Thermodynamics: Examples for chapter 8.

1. Derive expressions for C_V and C_P using the ideal gas result for internal energy $U = \frac{3}{2}nRT$.

   Solution:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}nR$$
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{5}{2}nR$$

   In the latter equation we have use the fact that $H = U + PV = U + nRT = \frac{5}{2}nRT$.

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2. Derive the expression for entropy S using the ideal gas partition function.

   Solution:

   Entropy is given by:

$$S = \frac{U}{T} + k\ln\left(Z_{tr}\right)$$

   where we need to use the following (N is number of atoms):

$$U = \frac{3}{2}NkT$$

$$\ln\left(Z_{tr}\right) = N \times \left[\frac{3}{2}\ln\left(2\pi mk/h^2\right) + \frac{3}{2}\ln(T) + ln(V)\right] - \ln(N!)$$

   Inserting these into the expression for entropy, we get:

$$S = \frac{3}{2}Nk + Nk \times \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] + \ln\left(\frac{V^{Nk}}{N!^k}\right)$$

To simplify this expression we use $N! = N^N/e^N$:

$$S = \frac{3}{2}nK + Nk \times \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} + \ln\left(\frac{V}{N}\right) + \ln(1)\right]$$

This further simplifies as:

$$S = nK\left\{\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \times \frac{V}{N}\right] + \frac{5}{2}\right\}$$

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3. Consider 2 mol of N_2(g) at 2 bar pressure and 209.18 K temperature. Calculate U, H, and S using the statistical thermodynamics expressions.

   <u>Solution:</u>

   The mass of N_2 can be calculated from the molar mass:

$$m = \frac{M_{\mathrm{N}_2}}{N_A} = \frac{28.01 \times 10^{-3}\ \mathrm{kg\ mol}^{-1}}{6.022 \times 10^{23}\ \mathrm{mol}^{-1}} = 4.651 \times 10^{-26}\ \mathrm{kg}$$

   The internal energy is given by:

$$U = \frac{3}{2}RT = 3.72\ \mathrm{kJ\ mol}^{-1}$$

   and the entropy (in terms of moles rather than number of atoms):

$$S = R\left(\frac{5}{2} + \ln\left(\frac{q_t}{N_A}\right)\right) = 8.315\ \mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}\left(2.5 + \ln\left(5.829 \times 10^6\right)\right)$$

$$= 150.3\ \mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}$$

   where $q_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V = 3.510 \times 10^{30}$.
