

5.4: Specific Heat of a Hetero-nuclear Diatomic Ideal Gas

The classical partition function is

$$Z = \frac{1}{N!} \left[\frac{V}{\lambda^3(T)} \frac{1}{h^2} \int_0^\pi d\theta \int_0^{2\pi} d\varphi \int_{-\infty}^{+\infty} d\ell_\theta \int_{-\infty}^{+\infty} d\ell_\varphi e^{-\beta(\ell_\theta^2 + \ell_\varphi^2)/2I} \right]^N. \quad (5.4.1)$$

Let's make sure we have the quantum mechanics of one molecule straight before we jump into treating 6.02×10^{23} molecules: First of all, we consider *hetero*-nuclear rather than homo-nuclear diatomic molecules (such as CO or HCl rather than H₂ or N₂) because in the latter there are additional issues due to the Pauli principle. Let's just avoid these issues on our first encounter. The quantal eigenvalues are

$$\epsilon_{\text{rot}} = \ell(\ell+1) \frac{\hbar^2}{2I} \quad \ell = 0, 1, 2, \dots \quad (5.4.2)$$

with

$$\text{degeneracy}_\ell = 2\ell + 1. \quad (5.4.3)$$

Thus the quantal “characteristic temperature” θ (or Θ_{rot}) is

$$k_B \theta \equiv \epsilon_1 - \epsilon_0 = \frac{\hbar^2}{I}. \quad (5.4.4)$$

And, finally, the quantal partition function is

$$Z = \frac{1}{N!} \left[\frac{V}{\lambda^3(T)} \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\beta \ell(\ell+1) \hbar^2 / 2I} \right]^N. \quad (5.4.5)$$

It saves a lot of writing to define the “rotational partition function”

$$\zeta(T) \equiv \zeta^{\text{rot}}(T) \equiv \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\beta \ell(\ell+1) \hbar^2 / 2I} = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\ell(\ell+1) \theta / 2T}. \quad (5.4.6)$$

The expression on the far right is the one that I like to use. . . instead of having a lot of variables like T , \hbar , and I floating around just waiting to get misplaced, everything is neatly packaged into the ratio θ/T , which is obviously dimensionless.

Now, for *any* partition function of the form

$$Z = \frac{1}{N!} \left[\frac{V}{\lambda^3(T)} \zeta(T) \right]^N = Z_{\text{mono}} \zeta^N(T). \quad (5.4.7)$$

We have

$$F = -k_B T \ln Z = \underbrace{-k_B T \ln Z_{\text{mono}}}_{F_{\text{mono}}} - \underbrace{k_B T N \ln \zeta}_{N f^{\text{rot}}} \quad (5.4.8)$$

and

$$e^{\text{rot}} = \frac{\partial (f^{\text{rot}}/T)}{\partial (1/T)} = -\frac{\partial \ln \zeta}{\partial \beta} \quad c_V^{\text{rot}} = \frac{\partial e^{\text{rot}}}{\partial T}. \quad (5.4.9)$$

Because the rotational partition function depends on temperature only through the combination θ/T , it makes sense to use that variable for derivatives:

$$e^{\text{rot}} = \frac{\partial (f^{\text{rot}}/T)}{\partial (1/T)} = \frac{\partial (-k_B T \ln \zeta / T)}{\partial (1/T)} = -k_B \frac{\partial \ln \zeta}{\partial (1/T)} = -k_B \theta \frac{\partial \ln \zeta}{\partial (\theta/T)} \quad (5.4.10)$$

and

$$c_V^{\text{rot}} = \frac{\partial e^{\text{rot}}}{\partial T} = \frac{\partial e^{\text{rot}}}{\partial(\theta/T)} \frac{\partial(\theta/T)}{\partial T} = -\frac{\theta}{T^2} \frac{\partial e^{\text{rot}}}{\partial(\theta/T)}. \quad (5.4.11)$$

Now back to the evaluation of $\zeta(T)$. It is quite easy to prove that the infinite sum for $\zeta(T)$ converges. You will then be tempted to find an expression for $\zeta(T)$ in terms of well-known functions like polynomials or exponentials. If you try this, you will not find any simple expression. Instead of manipulating $\zeta(T)$ into some combination of familiar functions, we will have to become familiar with it on our own. It can be evaluated and plotted on a computer just by adding up a finite number of terms in the defining infinite sum. But doing so is not the most productive way to approach an understanding of this function. . . given a plot of $\zeta(T)$, how would you find the specific heat due to rotation? A better way to approach the problem is to find how the partition function $\zeta(T)$ (and hence the specific heat $c_V^{\text{rot}}(T)$) behaves at low and high temperatures.

At low temperatures, we expand in terms of the small variable $e^{-\theta/T}$ to find

$$\begin{aligned} \zeta(T) &= 1 + 3e^{-\theta/T} + 5e^{-3\theta/T} + 7e^{-6\theta/T} + \dots \\ &= 1 + 3e^{-\theta/T} + 5e^{-3\theta/T} + \mathcal{O}(e^{-6\theta/T}) \end{aligned}$$

The notation $\mathcal{O}(x^N)$ is read “terms of order x^N ”. (See the box on page 129.) Now for small variables the logarithm is

$$\ln(1 + \epsilon) = \epsilon - \frac{1}{2}\epsilon^2 + \frac{1}{3}\epsilon^3 - \frac{1}{4}\epsilon^4 + \mathcal{O}(\epsilon^5) \quad (5.4.12)$$

whence

$$\begin{aligned} \ln \zeta(T) &= 3e^{-\theta/T} + 5e^{-3\theta/T} + \mathcal{O}(e^{-6\theta/T}) \\ &\quad - \frac{1}{2} \left[3e^{-\theta/T} + 5e^{-3\theta/T} + \mathcal{O}(e^{-6\theta/T}) \right]^2 \\ &\quad + \frac{1}{3} \left[3e^{-\theta/T} + 5e^{-3\theta/T} + \mathcal{O}(e^{-6\theta/T}) \right]^3 \\ &\quad + \mathcal{O}(e^{-4\theta/T}) \\ &= 3e^{-\theta/T} + 5e^{-3\theta/T} + \mathcal{O}(e^{-6\theta/T}) \\ &\quad - \frac{1}{2} \left[9e^{-2\theta/T} + 30e^{-4\theta/T} + \mathcal{O}(e^{-6\theta/T}) \right] \\ &\quad + \frac{1}{3} \left[27e^{-3\theta/T} + 135e^{-5\theta/T} + \mathcal{O}(e^{-6\theta/T}) \right] \\ &\quad + \mathcal{O}(e^{-4\theta/T}) \\ &= 3e^{-\theta/T} - \frac{9}{2}e^{-2\theta/T} + 14e^{-3\theta/T} + \mathcal{O}(e^{-4\theta/T}) \end{aligned} \quad (5.4.13)$$

Note that in going from equation (5.67) to equation (5.68) it would have been impossible to make sure that all of the several expansions were kept to equivalent orders of accuracy had we used $+ \dots$ rather than the $\text{\textcolor{red}{matcal}}\mathcal{O}$ notation.

Now it is easy to use equations (5.62) and (5.63) to find

$$e^{\text{rot}} = -k_B \theta \left[-3e^{-\theta/T} - 9e^{-2\theta/T} - 42e^{-3\theta/T} + \mathcal{O}(e^{-4\theta/T}) \right] \quad (5.4.14)$$

and

$$c^{\text{rot}} = k_B \left(\frac{\theta}{T} \right)^2 \left[3e^{-\theta/T} - 18e^{-2\theta/T} + 126e^{-3\theta/T} + \mathcal{O}(e^{-4\theta/T}) \right] \quad (5.4.15)$$

(Note that if we had used equations (5.61) instead, it would have been a lot more work.) The specific heat vanishes at zero temperature, and it increases *exponentially* slowly with increasing temperature. This is a very slow growth indeed. . . not only is the slope zero, but the second derivative is zero, the third derivative is zero, indeed *all* orders of derivative vanish at the origin.

What about high temperatures? We have discussed the fact that at high temperatures the rotational specific heat will approach the classical equipartition value of k_B , but *how* will it approach the limiting value? In other words, what are the deviations from the

high temperature limit? We can answer these questions by approximating the sum by an integral. The *Euler-MacLaurin formula* states that if $f(x) \rightarrow 0$, $f'(x) \rightarrow 0$, $f''(x) \rightarrow 0$, etc. as $x \rightarrow \infty$, then

$$\sum_{\ell=0}^{\infty} f(\ell) \approx \int_0^{\infty} f(x) dx + \frac{1}{2} f(0) - \frac{1}{12} f'(0) + \frac{1}{720} f'''(0) - \frac{1}{30240} f^{(5)}(0) + \dots \quad (5.4.16)$$

In our case,

$$f(x) = (2x + 1)e^{-x(x+1)\theta/2T}, \quad (5.4.17)$$

so

$$\int_0^{\infty} f(x) dx = 2 \frac{T}{\theta} \quad (5.4.18)$$

$$f(0) = 1$$

$$f'(0) = 2 - \frac{\theta}{2T}$$

$$f'''(0) = -6 \frac{\theta}{T} + \mathcal{O}\left(\frac{\theta}{T}\right)^2$$

$$f^{(5)}(0) = \mathcal{O}\left(\frac{\theta}{T}\right)^2$$

Thus we have

$$\zeta(T) \approx 2 \frac{T}{\theta} + \frac{1}{3} + \frac{1}{30} \frac{\theta}{T} + \mathcal{O}\left(\frac{\theta}{T}\right)^2 \quad (5.4.19)$$

$$\ln \zeta(T) \approx -\ln \frac{\theta}{2T} + \frac{1}{6} \frac{\theta}{T} + \frac{1}{360} \left(\frac{\theta}{T}\right)^2 + \mathcal{O}\left(\frac{\theta}{T}\right)^3 \quad (5.4.20)$$

$$e^{\text{rot}} \approx -k_B \theta \left[-\frac{T}{\theta} + \frac{1}{6} + \frac{1}{180} \frac{\theta}{T} + \mathcal{O}\left(\frac{\theta}{T}\right)^2 \right] \quad (5.4.21)$$

$$c_V^{\text{rot}} \approx k_B \left[1 + \frac{1}{180} \left(\frac{\theta}{T}\right)^2 + \mathcal{O}\left(\frac{\theta}{T}\right)^3 \right] \quad (5.4.22)$$

For high temperatures the specific heat is nearly equal to its classical value, and the quantity grows slightly larger as the temperature decreases.

Note: The \approx sign in the above formulas represents “asymptotic equality”. The infinite series on the right does not necessarily converge, and even if it does then it might not converge to the quantity on the left. However a finite truncation of the sum can be a good approximation for the quantity on the left, and that approximation grows better and better with increasing temperature (i.e. smaller values of θ/T).

This page titled [5.4: Specific Heat of a Hetero-nuclear Diatomic Ideal Gas](#) is shared under a [CC BY-SA](#) license and was authored, remixed, and/or curated by [Daniel F. Styer](#).