Quiz 8, Chemistry 481, 15 Nov 2019

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Possibly useful relations:

$k_B = 1.3807 \times 10^{-23}$ J·K^{-1}; R (molar gas constant) $= 8.314$ J·K^{-1}·mol^{-1}

$\ln(1+x) = x - x^2/2 + \ldots$

$(1+x)^{-1} = 1 - x + x^2 + \ldots$

1. A three-level system has energy levels $-\varepsilon$, 0, and and $+\varepsilon$, where ε is a positive number. There are no degeneracies. In terms of the variable $x = \exp(-\varepsilon\beta) = \exp(-\varepsilon/k_BT)$ the partition function and average energy are given by

$$q = 1/x + 1 + x \text{ and } \langle E\rangle = \frac{x^2-1}{1+x+x^2}\varepsilon$$

   a. What is the high temperature limit of the entropy? (3 pts) We know that $S = \langle E\rangle/T + k\ln q$. At high temperature $x \to 1$ and the $\langle E\rangle/T$ term goes to zero, so $\lim_{T\to\infty} S = k\lim_{x\to 1}\ln q = k\ln 3$.

   You could also say that at high temperature $\Omega = 3$, so that $S = k\ln\Omega = k\ln 3$

   b. Determine a power series expansion (in x) for S valid at low temperature. Retain only terms up through order x^2. (7 pts) First evaluate $\ln q = -\ln x + \ln(1+x+x^2) = -\ln x + x + x^2 + \ldots$ From the definition of x we know that $\ln x = -\varepsilon/kT$, thus

$$k\ln q = \frac{\varepsilon}{T} + x + x^2 + \ldots \tag{1}$$

   Now, expanding the denominator of the expression for $\langle E\rangle$, we find

$$\frac{\langle E\rangle}{T} = \frac{\varepsilon}{T}(x^2-1)(1-x-x^2+\ldots) = \frac{\varepsilon}{T}(-1+x+2x^2+\ldots) \tag{2}$$

   Combining Eqs. (1) and (2), we obtain

$$S = \frac{\langle E\rangle}{T} + k\ln q = x(k+\varepsilon/T) + x^2(k+2\varepsilon/T) + \ldots$$

   We also know that

$$\lim_{T\to 0}\frac{x}{T} = \frac{\exp(-\varepsilon/kT}{T} = 0$$

The exponential goes to zero much faster than (1/T) goes to infinity. Thus, since $\lim_{T\to 0} x = 0$, $\lim_{T\to 0} S = 0$, which is expected, since the lowest level is non-degenerate.