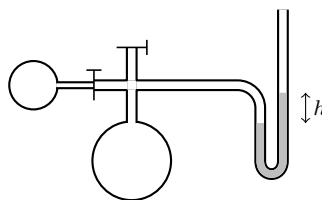


## 2 The First and Second Laws of Thermodynamics

- 2/8: 1. Consider the following experiment with an ideal gas, and derive the relation between  $\gamma$ ,  $h$ , and  $h'$ .

Let the system sit at  $P_0, T_0$  where  $h = 0$ . Pump a little gas in (add  $\Delta n$ ) and wait so that  $T$  is back to  $T_0$ ; measure  $h$ . Open the valve to air quickly to  $P_0$  and close again. Justify why this can be considered a reversible adiabatic expansion. Wait so that  $T$  is back to  $T_0$ ; measure  $h'$ .



*Answer.* State 1 is  $P_0 V_0 = nRT_0$ , state 2 is  $(P_0 + h)V_0 = (n + \Delta n_1)RT_0$ , and state 3 is  $(P_0 + h')V_0 = (n + \Delta n_1 + \Delta n_2)RT_0$ . It follows that

$$\begin{aligned}(P_0 + h)V_0 &= (n + \Delta n_1)RT_0 \\ P_0 V_0 + hV_0 &= nRT_0 + \Delta n_1 RT_0 \\ hV_0 &= \Delta n_1 RT_0 \\ hV_0 &= \Delta n_1 \cdot \frac{P_0 V_0}{n} \\ \frac{h}{P_0} &= \frac{\Delta n_1}{n}\end{aligned}$$

$$\begin{aligned}(P_0 + h')V_0 &= (n + \Delta n_1 + \Delta n_2)RT_0 \\ P_0 V_0 + h'V_0 &= nRT_0 + \Delta n_1 RT_0 + \Delta n_2 RT_0 \\ h'V_0 &= \Delta n_1 RT_0 + \Delta n_2 RT_0 \\ h'V_0 &= \frac{nh}{P_0} \cdot RT_0 + \Delta n_2 RT_0 \\ h'V_0 &= \frac{nh}{P_0} \cdot \frac{P_0 V_0}{n} + \Delta n_2 \cdot \frac{P_0 V_0}{n} \\ h' &= h + \frac{P_0 \Delta n_2}{n} \\ \frac{\Delta n_2}{n} &= \frac{h - h'}{P_0} = \frac{C_P}{C_V} \frac{h}{P_0}\end{aligned}$$

$$\begin{aligned}h - h' &= \frac{hC_P}{C_V} \\ C_V(h - h') &= hC_P \\ h(C_V - C_P) &= h'C_V \\ \frac{h'}{h} &= \frac{C_V - C_P}{C_V} \\ &= 1 - \gamma\end{aligned}$$

□

2. (a)  $n$  moles of an ideal gas with a given  $\gamma$  undergo an adiabatic expansion from  $V_a$  to  $V_b$ . Calculate the work done and the total energy change.

*Answer.* Let the initial pressure of the gas be  $P_a$ . Then

$$\begin{aligned} w &= - \int_{V_a}^{V_b} P \, dV \\ &= - \int_{V_a}^{V_b} \frac{P_a V_a^\gamma}{V^\gamma} \, dV \\ \boxed{w &= \frac{P_a V_a^\gamma}{\gamma - 1} (V_b^{1-\gamma} - V_a^{1-\gamma})} \end{aligned}$$

Additionally, since the process is adiabatic (i.e.,  $\delta q = 0$ ), we know that  $\Delta U = w$ . Thus,

$$\boxed{\Delta U = \frac{P_a V_a^\gamma}{\gamma - 1} (V_b^{1-\gamma} - V_a^{1-\gamma})}$$

□

- (b)  $n$  moles of an ideal gas with a given  $\gamma$  undergo an isobaric expansion from  $V_a$  to  $V_b$ . Calculate the work done and the total energy change.

*Answer.* Let the constant pressure throughout the expansion be  $P$ . Then

$$\boxed{w = P(V_b - V_a)}$$

Additionally, since  $PV_a = nRT_a$  and  $PV_b = nRT_b$ , we have that

$$\begin{aligned} \Delta U &= \int_{T_a}^{T_b} C_V \, dT \\ &= C_V (T_b - T_a) \\ \boxed{\Delta U &= \frac{C_V P}{nR} (V_b - V_a)} \end{aligned}$$

□

3. (a) Consider a Carnot cycle for an ideal gas. Derive the relation  $Q_1/T_1 + Q_2/T_2 = 0$  where  $Q_1, Q_2$  are the heat transferred to the system along the isotherms at  $T_1, T_2$ .

*Answer.* The Carnot cycle is a four step process. The four steps are isothermal expansion (at  $T_1$ ; we let  $Q_1$  be the heat absorbed during this process), adiabatic expansion (the amount  $Q$  of heat absorbed or released is zero), isothermal compression ( $Q_2$  at  $T_2$ ), and adiabatic compression ( $Q = 0$ ). During each of these reversible processes, there is a change in entropy  $dS = \delta q_{\text{rev}}/T$ . Thus, the total change in entropy  $\Delta S$  is given by

$$\begin{aligned} \Delta S &= \int_{T_1}^{T_1} \frac{Q_1}{T_1} \, dT + \int_{T_1}^{T_2} \frac{0}{T} \, dT + \int_{T_2}^{T_2} \frac{Q_2}{T_2} \, dT + \int_{T_2}^{T_1} \frac{0}{T} \, dT \\ &= \frac{Q_1}{T_1} + \frac{Q_2}{T_2} \end{aligned}$$

But since  $\Delta S = 0$  around a closed loop (such as the Carnot cycle), we have that

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

as desired.

□

- (b) Consider an ideal gas going from  $V_1, T_1$  to  $V_2, T_2$ . Calculate the entropy change in terms of  $V_1, V_2, T_2, T_1$ .

*Answer.* We will calculate the entropy change along two separate paths (reversible processes) that together move an ideal gas from  $V_1, T_1$  to  $V_2, T_2$ . In particular, we go from  $V_1, T_1$  to  $V_2, T_1$  isothermally and then from  $V_2, T_1$  to  $V_2, T_2$  isochorically. If we call these processes  $A$  and  $B$ , it follows that

$$\begin{aligned}\Delta S &= \Delta S_A + \Delta S_B \\ &= nR \ln \frac{V_2}{V_1} + \int_{T_1}^{T_2} \frac{C_V}{T} dT\end{aligned}$$

$$\boxed{\Delta S = nR \ln \frac{V_2}{V_1} + C_V \ln \frac{T_2}{T_1}}$$

□

#### 4. Practicing with partial derivatives.

By expressing the internal energy state function  $U$  in terms of  $V$  and  $T$  variables and alternatively with  $P$  and  $T$  variables, show that

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T \quad \left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial U}{\partial V}\right)_T$$

Then derive that

$$C_P - C_V = \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_P$$

Show that

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

for an ideal gas. And then show that

$$C_P - C_V = nR$$

*Answer.* The total differential for  $U(P, T)$  is

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT$$

It contains the two partial derivatives for which we want to find expressions. Thus, we need only manipulate an analogous equation into the above form. To do so, we use the total differential for  $U(V, T)$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

This is close, but we need  $dP$ , not  $dV$ . Thus, we substitute the total differential for  $V(P, T)$

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

into the above expression to get

$$\begin{aligned}dU &= \left(\frac{\partial U}{\partial V}\right)_T \left[ \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \right] + \left(\frac{\partial U}{\partial T}\right)_V dT \\ &= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial T}\right)_V dT \\ &= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP + \left[ \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V \right] dT\end{aligned}$$

The first two equations follow by comparing the above with the total differential for  $U(P, T)$ .

It follows from the second equation and the definition of enthalpy that

$$\begin{aligned}\left(\frac{\partial}{\partial T}(H - PV)\right)_P &= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V \\ \left(\frac{\partial H}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial T}\right)_P - V \left(\frac{\partial P}{\partial T}\right)_P &= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V\end{aligned}$$

Noting that  $\partial P/\partial T = 0$  for  $P$  a constant function (the derivative is taken at constant pressure) and employing the definitions of  $C_P, C_V$  gives us

$$\begin{aligned}C_P - P \left(\frac{\partial V}{\partial T}\right)_P - V \cdot 0 &= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + C_V \\ C_P - C_V &= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P \\ &= \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_P\end{aligned}$$

as desired.

Since the internal energy  $U$  of an ideal gas is solely a function of temperature  $T$ , taking the partial derivative of  $U$  with respect to  $V$  is equivalent to taking the derivative of a constant function, and thus we clearly have

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

It follows since  $V = nRT/P$  by the ideal gas law that

$$\begin{aligned}C_P - C_V &= \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_P \\ &= [P + 0] \frac{nR}{P} \\ &= nR\end{aligned}$$

as desired. □

5. Write that  $dU = T dS - P dV$  and derive the following two relations.

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

*Answer.* The total differential of  $U(T, V)$  is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Thus, we have that

$$\begin{aligned}T dS - P dV &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ dS &= \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \\ &= \frac{C_V}{T} dT + \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV\end{aligned}$$

The two equations follow by comparing the above with the total differential for  $S(T, V)$ , given by

$$dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV$$

□

6. Problem 21-10. Show your work.

It has been found experimentally that  $\Delta_{\text{vap}}\bar{S} \approx 88 \text{ J K}^{-1} \text{ mol}^{-1}$  for many nonassociated liquids. This rough rule of thumb is called **Trouton's rule**. Use the following data to test the validity of Trouton's rule.

Substance	$t_{\text{fus}}/^{\circ}\text{C}$	$t_{\text{vap}}/^{\circ}\text{C}$	$\Delta_{\text{fus}}\bar{H}/\text{kJ mol}^{-1}$	$\Delta_{\text{vap}}\bar{H}/\text{kJ mol}^{-1}$
Pentane	-129.7	36.06	8.42	25.79
Hexane	-95.3	68.73	13.08	28.85
Heptane	-90.6	98.5	14.16	31.77
Ethylene oxide	-111.7	10.6	5.17	25.52
Benzene	5.53	80.09	9.95	30.72
Diethyl ether	-116.3	34.5	7.27	26.52
Tetrachloromethane	-23	76.8	3.28	29.82
Mercury	-38.83	356.7	2.29	59.11
Bromine	-7.2	58.8	10.57	29.96

*Answer.* We know that

$$\Delta_{\text{vap}}\bar{S} = \frac{\Delta_{\text{vap}}\bar{H}}{t_{\text{vap}}}$$

Thus, for pentane (for example), we have that

$$\Delta_{\text{vap}}\bar{S}(\text{pentane}) = \frac{25.79 \text{ kJ mol}^{-1}}{36.06 ^{\circ}\text{C}} = \frac{2.579 \times 10^4 \text{ J mol}^{-1}}{309.21 \text{ K}} = 83.41 \text{ J K}^{-1} \text{ mol}^{-1}$$

We can run the same calculation for all of the other values to learn that

$$\begin{aligned}\Delta_{\text{vap}}\bar{S}(\text{hexane}) &= 84.39 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta_{\text{vap}}\bar{S}(\text{heptane}) &= 85.47 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta_{\text{vap}}\bar{S}(\text{ethylene oxide}) &= 89.92 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta_{\text{vap}}\bar{S}(\text{benzene}) &= 86.97 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta_{\text{vap}}\bar{S}(\text{diethyl ether}) &= 86.19 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta_{\text{vap}}\bar{S}(\text{tetrachloromethane}) &= 85.20 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta_{\text{vap}}\bar{S}(\text{mercury}) &= 93.84 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta_{\text{vap}}\bar{S}(\text{bromine}) &= 90.24 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Since the mean of this set of values of  $\Delta_{\text{vap}}\bar{S}$  is  $87.29 \approx 88$  and the standard deviation is relatively small, the given data supports Trouton's rule. □

7. Problem 21-37. Show your reasoning.

Given that  $\tilde{\nu}_1 = 1321.3 \text{ cm}^{-1}$ ,  $\tilde{\nu}_2 = 750.8 \text{ cm}^{-1}$ ,  $\tilde{\nu}_3 = 1620.3 \text{ cm}^{-1}$ ,  $\tilde{A}_0 = 7.9971 \text{ cm}^{-1}$ ,  $\tilde{B}_0 = 0.4339 \text{ cm}^{-1}$ , and  $\tilde{C}_0 = 0.4103 \text{ cm}^{-1}$ , calculate the standard molar entropy of  $\text{NO}_{2(g)}$  at 298.15 K. (Note that  $\text{NO}_{2(g)}$  is a bent triatomic molecule.) How does your value compare with that in Table 21.2?

*Answer.* Given molecular data, it will be easiest to calculate the standard molar entropy by means of the partition function  $Q$ . We can do this with the help of the equation

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

To see if we can employ the  $Q = q^N/N!$  approximation, we apply the following condition, where  $P = 1$  bar,  $T = 298.15$  K,  $m = 46.01$  g/mol  $= 7.640 \times 10^{-26}$  kg, and the rest of the terms are fundamental constants.

$$\begin{aligned} \frac{N}{V} \left( \frac{h^2}{8mk_B T} \right)^{3/2} &\stackrel{?}{\ll} 1 \\ \frac{P}{RT} \left( \frac{h^2}{8mk_B T} \right)^{3/2} &\stackrel{?}{\ll} 1 \\ 5.596 \times 10^{-8} &\stackrel{\checkmark}{\ll} 1 \end{aligned}$$

Indeed we can, so thus we write

$$\begin{aligned} S &= k_B \ln \frac{q^N}{N!} + k_B T \left( \frac{\partial \ln q^N/N!}{\partial T} \right)_V \\ &= Nk_B \ln q - k_B \ln N! + k_B T N \left( \frac{\partial \ln q}{\partial T} \right)_V - k_B T N \left( \frac{\partial \ln N!}{\partial T} \right)_V \\ &= Nk_B \ln q - Nk_B \ln N + Nk_B + Nk_B T \left( \frac{\partial \ln q}{\partial T} \right)_V \\ &= Nk_B + Nk_B \ln \frac{q}{N} + Nk_B T \left( \frac{\partial \ln q}{\partial T} \right)_V \end{aligned}$$

Now for a nonlinear polyatomic molecule,

$$q(V, T) = \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \cdot \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\Theta_{\text{rot},A} \Theta_{\text{rot},B} \Theta_{\text{rot},C}}} \cdot \prod_{j=1}^{3n-6} \frac{e^{-\Theta_{\text{vib},j}/2T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \cdot g_e e^{D_e/k_B T}$$

It follows that for  $\text{NO}_2$  in particular,

$$q(V, T) = \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \cdot \frac{\sqrt{\pi}}{2} \sqrt{\frac{T^3}{\Theta_{\text{rot},A} \Theta_{\text{rot},B} \Theta_{\text{rot},C}}} \cdot \prod_{j=1}^3 \frac{e^{-\Theta_{\text{vib},j}/2T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \cdot e^{D_e/k_B T}$$

Then since

$$\begin{aligned} \ln q &= \ln \left[ \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \cdot \frac{\sqrt{\pi}}{2} \sqrt{\frac{T^3}{\Theta_{\text{rot},A} \Theta_{\text{rot},B} \Theta_{\text{rot},C}}} \cdot \prod_{j=1}^3 \frac{e^{-\Theta_{\text{vib},j}/2T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \cdot e^{D_e/k_B T} \right] \\ &= \ln \left[ \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \right] + \frac{1}{2} \ln \frac{T^3 \pi}{4 \Theta_{\text{rot},A} \Theta_{\text{rot},B} \Theta_{\text{rot},C}} + \sum_{j=1}^3 \ln \left[ \frac{e^{-\Theta_{\text{vib},j}/2T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \right] + \frac{D_e}{k_B T} \\ &= \frac{3}{2} \ln T + \frac{1}{2} \cdot 3 \ln T + \sum_{j=1}^3 \left[ -\frac{\Theta_{\text{vib},j}}{2T} - \ln \left( 1 - e^{-\Theta_{\text{vib},j}/T} \right) \right] + \frac{D_e}{k_B T} + \text{terms not involving } T \\ &= 3 \ln T + \sum_{j=1}^3 \left[ -\frac{\Theta_{\text{vib},j}}{2T} - \ln \left( 1 - e^{-\Theta_{\text{vib},j}/T} \right) \right] + \frac{D_e}{k_B T} + \text{terms not involving } T \end{aligned}$$

and

$$\left(\frac{\partial \ln q}{\partial T}\right)_V = \frac{3}{T} + \sum_{j=1}^3 \left[ \frac{\Theta_{\text{vib},j}}{2T^2} + \frac{(\Theta_{\text{vib},j}/T^2)e^{-\Theta_{\text{vib},j}/T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \right] - \frac{D_e}{k_B T^2}$$

$$Nk_B T \left(\frac{\partial \ln q}{\partial T}\right)_V = 3Nk_B + Nk_B \sum_{j=1}^3 \left[ \frac{\Theta_{\text{vib},j}}{2T} + \frac{(\Theta_{\text{vib},j}/T)e^{-\Theta_{\text{vib},j}/T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \right] - \frac{ND_e}{T}$$

we have that

$$\begin{aligned} S &= Nk_B + Nk_B \ln q - Nk_B \ln N + Nk_B T \left(\frac{\partial \ln q}{\partial T}\right)_V \\ &= Nk_B + Nk_B \left\{ \ln \left[ \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \right] + \frac{1}{2} \ln \frac{T^3 \pi}{4\Theta_{\text{rot},A}\Theta_{\text{rot},B}\Theta_{\text{rot},C}} \right. \\ &\quad \left. + \sum_{j=1}^3 \ln \left[ \frac{e^{-\Theta_{\text{vib},j}/2T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \right] + \frac{D_e}{k_B T} \right\} \\ &\quad - Nk_B \ln N + 3Nk_B + Nk_B \sum_{j=1}^3 \left[ \frac{\Theta_{\text{vib},j}}{2T} + \frac{(\Theta_{\text{vib},j}/T)e^{-\Theta_{\text{vib},j}/T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \right] - \frac{ND_e}{T} \\ &= 4Nk_B + Nk_B \left\{ \ln \left[ \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \right] + \frac{1}{2} \ln \frac{T^3 \pi}{4\Theta_{\text{rot},A}\Theta_{\text{rot},B}\Theta_{\text{rot},C}} \right. \\ &\quad \left. + \sum_{j=1}^3 \left[ -\frac{\Theta_{\text{vib},j}}{2T} - \ln \left( 1 - e^{-\Theta_{\text{vib},j}/T} \right) \right] + \frac{D_e}{k_B T} \right\} \\ &\quad - Nk_B \ln N + Nk_B \sum_{j=1}^3 \left[ \frac{\Theta_{\text{vib},j}}{2T} + \frac{(\Theta_{\text{vib},j}/T)e^{-\Theta_{\text{vib},j}/T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \right] - \frac{ND_e}{T} \\ &= Nk_B \left\{ 4 + \ln \left[ \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{V}{N} \right] + \frac{1}{2} \ln \frac{T^3 \pi}{4\Theta_{\text{rot},A}\Theta_{\text{rot},B}\Theta_{\text{rot},C}} \right. \\ &\quad \left. + \sum_{j=1}^3 \left[ -\ln \left( 1 - e^{-\Theta_{\text{vib},j}/T} \right) \right] \right. \\ &\quad \left. + \sum_{j=1}^3 \left[ \frac{(\Theta_{\text{vib},j}/T)e^{-\Theta_{\text{vib},j}/T}}{1 - e^{-\Theta_{\text{vib},j}/T}} \right] \right\} \\ \frac{\bar{S}}{R} &= 4 + \ln \left[ \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{RT}{PN_A} \right] + \frac{1}{2} \ln \frac{T^3 \pi}{4\Theta_{\text{rot},A}\Theta_{\text{rot},B}\Theta_{\text{rot},C}} \\ &\quad + \sum_{j=1}^3 \left[ \frac{(\Theta_{\text{vib},j}/T)e^{-\Theta_{\text{vib},j}/T}}{1 - e^{-\Theta_{\text{vib},j}/T}} - \ln \left( 1 - e^{-\Theta_{\text{vib},j}/T} \right) \right] \end{aligned}$$

We now construct the needed values from the given data on NO<sub>2</sub>. In particular, since  $\Theta_{\text{vib}} = h\nu/k_B = hc\tilde{\nu}/k_B$ , we have that

$$\begin{aligned} \Theta_{\text{vib},1} &= \frac{hc\tilde{\nu}_1}{k_B} & \Theta_{\text{vib},2} &= \frac{hc\tilde{\nu}_2}{k_B} & \Theta_{\text{vib},3} &= \frac{hc\tilde{\nu}_3}{k_B} \\ &= 1901 \text{ K} & &= 1080 \text{ K} & &= 2331 \text{ K} \end{aligned}$$

Additionally, since  $\Theta_{\text{rot}} = \hbar^2/2Ik_B$  and  $\tilde{X}_0 = h/8\pi^2 cI$ , we have that

$$\Theta_{\text{rot}} = \frac{\hbar^2}{8\pi^2 I k_B} = \frac{hc}{k_B} \cdot \frac{h}{8\pi^2 cI} = \frac{hc\tilde{X}_0}{k_B}$$

Thus,

$$\begin{aligned}\Theta_{\text{rot},A} &= \frac{hc\tilde{A}_0}{k_B} & \Theta_{\text{rot},B} &= \frac{hc\tilde{B}_0}{k_B} & \Theta_{\text{rot},C} &= \frac{hc\tilde{C}_0}{k_B} \\ &= 11.50 \text{ K} & &= 0.6241 \text{ K} & &= 0.5902 \text{ K}\end{aligned}$$

The value of  $M$  was given above (as  $m$  in the molecular partition function criterion), and everything else is a fundamental constant. The one exception is pressure, which we take to be standard (i.e., 1 bar =  $1 \times 10^5$  Pa). Choosing values such that all units cancel gives us

$$\boxed{\bar{S} = 234.3 \text{ J mol}^{-1} \text{ K}^{-1}}$$

□

#### 8. Problem 19-55.

Use the rigid rotator-harmonic oscillator model and the data in Table 18.2 to plot  $\bar{C}_P(T)$  for  $\text{CO}_{(g)}$  from 300 K to 1000 K. Compare your result with the expression given in Problem 19-43.

*Answer.* For a linear molecule,

$$\frac{C_V}{Nk_B} = \frac{5}{2} + \sum_{j=1}^{3n-5} \left( \frac{\Theta_{\text{vib},j}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib},j}/T}}{(1 - e^{-\Theta_{\text{vib},j}/T})^2}$$

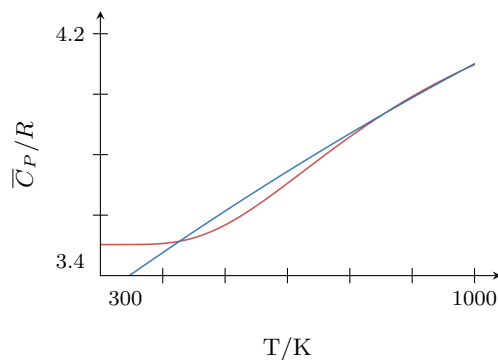
In particular, for a linear diatomic molecule,

$$\frac{C_V}{Nk_B} = \frac{5}{2} + \left( \frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^2}$$

Thus, since  $C_P - C_V = Nk_B$ , we have that

$$\begin{aligned}C_P &= \frac{7}{2}Nk_B + Nk_B \left( \frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^2} \\ \bar{C}_V(T) &= \frac{7}{2}R + R \left( \frac{\Theta_{\text{vib}}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{(1 - e^{-\Theta_{\text{vib}}/T})^2}\end{aligned}$$

where  $\Theta_{\text{vib}} = 3103 \text{ K}$  by Table 18.2. This function is plotted below in red, and the expression given in Problem 19-43 is plotted below in blue. They clearly follow the same general trend but nevertheless display not insignificant differences in their trajectory.



□