned} Q &= \sum_n g_n e^{-E_n / k_\mathrm{B} T} \\ &= e^{-E_0 / k_\mathrm{B} T} \sum_n g_n e^{-(E_n - E_0) / k_\mathrm{B} T} \end{aligned}$$

As T goes to zero, the argument of the exponential inside the summation goes to $-\infty$ for all levels other than $n = 0$, so

$$\lim_{T \to 0} Q = g_0 e^{-E_0 / k_\mathrm{B} T}$$

LOW T BEHAVIOR OF ENTROPY

Using:

$$\lim_{T\to 0} Q = g_0 e^{-E_0/k_\mathrm{B}T}$$

in

$$S = k_\mathrm{B} \ln \sum_j e^{-E_j/k_\mathrm{B}T} + \frac{1}{T}\frac{\sum_j E_j e^{-E_j/k_\mathrm{B}T}}{\sum_j e^{-E_j/k_\mathrm{B}T}}$$

gives:

$$S = k_\mathrm{B} \ln g_0 e^{-E_0/k_\mathrm{B}T} + \frac{1}{T}\frac{g_0 E_0 e^{-E_0/k_\mathrm{B}T}}{g_0 e^{-E_0/k_\mathrm{B}T}}$$

$$= k_\mathrm{B} \ln g_0 - \frac{E_0}{T} + \frac{E_0}{T} = \boxed{k_\mathrm{B} \ln g_0}$$

So, as T goes to zero, the entropy determined from the partition function also goes to zero, to within ground-state degeneracy

FIRST PRINCIPLES COMPUTATION OF S

$$S = k_{\mathrm{B}} \ln Q + k_{\mathrm{B}} T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \qquad Q(N,V,T) = \frac{\left[q(V,T) \right]^N}{N!}$$

$$\underbrace{q(V,T) = \left(\frac{2\pi \left(m_1 + m_2 \right) k_{\mathrm{B}} T}{h^2} \right)^{3/2} V \cdot \frac{T}{\sigma \Theta_{\mathrm{rot}}} \cdot \frac{e^{-\Theta_{\mathrm{vib}}/2T}}{1 - e^{-\Theta_{\mathrm{vib}}/T}} \cdot g_1 e^{D_e / k_{\mathrm{B}} T}}_{\text{partition function for a diatomic ideal gas (cf. Video 4.6)}}$$

$\Downarrow$ Great math exercise!

$$\frac{\overline{S}}{R} = \ln \left\{ \left[\frac{2\pi \left(m_1 + m_2 \right) k_{\mathrm{B}} T}{h^2} \right]^{3/2} \frac{\overline{V} e^{5/2}}{N_{\mathrm{A}}} \right\} + \ln \frac{Te}{\sigma \Theta_{\mathrm{rot}}} - \ln \left(1 - e^{-\Theta_{\mathrm{vib}}/T} \right) + \frac{\Theta_{\mathrm{vib}}/T}{e^{\Theta_{\mathrm{vib}}/T} - 1} + \ln g_1$$

EXAMPLE FOR NITROGEN

$$\frac{\bar{S}}{R} = \ln\underbrace{\left\{\left[\frac{2\pi\left(m_1+m_2\right)k_{\mathrm{B}}T}{h^2}\right]^{3/2}\frac{\bar{V}e^{5/2}}{N_{\mathrm{A}}}\right\}}_{\text{trans}} + \underbrace{\ln\frac{Te}{\sigma\Theta_{\mathrm{rot}}}}_{\text{rot}} \underbrace{- \ln\left(1-e^{-\Theta_{\mathrm{vib}}/T}\right) + \frac{\Theta_{\mathrm{vib}}/T}{e^{\Theta_{\mathrm{vib}}/T}-1}}_{\text{vib}} + \underbrace{\ln g_1}_{\text{elec}}$$

For N_2:

$m_1 + m_2 \sim 28\text{ amu}$

$\sigma = 2$

$\Theta_{rot} = 2.88\text{ K}$

$\Theta_{vib} = 3374\text{ K}$

$g_1 = 1$

Using data for N_2 at 298.15 K and 1 bar:

$$S^\circ = S^\circ_{trans} + S^\circ_{rot} + S^\circ_{vib} + S^\circ_{elec}$$

$$S^\circ = \left(150.4 + 41.13 + 1.15\times10^{-3} + 0\right)\ \mathrm{J\bullet K^{-1}\bullet mol^{-1}}$$

$$S^\circ = 191.5\ \mathrm{J\bullet K^{-1}\bullet mol^{-1}}$$

Cf. Video 7.3, Expt = $191.6\ \mathrm{J{\bullet}K^{-1}{\bullet}mol^{-1}}$ Quantitative agreement!

And, from the above analysis, we know *where* the entropy is.