Entropy and the Third Law of Thermodynamics

PROBLEMS AND SOLUTIONS

21–1. Form the total derivative of H as a function of T and P and equate the result to dH in Equation 21.6 to derive Equations 21.7 and 21.8.

The total derivative of $S(T, P)$ is

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

We can substitute this in Equation 21.6 to obtain

$$dH = TdS + VdP$$
$$dH = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP + VdP$$
$$= T\left(\frac{\partial S}{\partial T}\right)_P dT + \left[V + T\left(\frac{\partial S}{\partial P}\right)_T\right]dP \qquad (1)$$

We now write the total derivative of $H(T, P)$ as

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$
$$dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad (2)$$

Set the coefficients of dT in Equations 1 and 2 equal to each other to find Equation 21.7

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

and set the coefficients of dP equal to each other to obtain Equation 21.8:

$$\left[V + T\left(\frac{\partial S}{\partial P}\right)_T\right] = \left(\frac{\partial H}{\partial P}\right)_T$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \qquad (21.8)$$

21–2. The molar heat capacity of $H_2O(l)$ has an approximately constant value of $\overline{C}_p = 75.4 \ \text{J·K}^{-1}\text{·mol}^{-1}$ from 0°C to 100°C. Calculate ΔS if two moles of $H_2O(l)$ are heated from 10°C to 90°C at constant pressure.

We use Equation 21.9 to write

$$\Delta S = \int_{T_1}^{T_2} \frac{n\overline{C}_P}{T} dT = \int_{283 \text{ K}}^{363 \text{ K}} \frac{(2 \text{ mol})(75.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})}{T} dT$$

$$= (150.8 \text{ J}\cdot\text{K}^{-1}) \ln\frac{363}{283} = 37.5 \text{ J}\cdot\text{K}^{-1}$$

21–3. The molar heat capacity of butane can be expressed by

$$\overline{C}_P/R = 0.05641 + (0.04631 \text{ K}^{-1})T - (2.392 \times 10^{-5} \text{ K}^{-2})T^2 + (4.807 \times 10^{-9} \text{ K}^{-3})T^3$$

over the temperature range $300 \text{ K} \leq T \leq 1500 \text{ K}$. Calculate ΔS if one mole of butane is heated from 300 K to 1000 K at constant pressure.

We can use Equation 21.9 to write

$$\Delta S = \int_{T_1}^{T_2} \frac{n\overline{C}_P}{T} dT$$

$$= nR \int_{300 \text{ K}}^{1000 \text{ K}} \left[\frac{0.05641}{T} + 0.04631 \text{ K}^{-1} - (2.392 \times 10^{-5} \text{ K}^{-2})T \right.$$

$$\left. + (4.807 \times 10^{-9} \text{ K}^{-3})T^2 \right] dT$$

$$= (23.16R)(1 \text{ mol}) = 192.6 \text{ J}\cdot\text{K}^{-1}$$

21–4. The molar heat capacity of $C_2H_4(g)$ can be expressed by

$$\overline{C}_V(T)/R = 16.4105 - \frac{6085.929 \text{ K}}{T} + \frac{822\,826 \text{ K}^2}{T^2}$$

over the temperature range $300 \text{ K} < T < 1000 \text{ K}$. Calculate ΔS if one mole of ethene is heated from 300 K to 600 K at constant volume.

We can use Equation 21.5 to write

$$\Delta S = \int_{T_1}^{T_2} \frac{n\overline{C}_V}{T} dT$$

$$= nR \int_{300 \text{ K}}^{600 \text{ K}} \left[\frac{16.4105}{T} - \frac{6085.929 \text{ K}}{T^2} + \frac{822\,826 \text{ K}^2}{T^3} \right] dT$$

$$= (4.660R)(1 \text{ mol}) = 38.75 \text{ J}\cdot\text{K}^{-1}$$

21–5. Use the data in Problem 21–4 to calculate ΔS if one mole of ethene is heated from 300 K to 600 K at constant pressure. Assume ethene behaves ideally.

For an ideal gas, $\overline{C}_P - \overline{C}_V = R$, so we can express $\overline{C}_P$ as

$$\overline{C}_P/R = 1 + 16.4105 - \frac{6085.929 \text{ K}}{T} + \frac{822\,826 \text{ K}^2}{T^2}$$

Then we can use Equation 21.9 to calculate ΔS:

$$\Delta S = \int_{T_1}^{T_2} \frac{n\overline{C}_P}{T} dT$$

$$= nR \int_{300 \text{ K}}^{600 \text{ K}} \left[\frac{17.4105}{T} - \frac{6085.929 \text{ K}}{T^2} + \frac{822\,826 \text{ K}^2}{T^3} \right] dT$$

$$= (5.353R)(1 \text{ mol}) = 44.51 \text{ J}\cdot\text{K}^{-1}$$

21–6. We can calculate the difference in the results of Problems 21–4 and 21–5 in the following way. First, show that because $\overline{C}_P - \overline{C}_V = R$ for an ideal gas,

$$\Delta\overline{S}_P = \Delta\overline{S}_V + R \ln\frac{T_2}{T_1}$$

Check to see numerically that your answers to Problems 21–4 and 21–5 differ by $R \ln 2 = 0.693R = 5.76 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

For an ideal gas, $\overline{C}_P - \overline{C}_V = R$. Equations 21.6 and 21.9 state that

$$\Delta\overline{S}_V = \int_{T_1}^{T_2} \frac{\overline{C}_V}{T} dT \qquad \text{and} \qquad \Delta\overline{S}_P = \int_{T_1}^{T_2} \frac{\overline{C}_P}{T} dT$$

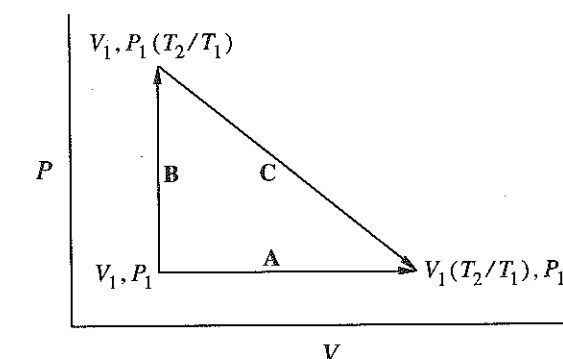Subtracting $\Delta\overline{S}_P$ from $\Delta\overline{S}_V$ gives

$$\Delta\overline{S}_P - \Delta\overline{S}_V = \int_{T_1}^{T_2} \frac{\overline{C}_P - \overline{C}_V}{T} dT = \int_{T_1}^{T_2} \frac{R}{T} dT = R \ln\frac{T_2}{T_1}$$

and so $\Delta\overline{S}_P$ can be written as

$$\Delta\overline{S}_P = \Delta\overline{S}_V + R \ln\frac{T_2}{T_1}$$

The answers to Problems 21–4 and 21–5 differ by $R \ln 2$, as required.

21–7. The results of Problems 21–4 and 21–5 must be connected in the following way. Show that the two processes can be represented by the diagram

where paths A and B represent the processes in Problems 21–5 and 21–4, respectively.

Now, path A is equivalent to the sum of paths B and C. Show that ΔS_C is given by

$$\Delta S_C = nR \ln \frac{V_1\left(\frac{T_2}{T_1}\right)}{V_1} = nR \ln \frac{P_1\left(\frac{T_2}{T_1}\right)}{P_1} = nR \ln \frac{T_2}{T_1}$$

and that the result given in Problem 21–6 follows.

In Problem 21–4, ethane is heated at constant volume, so (assuming ideal behavior)

$$P_2 = P_1\left(\frac{T_2}{T_1}\right)$$

Likewise, in Problem 21–5, the system is kept at constant pressure and so (assuming ideal behavior)

$$V_2 = V_1\left(\frac{T_2}{T_1}\right)$$

These values correspond to those shown in the diagram. Now, path C represents an isothermal process. Because we are assuming ideal behavior, $dU = 0$, which means that $\delta q_{rev} = -\delta w = nRT/V\,dV$. Then we can write ΔS_C as (Equation 20.22)

$$\Delta S_C = \int \frac{\delta q_{rev}}{T} = nR \ln \frac{V_2}{V_1} = R \ln \frac{V_1(T_2/T_1)}{V_1} = R \ln \frac{T_2}{T_1}$$

Note that path A is equivalent to the sums of paths B and C, so $\Delta S_A = \Delta S_B + \Delta S_C$. Because $\Delta S_A = \Delta S_P$ and $\Delta S_B = \Delta S_V$, we can write

$$\Delta S_C = \Delta S_P - \Delta S_V$$

and the result given in Problem 21–6 follows.

21–8. Use Equations 20.23 and 20.24 to show that $S = 0$ at 0 K, where every system will be in its ground state.

We begin with Equations 20.23 and 20.24,

$$W = \frac{A}{a_1!a_2!\dots} \qquad \text{and} \qquad S = k_B \ln W$$

Let a_1 represent the ground state, so all other $a_j = 0$ when the system is in the ground state. Then $A = \sum_j a_j = a_1 + 0 = a_1$, and Equation 20.23 becomes

$$W = \frac{a_1!}{a_1!} = 1$$

Substitute this into Equation 20.24 for S to find

$$S = k_B \ln 1 = 0$$

21–9. Prove that $S = -k \sum p_j \ln p_j = 0$ when $p_1 = 1$ and all the other $p_j = 0$. In other words, prove that $x \ln x \to 0$ as $x \to 0$.

Let $p_1 = 1$ and all other $p_j = 0$. Then Equation 20.40 becomes

$$S = -k_B \sum p_j \ln p_j = 0 - k_B \sum x \ln x$$

where $x \to 0$. In Problem J–8, we proved that $x \ln x \to 0$ as $x \to 0$, so $S = 0 - 0 = 0$ under the conditions given.

21–10. It has been found experimentally that $\Delta_{vap}\overline{S} \approx 88 \text{ J·K}^{-1}\text{·mol}^{-1}$ 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	$t_{fus}/°C$	$t_{vap}/°C$	$\Delta_{fus}\overline{H}/\text{kJ·mol}^{-1}$	$\Delta_{vap}\overline{H}/\text{kJ·mol}^{-1}$
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

Use Equation 21.16,

$$\Delta_{vap}\overline{S} = \frac{\Delta_{vap}\overline{H}}{T_{vap}}$$

to construct a table of values of $\Delta_{vap}\overline{S}$.

Substance	$\Delta_{vap}\overline{S}/\text{J·mol}^{-1}\text{·K}^{-1}$
Pentane	83.41
Hexane	84.39
Heptane	85.5
Ethylene oxide	89.9
Benzene	86.97
Diethyl ether	86.2
Tetrachloromethane	85.2
Mercury	93.85
Bromine	90.3

21–11. Use the data in Problem 21–10 to calculate the value of $\Delta_{fus}\overline{S}$ for each substance.

Use Equation 21.16,

$$\Delta_{fus}\overline{S} = \frac{\Delta_{fus}\overline{H}}{T_{fus}}$$

to construct a table of values of $\Delta_{fus}\overline{S}$.

Substance	$\Delta_{fus}\overline{S}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
Pentane	58.7
Hexane	73.5
Heptane	77.6
Ethylene oxide	32.0
Benzene	35.7
Diethyl ether	46.3
Tetrachloromethane	13
Mercury	9.77
Bromine	40

21–12. Why is $\Delta_{vap}\overline{S} > \Delta_{fus}\overline{S}$?

$\Delta_{vap}\overline{S} \gg \Delta_{fus}\overline{S}$ because gases are essentially completely unordered; the molecules of a gas travel more or less randomly within the gas's container. Liquids, however, are much more cohesive and structured, and solids are very structured. The difference between the entropy of a liquid and that of a solid is less than the difference between the entropy of a liquid and that of a gas.

21–13. Show that if $C_P^s(T) \to T^\alpha$ as $T \to 0$, where α is a positive constant, then $S(T) \to 0$ as $T \to 0$.

We assume in the statement of the problem that

$$\lim_{T\to 0} C_P^s(T) = T^\alpha$$

where α is a positive constant. Then express S using Equation 21.10 and take the limit of S as $T \to 0$:

$$\lim_{T\to 0} S(T) = S(0\,\text{K}) + \lim_{T\to 0}\int_0^T \frac{C_P(T)}{T}dT = \lim_{T\to 0}\int_0^T \frac{T^\alpha}{T}dT = \lim_{T\to 0}\frac{T^\alpha}{T} = 0$$

as long as $S(0\,\text{K}) = 0$ and $\alpha > 0$ (as stipulated in the statement of the problem).

21–14. Use the following data to calculate the standard molar entropy of $N_2(g)$ at 298.15 K.

$$C_P^\circ[N_2(s_1)]/R = -0.03165 + (0.05460\text{ K}^{-1})T + (3.520 \times 10^{-3}\text{ K}^{-2})T^2 \\ - (2.064 \times 10^{-5}\text{ K}^{-3})T^3$$

$$10\text{ K} \le T \le 35.61\text{ K}$$

$$C_P^\circ[N_2(s_2)]/R = -0.1696 + (0.2379\text{ K}^{-1})T - (4.214 \times 10^{-3}\text{ K}^{-2})T^2 \\ + (3.036 \times 10^{-5}\text{ K}^{-3})T^3$$

$$35.61\text{ K} \le T \le 63.15\text{ K}$$

$$C_P^\circ[N_2(l)]/R = -18.44 + (1.053\text{ K}^{-1})T - (0.0148\text{ K}^{-2})T^2 \\ + (7.064 \times 10^{-5}\text{ K}^{-3})T^3$$

$$63.15\text{ K} \le T \le 77.36\text{ K}$$

$C_P^\circ[N_2(g)]/R = 3.500$ from $77.36\text{ K} \le T \le 1000\text{ K}$, $C_P(T = 10.0\text{ K}) = 6.15\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $T_{trs} = 35.61\text{ K}$, $\Delta_{trs}\overline{H} = 0.2289\text{ kJ}\cdot\text{mol}^{-1}$, $T_{fus} = 63.15\text{ K}$, $\Delta_{fus}\overline{H} = 0.71\text{ kJ}\cdot\text{mol}^{-1}$, $T_{vap} = 77.36\text{ K}$, and $\Delta_{vap}\overline{H} = 5.57\text{ kJ}\cdot\text{mol}^{-1}$. The correction for nonideality (Problem 22–20) = $0.02\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

The easiest way to do this series of problems is to input the given data into a program like *Mathematica* and use Equation 21.17. For temperatures below the minimum value for which the formulae provided are valid, we can use the expression from Example 21–3, $\overline{S}(T) = \overline{C}_P(T)/3$. Here, we solve the formula

$$\overline{S}(T) = \frac{\overline{C}_P(10\text{ K})}{3} + \int_{10}^{35.61} \frac{\overline{C}_P[N_2(s_1)]}{T}dT + \frac{\Delta_{trs}\overline{H}}{35.61\text{ K}} + \int_{35.61}^{63.15} \frac{\overline{C}_P[N_2(s_2)]}{T}dT$$

$$+ \frac{\Delta_{fus}\overline{H}}{63.15\text{ K}} + \int_{63.15}^{77.36} \frac{\overline{C}_P[N_2(l)]}{T}dT + \frac{\Delta_{vap}\overline{H}}{77.36\text{ K}}$$

$$+ \int_{77.36}^{298.15} \frac{\overline{C}_P[N_2(g)]}{T}dT + \text{correction}$$

$$= 2.05\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} + 25.86\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} + 6.428\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$+ 23.41\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} + 11.24\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} + 11.78\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$+ 72.00\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} + 39.26\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} + 0.02\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$= 192.05\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The literature value of the standard molar entropy is $191.6\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The slight discrepancy between these two values reflects the use of the ideal expression for $\overline{C}_P[N_2(g)]$. (Using the $\overline{C}_P[N_2(g)]$ that is given in the next problem, which is linear in T, gives a standard molar entropy of $191.04\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.)

21–15. Use the data in Problem 21–14 and $\overline{C}_P[N_2(g)]/R = 3.307 + (6.29 \times 10^{-4}\text{ K}^{-1})T$ for $T \ge 77.36\text{ K}$ to plot the standard molar entropy of nitrogen as a function of temperature from 0 K to 1000 K.

The function which describes the standard molar entropy of nitrogen must be defined differently for each phase and phase transition. Notice that the correction factor must be added to all functions to correct for nonideality.

From 0 K to 10 K,

$$\overline{S}(T) = \frac{\overline{C}_P(10\text{ K})}{3} + \text{corr}$$

From 10 K to 35.61 K,

$$\overline{S}(T) = \frac{\overline{C}_P(10\,\text{K})}{3} + \int_{10}^{T} \frac{\overline{C}_P[\text{N}_2(\text{s}_1)]}{T} dT + \text{corr}$$

At 35.61 K,

$$\overline{S}(T) = \frac{\overline{C}_P(10\,\text{K})}{3} + \int_{10}^{35.61} \frac{\overline{C}_P[\text{N}_2(\text{s}_1)]}{T} dT + \frac{\Delta_{\text{trs}}\overline{H}}{35.61\,\text{K}} + \text{corr}$$

From 35.61 K to 63.15 K,

$$\overline{S}(T) = \frac{\overline{C}_P(10\,\text{K})}{3} + \int_{10}^{35.61} \frac{\overline{C}_P[\text{N}_2(\text{s}_1)]}{T} dT + \frac{\Delta_{\text{trs}}\overline{H}}{35.61\,\text{K}} + \int_{35.61}^{T} \frac{\overline{C}_P[\text{N}_2(\text{s}_2)]}{T} dT + \text{corr}$$

At 63.15 K,

$$\overline{S}(T) = \frac{\overline{C}_P(10\,\text{K})}{3} + \int_{10}^{35.61} \frac{\overline{C}_P[\text{N}_2(\text{s}_1)]}{T} dT + \frac{\Delta_{\text{trs}}\overline{H}}{35.61\,\text{K}} + \int_{35.61}^{63.15} \frac{\overline{C}_P[\text{N}_2(\text{s}_2)]}{T} dT$$
$$+ \frac{\Delta_{\text{fus}}\overline{H}}{63.15\,\text{K}} + \text{corr}$$

From 63.15 K to 77.36 K,

$$\overline{S}(T) = \frac{\overline{C}_P(10\,\text{K})}{3} + \int_{10}^{35.61} \frac{\overline{C}_P[\text{N}_2(\text{s}_1)]}{T} dT + \frac{\Delta_{\text{trs}}\overline{H}}{35.61\,\text{K}} + \int_{35.61}^{63.15} \frac{\overline{C}_P[\text{N}_2(\text{s}_2)]}{T} dT$$
$$+ \frac{\Delta_{\text{fus}}\overline{H}}{63.15\,\text{K}} + \int_{63.15}^{T} \frac{\overline{C}_P[\text{N}_2(\text{l})]}{T} dT + \text{corr}$$

At 77.36 K,

$$\overline{S}(T) = \frac{\overline{C}_P(10\,\text{K})}{3} + \int_{10}^{35.61} \frac{\overline{C}_P[\text{N}_2(\text{s}_1)]}{T} dT + \frac{\Delta_{\text{trs}}\overline{H}}{35.61\,\text{K}} + \int_{35.61}^{63.15} \frac{\overline{C}_P[\text{N}_2(\text{s}_2)]}{T} dT$$
$$+ \frac{\Delta_{\text{fus}}\overline{H}}{63.15\,\text{K}} + \int_{63.15}^{77.36} \frac{\overline{C}_P[\text{N}_2(\text{l})]}{T} dT + \frac{\Delta_{\text{vap}}\overline{H}}{77.36\,\text{K}} + \text{corr}$$

From 77.36 K to 1000 K,

$$\overline{S}(T) = \frac{\overline{C}_P(10\,\text{K})}{3} + \int_{10}^{35.61} \frac{\overline{C}_P[\text{N}_2(\text{s}_1)]}{T} dT + \frac{\Delta_{\text{trs}}\overline{H}}{35.61\,\text{K}} + \int_{35.61}^{63.15} \frac{\overline{C}_P[\text{N}_2(\text{s}_2)]}{T} dT$$
$$+ \frac{\Delta_{\text{fus}}\overline{H}}{63.15\,\text{K}} + \int_{63.15}^{77.36} \frac{\overline{C}_P[\text{N}_2(\text{l})]}{T} dT + \frac{\Delta_{\text{vap}}\overline{H}}{77.36\,\text{K}} + \int_{77.36}^{T} \frac{\overline{C}_P[\text{N}_2(\text{g})]}{T} dT + \text{corr}$$
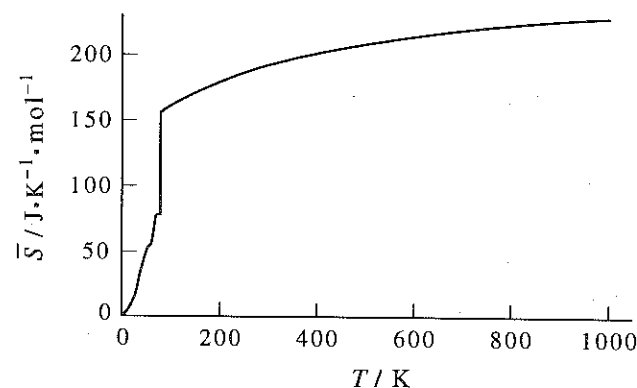
21–16. The molar heat capacities of solid, liquid, and gaseous chlorine can be expressed as

$$C_P^{\circ}[\text{Cl}_2(\text{s})]/R = -1.545 + (0.1502\,\text{K}^{-1})T - (1.179 \times 10^{-3}\,\text{K}^{-2})T^2$$
$$+ (3.441 \times 10^{-6}\,\text{K}^{-3})T^3$$
$$15\,\text{K} \leq T \leq 172.12\,\text{K}$$

$$C_P^{\circ}[\text{Cl}_2(\text{l})]/R = 7.689 + (5.582 \times 10^{-3}\,\text{K}^{-1})T - (1.954 \times 10^{-5}\,\text{K}^{-2})T^2$$
$$172.12\,\text{K} \leq T \leq 239.0\,\text{K}$$

$$C_P^{\circ}[\text{Cl}_2(\text{g})]/R = 3.812 + (1.220 \times 10^{-3}\,\text{K}^{-1})T - (4.856 \times 10^{-7}\,\text{K}^{-2})T^2$$
$$239.0\,\text{K} \leq T \leq 1000\,\text{K}$$

Use the above molar heat capacities and $T_{\text{fus}} = 172.12\,\text{K}$, $\Delta_{\text{fus}}\overline{H} = 6.406\,\text{kJ}\cdot\text{mol}^{-1}$, $T_{\text{vap}} = 239.0\,\text{K}$, $\Delta_{\text{vap}}\overline{H} = 20.40\,\text{kJ}\cdot\text{mol}^{-1}$, and $\Theta_{\text{D}} = 116\,\text{K}$. The correction for nonideality $= 0.502\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ to calculate the standard molar entropy of chlorine at 298.15 K. Compare your result with the value given in Table 21.2.

$$\overline{S}(T) = \int_0^{15} \frac{12\pi^4}{5T} R \left(\frac{T}{\Theta_{\text{D}}}\right)^3 dT + \int_{15}^{172.12} \frac{\overline{C}_P[\text{Cl}_2(\text{s})]}{T} dT + \frac{\Delta_{\text{fus}}\overline{H}}{172.12\,\text{K}}$$
$$+ \int_{172.12}^{239.0} \frac{\overline{C}_P[\text{Cl}_2(\text{l})]}{T} dT + \frac{\Delta_{\text{vap}}\overline{H}}{239.0\,\text{K}} + \int_{239.0}^{298} \frac{\overline{C}_P[\text{Cl}_2(\text{g})]}{T} dT + \text{correction}$$
$$= 1.401\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 69.37\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 37.22\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$
$$+ 21.86\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 85.36\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 7.54\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$
$$+ 0.502\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$= 223.2\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The result is extremely close to the value of $223.1\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ found in Table 21.2.

21–17. Use the data in Problem 21–16 to plot the standard molar entropy of chlorine as a function of temperature from 0 K to 1000 K.

Do this in the same manner as Problem 21–15, using the appropriate values from Problem 21–16 and changing the limits of integration as required.
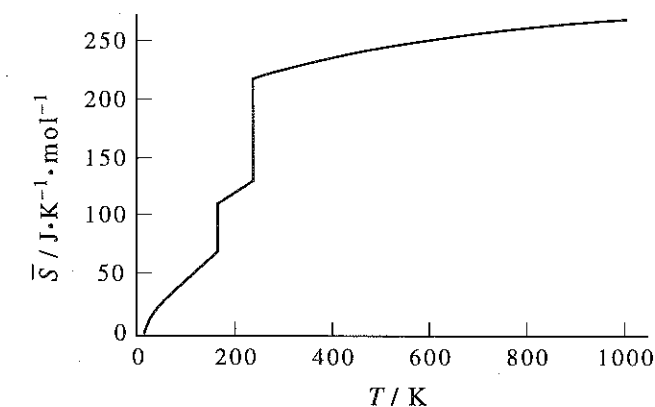
21–18. Use the following data to calculate the standard molar entropy of cyclopropane at 298.1 K.

$$C_P^\circ[C_3H_6(s)]/R = -1.921 + (0.1508\ K^{-1})T - (9.670 \times 10^{-4}\ K^{-2})T^2$$
$$+ (2.694 \times 10^{-6}\ K^{-3})T^3$$
$$15\ K \leq T \leq 145.5\ K$$

$$C_P^\circ[C_3H_6(l)]/R = 5.624 + (4.493 \times 10^{-2}\ K^{-1})T - (1.340 \times 10^{-4}\ K^{-2})T^2$$
$$145.5\ K \leq T \leq 240.3\ K$$

$$C_P^\circ[C_3H_6(g)]/R = -1.793 + (3.277 \times 10^{-2}\ K^{-1})T - (1.326 \times 10^{-5}\ K^{-2})T^2$$
$$240.3\ K \leq T \leq 1000\ K$$

$T_{fus} = 145.5$ K, $T_{vap} = 240.3$ K, $\Delta_{fus}\overline{H} = 5.44$ kJ·mol^{-1}, $\Delta_{vap}\overline{H} = 20.05$ kJ·mol^{-1}, and $\Theta_D = 130$ K. The correction for nonideality $= 0.54$ J·K^{-1}·mol^{-1}.

$$\overline{S}(T) = \int_0^{15} \frac{12\pi^4}{5T}R\left(\frac{T}{\Theta_D}\right)^3 dT + \int_{15}^{145.5} \frac{\overline{C}_P[C_3H_6(s)]}{T}dT + \frac{\Delta_{fus}\overline{H}}{145.5\ K}$$
$$+ \int_{145.5}^{240.3} \frac{\overline{C}_P[C_3H_6(l)]}{T}dT + \frac{\Delta_{vap}\overline{H}}{240.3\ K} + \int_{240.3}^{298.1} \frac{\overline{C}_P[C_3H_6(g)]}{T}dT$$
$$+ \text{correction}$$

$$= 0.995\ \text{J·K}^{-1}\text{·mol}^{-1} + 66.1\ \text{J·K}^{-1}\text{·mol}^{-1} + 37.4\ \text{J·K}^{-1}\text{·mol}^{-1}$$
$$+ 38.5\ \text{J·K}^{-1}\text{·mol}^{-1} + 83.4\ \text{J·K}^{-1}\text{·mol}^{-1} + 10.8\ \text{J·K}^{-1}\text{·mol}^{-1}$$
$$+ 0.54\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$= 237.8\ \text{J·K}^{-1}\text{·mol}^{-1}$$

This compares very well with the literature value of 237.5 J·K^{-1}·mol^{-1}.

21–19. Use the data in Problem 21–18 to plot the standard molar entropy of cyclopropane from 0 K to 1000 K.

Do this in the same manner as Problem 21–15, using the appropriate values from Problem 21–18 and changing the limits of integration as required.
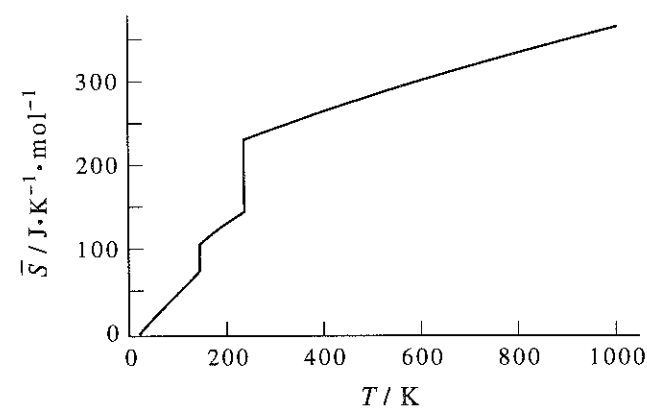

21–20. The constant-pressure molar heat capacity of N_2O as a function of temperature is tabulated below. Dinitrogen oxide melts at 182.26 K with $\Delta_{fus}\overline{H} = 6.54$ kJ·mol^{-1}, and boils at 184.67 K with $\Delta_{vap}\overline{H} = 16.53$ kJ·mol^{-1} at one bar. Assuming the heat capacity of solid dinitrogen oxide can be described by the Debye theory up to 15 K, calculate the molar entropy of $N_2O(g)$ at its boiling point.

T/K	$\overline{C}_P$/J·K^{-1}·mol^{-1}	T/K	$\overline{C}_P$/J·K^{-1}·mol^{-1}
15.17	2.90	120.29	45.10
19.95	6.19	130.44	47.32
25.81	10.89	141.07	48.91
33.38	16.98	154.71	52.17
42.61	23.13	164.82	54.02
52.02	28.56	174.90	56.99
57.35	30.75	180.75	58.83
68.05	34.18	182.26	Melting point
76.67	36.57	183.55	77.70
87.06	38.87	183.71	77.45
98.34	41.13	184.67	Boiling point
109.12	42.84		

We can do this problem in the same way we did Problems 21–14, 21–16, and 21–18. Because we are not given equations for the molar heat capacity, we can graph the heat capacity of the solid and liquid dinitrogen oxide, find a best-fit line, and use this to calculate the molar entropy of N_2O at the boiling point.

For solid dinitrogen oxide, a best-fit line gives the equation

$$\overline{C}_P[N_2O(s)]/\text{J·K}^{-1}\text{·mol}^{-1} = -13.153 + (1.1556\ K^{-1})T - (8.3372 \times 10^{-3}\ K^{-2})T^2$$
$$+ (2.3026 \times 10^{-5}\ K^{-3})T^3$$
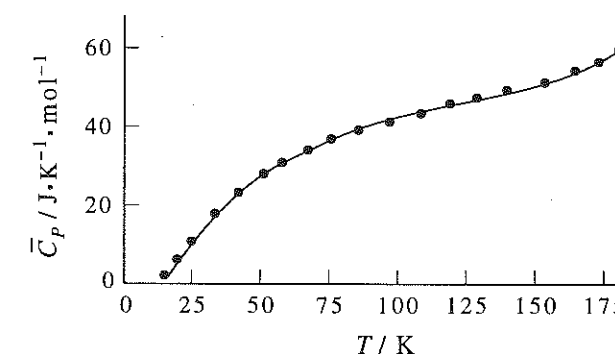
And for liquid dinitrogen oxide (with only two points), a line drawn between those two points has the equation

$$\overline{C}_P[N_2O(l)]/\text{J·K}^{-1}\text{·mol}^{-1} = 364.49 - (1.5625\ K^{-1})T$$

Note that, although we are given only two data points, the temperature varies by only 2° for dinitrogen oxide. From the Debye theory (Example 21–3) we can write the low temperature entropy as

$$\overline{S}(15\ K) = \frac{\overline{C}_P(15\ K)}{3} \qquad 0 < T \leq 15\ K$$

Now we can substitute into Equation 21.17, as before.

$$\overline{S}(T) = \frac{\overline{C}_P(15\text{ K})}{3} + \int_{15}^{182.26} \frac{\overline{C}_P[N_2O(s)]}{T}dT + \frac{\Delta_{fus}\overline{H}}{182.26\text{ K}}$$

$$+ \int_{182.26}^{184.67} \frac{\overline{C}_P[N_2O(l)]}{T}dT + \frac{\Delta_{vap}\overline{H}}{184.67\text{ K}}$$

$$= 0.967\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 69.34\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 35.9\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$+1.02\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 89.5\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$= 196.7\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

21–21. Methylammonium chloride occurs as three crystalline forms, called β, γ, and α, between 0 K and 298.15 K. The constant-pressure molar heat capacity of methylammonium chloride as a function of temperature is tabulated below. The $\beta \to \gamma$ transition occurs at 220.4 K with $\Delta_{trs}\overline{H} = 1.779\text{ kJ}\cdot\text{mol}^{-1}$ and the $\gamma \to \alpha$ transition occurs at 264.5 K with $\Delta_{trs}\overline{H} = 2.818\text{ kJ}\cdot\text{mol}^{-1}$. Assuming the heat capacity of solid methylammonium chloride can be described by the Debye theory up to 12 K, calculate the molar entropy of methylammonium chloride at 298.15 K.

T/K	$\overline{C}_P/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$\overline{C}_P/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
12	0.837	180	73.72
15	1.59	200	77.95
20	3.92	210	79.71
30	10.53	220.4	$\beta \to \gamma$ transition
40	18.28	222	82.01
50	25.92	230	82.84
60	32.76	240	84.27
70	38.95	260	87.03
80	44.35	264.5	$\gamma \to \alpha$ transition
90	49.08	270	88.16
100	53.18	280	89.20
120	59.50	290	90.16
140	64.81	295	90.63
160	69.45		

We can this problem in the same way as Problem 21–20, graphing the molar heat capacities of the β, α, and γ crystalline forms versus temperature:
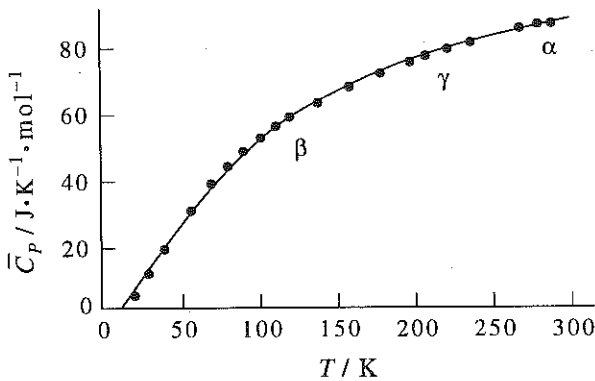
Fitting the curves to a polynomial, we find the following expressions for $\overline{C}_P$:

$$\overline{C}_P[\beta]/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -12.432 + (0.93892\text{ K}^{-1})T - (3.4126\times10^{-3}\text{ K}^{-2})T^2$$
$$+ (4.8562\times10^{-6}\text{ K}^{-3})T^3$$
$$12\text{ K} \leq T \leq 220.4\text{ K}$$

$$\overline{C}_P[\gamma]/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 78.265 - (8.2955\times10^{-2}\text{ K}^{-1})T + (4.4885\times10^{-4}\text{ K}^{-2})T^2$$
$$220.4\text{ K} \leq T \leq 264.5\text{ K}$$

$$\overline{C}_P[\alpha]/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 35.757 + (0.28147\text{ K}^{-1})T - (3.2362\times10^{-4}\text{ K}^{-2})T^2$$
$$264.5\text{ K} \leq T$$

From the Debye theory (Example 21–3),

$$\overline{S}(12\text{ K}) = \frac{\overline{C}_P(12\text{ K})}{3} \qquad 0 < T \leq 12\text{ K}$$

Now we can write the molar entropy of methylammonium chloride as

$$\overline{S}(298.15\text{ K}) = \frac{\overline{C}_P(12\text{ K})}{3} + \int_{12}^{220.4} \frac{\overline{C}_P[\beta]}{T}dT + \frac{\Delta_{\beta\to\gamma}\overline{H}}{220.4\text{ K}} + \int_{220.4}^{264.5} \frac{\overline{C}_P[\gamma]}{T}dT$$

$$+\frac{\Delta_{\gamma\to\alpha}\overline{H}}{264.5\text{ K}} + \int_{264.5}^{298.15} \frac{\overline{C}_P[\alpha]}{T}dT$$

$$= 0.279\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 94.17\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 8.07\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$+15.42\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 10.65\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 10.69\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$= 139.3\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

21–22. The constant-pressure molar heat capacity of chloroethane as a function of temperature is tabulated below. Chloroethane melts at 134.4 K with $\Delta_{fus}\overline{H} = 4.45\text{ kJ}\cdot\text{mol}^{-1}$, and boils at 286.2 K with $\Delta_{vap}\overline{H} = 24.65\text{ kJ}\cdot\text{mol}^{-1}$ at one bar. Furthermore, the heat capacity of solid chloroethane can be described by the Debye theory up to 15 K. Use these data to calculate the molar entropy of chloroethane at its boiling point.

T/K	$\overline{C}_P/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	T/K	$\overline{C}_P/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
15	5.65	130	84.60
20	11.42	134.4	90.83 (solid)
25	16.53		97.19 (liquid)
30	21.21	140	96.86
35	25.52	150	96.40
40	29.62	160	96.02
50	36.53	180	95.65
60	42.47	200	95.77
70	47.53	220	96.04
80	52.63	240	97.78
90	55.23	260	99.79
100	59.66	280	102.09
110	65.48	286.2	102.13
120	73.55		

Do this problem in the same way as Problem 21–20, graphing the molar heat capacities of solid and liquid chloroethane versus temperature:
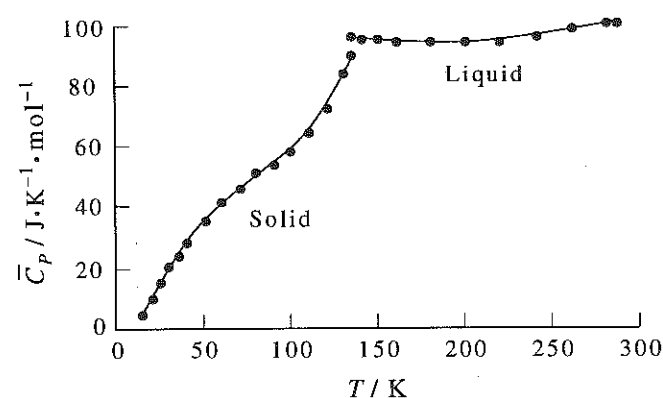
Fitting the curves to a polynomial, we find the following expressions for $\overline{C}_p$:

$$\overline{C}_p[\text{solid}]/\,\text{J·K}^{-1}\text{·mol}^{-1} = -19.195 + (1.863\ \text{K}^{-1})T - (1.8997 \times 10^{-2}\ \text{K}^{-2})T^2 \\ + (8.3132 \times 10^{-5}\ \text{K}^{-3})T^3$$

$$15\ \text{K} \le T \le 134.4\ \text{K}$$

$$\overline{C}_p[\text{liquid}]/\,\text{J·K}^{-1}\text{·mol}^{-1} = 118.15 - (0.24544\ \text{K}^{-1})T + (6.675 \times 10^{-4}\ \text{K}^{-2})T^2$$

$$134.4\ \text{K} \le T \le 298.15\ \text{K}$$

From the Debye theory (Example 21–3),

$$\overline{S}(15\ \text{K}) = \frac{\overline{C}_p(15\ \text{K})}{3} \qquad 0 < T \le 15\ \text{K}$$

Now

$$\overline{S}(T) = \frac{\overline{C}_p(15\ \text{K})}{3} + \int_{15}^{134.4} \frac{\overline{C}_p[\text{solid}]}{T}dT + \frac{\Delta_{\text{fus}}\overline{H}}{134.4\ \text{K}} + \int_{134.4}^{286.2} \frac{\overline{C}_p[\text{liquid}]}{T}dT + \frac{\Delta_{\text{vap}}\overline{H}}{286.2\ \text{K}}$$

$$= 1.88\ \text{J·K}^{-1}\text{·mol}^{-1} + 78.1\ \text{J·K}^{-1}\text{·mol}^{-1} + 33.1\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$+73.4\ \text{J·K}^{-1}\text{·mol}^{-1} + 86.1\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$= 272.6\ \text{J·K}^{-1}\text{·mol}^{-1}$$

21–23. The constant-pressure molar heat capacity of nitromethane as a function of temperature is tabulated below. Nitromethane melts at 244.60 K with $\Delta_{\text{fus}}\overline{H} = 9.70\ \text{kJ·mol}^{-1}$, and boils at 374.34 K at one bar with $\Delta_{\text{vap}}\overline{H} = 38.27\ \text{kJ·mol}^{-1}$ at 298.15 K. Furthermore, the heat capacity of solid nitromethane can be described by the Debye theory up to 15 K. Use these data to calculate the molar entropy of nitromethane at 298.15 K and one bar. The vapor pressure of nitromethane

is 36.66 torr at 298.15 K. (Be sure to take into account ΔS for the isothermal compression of nitromethane from its vapor pressure to one bar at 298.15 K).

T/K	$\overline{C}_P/\text{J·K}^{-1}\text{·mol}^{-1}$	T/K	$\overline{C}_P/\text{J·K}^{-1}\text{·mol}^{-1}$
15	3.72	200	71.46
20	8.66	220	75.23
30	19.20	240	78.99
40	28.87	244.60	melting point
60	40.84	250	104.43
80	47.99	260	104.64
100	52.80	270	104.93
120	56.74	280	105.31
140	60.46	290	105.69
160	64.06	300	106.06
180	67.74		

Do this problem in the same way as Problems 21–20, but include ΔS for the isothermal compression of nitromethane. Graph the molar heat capacities of solid and liquid chloroethane versus temperature:
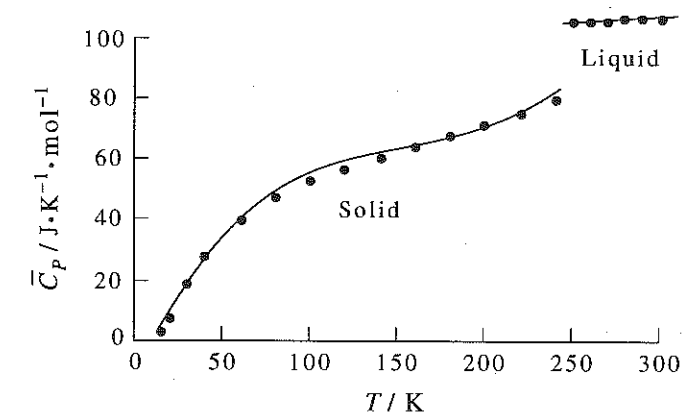
Fitting the curves to a polynomial, we find the following expressions for $\overline{C}_p$:

$$\overline{C}_p[\text{solid}]/\text{J·K}^{-1}\text{·mol}^{-1} = -11.177 + (1.1831\ \text{K}^{-1})T - (6.6826 \times 10^{-3}\ \text{K}^{-2})T^2 \\ + (1.3948 \times 10^{-5}\ \text{K}^{-3})T^3$$

$$15\ \text{K} \le T \le 244.60\ \text{K}$$

$$\overline{C}_p[\text{liquid}]/\text{J·K}^{-1}\text{·mol}^{-1} = 111.6 - (8.0557 \times 10^{-2}\ \text{K}^{-1})T + (2.0714 \times 10^{-4}\ \text{K}^{-2})T^2$$

$$244.60\ \text{K} \le T \le 300\ \text{K}$$

From the Debye theory (Example 21–3),

$$\overline{S}(T) = \frac{\overline{C}_p(15\ \text{K})}{3} \qquad 0 < T \le 15\ \text{K}$$

Assuming that nitromethane behaves ideally, $dU = 0$ for the isothermal compression and so $\delta q = PdV$. Then we can express the change in entropy for the isothermal compression as

$$\Delta \overline{S} = \int Pd\overline{V} = \int_{P_1}^{P_2} \frac{R}{P}dP$$

We can now write the molar entropy of nitromethane at the given conditions as

$$\overline{S}(T) = \frac{\overline{C}_P(15\ K)}{3} + \int_{15}^{244.60} \frac{\overline{C}_P[\text{solid}]}{T}dT + \frac{\Delta_{fus}\overline{H}}{244.60\ K} + \int_{244.60}^{374.34} \frac{\overline{C}_P[\text{liquid}]}{T}dT$$
$$+ \frac{\Delta_{vap}\overline{H}}{374.34\ K} - \int_{0.0489\ bar}^{1\ bar} \frac{R}{P}dP$$
$$= 1.24\ J\cdot K^{-1}\cdot mol^{-1} + 109.3\ J\cdot K^{-1}\cdot mol^{-1} + 39.66\ J\cdot K^{-1}\cdot mol^{-1}$$
$$+ 20.79\ J\cdot K^{-1}\cdot mol^{-1} + 128.4\ J\cdot K^{-1}\cdot mol^{-1} - 25.1\ J\cdot K^{-1}\cdot mol^{-1}$$
$$= 274.26\ J\cdot K^{-1}\cdot mol^{-1}$$

21–24. Use the following data to calculate the standard molar entropy of CO(g) at its normal boiling point. Carbon monoxide undergoes a solid-solid phase transition at 61.6 K. Compare your result with the calculated value of 160.3 J·K⁻¹·mol⁻¹. Why is there a discrepancy between the calculated value and the experimental value?

$$\overline{C}_P[CO(s_1)]/R = -2.820 + (0.3317\ K^{-1})T - (6.408 \times 10^{-3}\ K^{-2})T^2$$
$$+ (6.002 \times 10^{-5}\ K^{-3})T^3$$
$$10\ K \leq T \leq 61.6\ K$$

$$\overline{C}_P[CO(s_2)]/R = 2.436 + (0.05694\ K^{-1})T$$
$$61.6\ K \leq T \leq 68.1\ K$$

$$\overline{C}_P[CO(l)]/R = 5.967 + (0.0330\ K^{-1})T - (2.088 \times 10^{-4}\ K^{-2})T^2$$
$$68.1\ K \leq T \leq 81.6\ K$$

and $T_{trs}(s_1 \rightarrow s_2) = 61.6$ K, $T_{fus} = 68.1$ K, $T_{vap} = 81.6$ K, $\Delta_{fus}\overline{H} = 0.836$ kJ·mol⁻¹, $\Delta_{trs}\overline{H} = 0.633$ kJ·mol⁻¹, $\Delta_{vap}\overline{H} = 6.04$ kJ·mol⁻¹, $\Theta_D = 79.5$ K, and the correction for nonideality $= 0.879$ J·K⁻¹·mol⁻¹.

$$\overline{S}(T) = \int_0^{10} \frac{12\pi^4}{5T}R\left(\frac{T}{\Theta_D}\right)^3 dT + \int_{10}^{61.6} \frac{\overline{C}_P[CO(s_1)]}{T}dT + \frac{\Delta_{trs}\overline{H}}{61.6\ K}$$
$$+ \int_{61.6}^{68.1} \frac{\overline{C}_P[CO(s_2)]}{T}dT + \frac{\Delta_{fus}\overline{H}}{68.1\ K} + \int_{68.1}^{81.6} \frac{\overline{C}_P[CO(l)]}{T}dT + \frac{\Delta_{vap}\overline{H}}{81.6\ K} + \text{correction}$$
$$= 1.29\ J\cdot K^{-1}\cdot mol^{-1} + 40.0\ J\cdot K^{-1}\cdot mol^{-1} + 10.3\ J\cdot K^{-1}\cdot mol^{-1} + 5.11\ J\cdot K^{-1}\cdot mol^{-1}$$
$$+ 12.3\ J\cdot K^{-1}\cdot mol^{-1} + 10.9\ J\cdot K^{-1}\cdot mol^{-1} + 74.0\ J\cdot K^{-1}\cdot mol^{-1} + 0.879\ J\cdot K^{-1}\cdot mol^{-1}$$
$$= 154.7\ J\cdot K^{-1}\cdot mol^{-1}$$

We have found an experimental value for $\overline{S}$ of 154.7 J·K⁻¹·mol⁻¹. The difference between this and the calculated value is the residual entropy of the crystal, which is approximately $R\ln 2$, or 5.8 J·K⁻¹·mol⁻¹ (in agreement with the difference calculated here of 5.6 J·K⁻¹·mol⁻¹).

21–25. The molar heat capacities of solid and liquid water can be expressed by

$$\overline{C}_P[H_2O(s)]/R = -0.2985 + (2.896 \times 10^{-2}\ K^{-1})T - (8.6714 \times 10^{-5}\ K^{-2})T^2$$
$$+ (1.703 \times 10^{-7}\ K^{-3})T^3$$
$$10\ K \leq T \leq 273.15\ K$$

$$\overline{C}_P[H_2O(l)]/R = 22.447 - (0.11639\ K^{-1})T + (3.3312 \times 10^{-4}\ K^{-2})T^2$$
$$- (3.1314 \times 10^{-7}\ K^{-3})T^3$$
$$273.15\ K \leq T \leq 298.15\ K$$

and $T_{fus} = 273.15$ K, $\Delta_{fus}\overline{H} = 6.007$ kJ·mol⁻¹, $\Delta_{vap}\overline{H}(T = 298.15$ K$) = 43.93$ kJ·mol⁻¹, $\Theta_D = 192$ K, the correction for nonideality $= 0.32$ J·K⁻¹·mol⁻¹, and the vapor pressure of H_2O at 298.15 K $= 23.8$ torr. Use these data to calculate the standard molar entropy of $H_2O(g)$ at 298.15 K. You need the vapor pressure of water at 298.15 K because that is the equilibrium pressure of $H_2O(g)$ when it is vaporized at 298.15 K. You must include the value of ΔS that results when you compress the $H_2O(g)$ from 23.8 torr to its standard value of one bar. Your answer should come out to be 185.6 J·K⁻¹·mol⁻¹, which does not agree exactly with the value in Table 21.2. There is a residual entropy associated with ice, which a detailed analysis of the structure of ice gives as $\Delta S_{residual} = R\ln(3/2) = 3.4$ J·K⁻¹·mol⁻¹, which is in good agreement with $\overline{S}_{calc} - \overline{S}_{exp}$.

We can do this problem in the same way as Problems 21–14, 21–16, and 21–18, taking into account ΔS for the isothermal compression of water. For an isothermal reaction, $\delta w = -\delta q$, so $\delta q = PdV$ and we assume that the gas is ideal. Then

$$\overline{S}(T) = \int_0^{10} \frac{12\pi^4}{5T}R\left(\frac{T}{\Theta_D}\right)^3 dT + \int_{10}^{273.15} \frac{\overline{C}_P[H_2O(s)]}{T}dT + \frac{\Delta_{fus}\overline{H}}{273.15\ K}$$
$$+ \int_{273.15}^{298.15} \frac{\overline{C}_P[H_2O(l)]}{T}dT + \frac{\Delta_{vap}\overline{H}}{298.15\ K}$$
$$- \int_{0.0317}^1 \frac{R}{P}dP + \text{correction}$$
$$= 0.0915\ J\cdot K^{-1}\cdot mol^{-1} + 37.9\ J\cdot K^{-1}\cdot mol^{-1} + 22.0\ J\cdot K^{-1}\cdot mol^{-1}$$
$$+ 6.62\ J\cdot K^{-1}\cdot mol^{-1} + 147.3\ J\cdot K^{-1}\cdot mol^{-1} - 28.69\ J\cdot K^{-1}\cdot mol^{-1}$$
$$+ 0.32\ J\cdot K^{-1}\cdot mol^{-1}$$
$$= 185.6\ J\cdot K^{-1}\cdot mol^{-1}$$

Adding in the residual entropy gives a molar entropy of 189 J·K⁻¹·mol⁻¹.

21–26. Use the data in Problem 21–25 and the empirical expression

$$\overline{C}_P[H_2O(g)]/R = 3.652 + (1.156 \times 10^{-3}\ K^{-1})T - (1.424 \times 10^{-7}\ K^{-2})T^2$$
$$300\ K \leq T \leq 1000\ K$$

to plot the standard molar entropy of water from 0 K to 500 K.

Do this in the same manner as Problem 21–15, using the appropriate values from Problem 21–25 and changing the limits of integration as required.
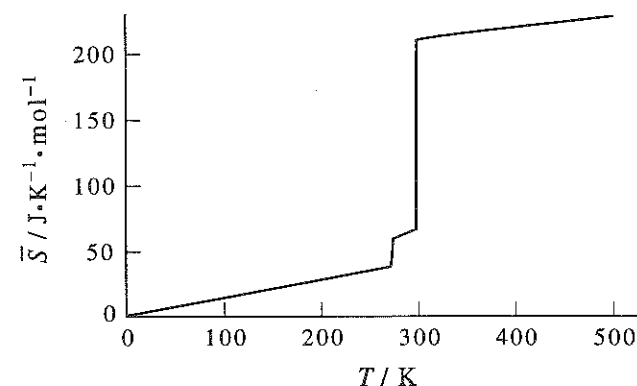
21–27. Show that

$$\overline{S} = R \ln \frac{qe}{N} + RT \left(\frac{\partial \ln q}{\partial T}\right)_V$$

We express the partition function of an ideal gas as (Equation 17.38)

$$Q(N, V, T) = \frac{q(V, T)^N}{N!}$$

and so

$$\ln Q(N, V, T) = N \ln q(V, T) - \ln N!$$

We substitute into Equation 21.19 to write

$$S = Nk_B \ln q - k_B \ln N + Nk_B T \left(\frac{\partial \ln q}{\partial T}\right)_V$$

We use Stirling's approximation and divide both sides of the equation by n to find

$$\overline{S} = N_A k_B \ln q - N_A k_B \ln N + k_B N_A + N_A k_B T \left(\frac{\partial \ln q}{\partial T}\right)_V$$

$$= R \ln \frac{q}{N} + R + RT \left(\frac{\partial \ln q}{\partial T}\right)_V$$

$$= R \ln \frac{qe}{N} + RT \left(\frac{\partial \ln q}{\partial T}\right)_V$$

21–28. Show that Equations 17.21 and 21.19 are consistent with Equations 21.2 and 21.3.

We begin with Equations 21.19 and 17.21,

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} \tag{21.19}$$

$$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} \tag{17.21}$$

We can substitute $k_B T (\partial Q / \partial T)$ from Equation 17.21 into Equation 21.19 to find

$$S = k_B \ln Q + \frac{\langle E \rangle}{T} \tag{1}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = k_B \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + \frac{1}{T} \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V - \frac{\langle E \rangle}{T^2}$$

Because $(\partial \langle E \rangle / \partial T)_V = C_V$, this becomes

$$\left(\frac{\partial S}{\partial T}\right)_V = k_B \left(\frac{\partial \ln Q}{\partial T}\right) + \frac{C_V}{T} - \frac{1}{T^2} k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right) = \frac{C_V}{T}$$

which is Equation 21.2. Now differentiate Equation 1 with respect to V:

$$S = k_B \ln Q + \frac{\langle E \rangle}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = k_B \left(\frac{\partial \ln Q}{\partial V}\right)_T + \frac{1}{T} \left(\frac{\partial \langle E \rangle}{\partial V}\right)_V$$

$$= \frac{1}{T} \left[k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

For an ideal gas, $k_B T = PV/N$, and $(\partial \ln Q / \partial V)_T = N/V$. Thus we have

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

which is Equation 21.3.

21–29. Substitute Equation 21.23 into Equation 21.19 and derive the equation (Problem 20–31)

$$\Delta \overline{S} = \overline{C}_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

for one mole of a monatomic ideal gas.

We know that $Q = q^N / N!$ for an ideal gas (Equation 21.22), so substituting Equation 21.23 into this equation gives

$$Q = \frac{1}{N!} \left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V \cdot g_{el} \right]^N$$

Then

$$\ln Q = N \ln \left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V \cdot g_{el} \right] - N!$$

so, if only temperature and volume vary,

$$\ln Q_2 - \ln Q_1 = \frac{3}{2} N \ln \frac{T_2}{T_1} + \ln \frac{V_2}{V_1}$$

Also, we can find $(\partial \ln Q / \partial T)_V$:

$$\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = \frac{3N}{2T}$$

Equation 21.19 states that

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

Let $\Delta \overline{S} = \overline{S}_2 - \overline{S}_1$. Then

$$\Delta \overline{S} = \frac{1}{n} \left[k_B \ln Q_2 + k_B T_2 \left(\frac{\partial \ln Q_2}{\partial T} \right)_{N,V} - k_B \ln Q_1 - k_B T_1 \left(\frac{\partial \ln Q_1}{\partial T} \right)_{N,V} \right]$$

$$= \frac{3}{2} R \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} + \frac{3R}{2T_2} T_2 - \frac{3R}{2T_1} T_1$$

$$= \frac{3}{2} R \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

where $3R/2$ is equal to $\overline{C}_V$ for a monatomic ideal gas (Equation 17.26).

21–30. Use Equation 21.24 and the data in Chapter 18 to calculate the standard molar entropy of $Cl_2(g)$ at 298.15 K. Compare your answer with the experimental value of 223.1 $J \cdot K^{-1} \cdot mol^{-1}$.

$$q = \left(\frac{2\pi M k_B T}{h^2} \right) V \frac{T}{\sigma \Theta_{rot}} \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}} g_{e1} e^{D_e/k_B T} \qquad (21.24)$$

Equation 21.28 (which is also for a diatomic ideal gas) can be written as

$$\frac{\overline{S}}{R} = \frac{7}{2} + \ln \left[\left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{\overline{V}}{N_A} \right] + \ln \frac{T}{\sigma \Theta_{rot}} - \ln(1 - e^{-\Theta_{vib}/T}) + \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} + \ln g_{e1}$$

(see also Problem 20–41).

For chlorine, $\Theta_{vib} = 805$ K, $\Theta_{rot} = 0.351$ K, $\sigma = 2$, and $g_{e1} = 1$. Then

$$\left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} = \left[\frac{2\pi (1.1774 \times 10^{-25} \text{ kg})(1.381 \times 10^{-23} \text{ J} \cdot K^{-1})(298.15 \text{ K})}{(6.626 \times 10^{34} \text{ J} \cdot \text{s})^2} \right]^{3/2} = 5.777 \times 10^{32} \text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot K^{-1})(298.15 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})(1 \text{ bar})} = 4.116 \times 10^{-26} \text{ m}^3$$

$$\ln \left(\frac{T}{\sigma \Theta_{rot}} \right) = \ln \left[\frac{298.15 \text{ K}}{2(0.351 \text{ K})} \right] = 6.051$$

$$\ln(1 - e^{-\Theta_{vib}/T}) = -0.06957$$

$$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} = 0.1945$$

The standard molar entropy is then

$$\frac{\overline{S}}{R} = 3.5 + 16.98 + 6.051 + 0.06954 + 0.1945 = 26.80$$

This is 222.8 $J \cdot K^{-1} \cdot mol^{-1}$, which is very close to the experimental value.

21–31. Use Equation 21.24 and the data in Chapter 18 to calculate the standard molar entropy of $CO(g)$ at its standard boiling point, 81.6 K. Compare your answer with the experimental value of 155.6 $J \cdot K^{-1} \cdot mol^{-1}$. Why is there a discrepancy of about 5 $J \cdot K^{-1} \cdot mol^{-1}$?

As in Problem 21–30,

$$\frac{\overline{S}}{R} = \frac{7}{2} + \ln \left[\left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{\overline{V}}{N_A} \right] + \ln \frac{T}{\sigma \Theta_{rot}} - \ln(1 - e^{-\Theta_{vib}/T}) + \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} + \ln g_{e1}$$

For carbon monoxide, $\Theta_{vib} = 3103$ K, $\Theta_{rot} = 2.77$ K, $\sigma = 1$, and $g_{e1} = 1$. Then

$$\left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} = \left[\frac{2\pi (4.651 \times 10^{-26} \text{ kg})(1.381 \times 10^{-23} \text{ J} \cdot K^{-1})(81.6 \text{ K})}{(6.626 \times 10^{34} \text{ J} \cdot \text{s})^2} \right]^{3/2} = 2.054 \times 10^{31} \text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot K^{-1})(81.6 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})(1 \text{ bar})} = 1.127 \times 10^{-26} \text{ m}^3$$

$$\ln \left(\frac{T}{\sigma \Theta_{rot}} \right) = \ln \left[\frac{81.6 \text{ K}}{(2.77 \text{ K})} \right] = 3.383$$

$$\ln(1 - e^{-\Theta_{vib}/T}) = -3.057 \times 10^{-17}$$

$$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} = 1.162 \times 10^{-15}$$

The standard molar entropy is then

$$\frac{\overline{S}}{R} = 3.5 + 12.352 + 3.383 + 3.057 \times 10^{-17} + 1.162 \times 10^{-15} = 19.23$$

This is 159.9 $J \cdot K^{-1} \cdot mol^{-1}$, which is about 4 $J \cdot K^{-1} \cdot mol^{-1}$ larger than the experimental value. The discrepancy is due to residual entropy.

21–32. Use Equation 21.26 and the data in Chapter 18 to calculate the standard molar entropy of $NH_3(g)$ at 298.15 K. Compare your answer with the experimental value of 192.8 $J \cdot K^{-1} \cdot mol^{-1}$.

See Problem 20–43. The value calculated is 193.1 $J \cdot K^{-1} \cdot mol^{-1}$.

21–33. Use Equation 21.24 and the data in Chapter 18 to calculate the standard molar entropy of $Br_2(g)$ at 298.15 K. Compare your answer with the experimental value of 245.5 $J \cdot K^{-1} \cdot mol^{-1}$.

As in Problem 21–30,

$$\frac{\overline{S}}{R} = \frac{7}{2} + \ln \left[\left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{\overline{V}}{N_A} \right] + \ln \frac{T}{\sigma \Theta_{rot}} - \ln(1 - e^{-\Theta_{vib}/T}) + \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} + \ln g_{e1}$$

For bromine, $\Theta_{vib} = 463$ K, $\Theta_{rot} = 0.116$ K, $\sigma = 2$, and $g_{e1} = 1$. Then

$$\left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} = \left[\frac{2\pi (2.654 \times 10^{-25} \text{ kg})(1.381 \times 10^{-23} \text{ J} \cdot K^{-1})(298.15 \text{ K})}{(6.626 \times 10^{34} \text{ J} \cdot \text{s})^2} \right]^{3/2} = 1.955 \times 10^{33} \text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot K^{-1})(298.15 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})(1 \text{ bar})} = 4.116 \times 10^{-26} \text{ m}^3$$

$$\ln \left(\frac{T}{\sigma \Theta_{rot}} \right) = \ln \left[\frac{298.15 \text{ K}}{2(0.116 \text{ K})} \right] = 7.159$$

$$\ln(1 - e^{-\Theta_{vib}/T}) = -0.2378$$

$$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} = 0.417$$

The standard molar entropy is then

$$\frac{\overline{S}}{R} = 3.5 + 18.203 + 7.158 + 0.238 + 0.417 = 29.52$$

This is 245.4 J·K^{-1}·mol^{-1}, almost identical to the experimental value.

21–34. The vibrational and rotational constants for HF(g) within the harmonic oscillator-rigid rotator model are $\tilde{\nu}_0 = 3959$ cm^{-1} and $\tilde{B}_0 = 20.56$ cm^{-1}. Calculate the standard molar entropy of HF(g) at 298.15 K. How does this value compare with that in Table 21.3?

We can use the equalities (given in Chapter 18)

$$\Theta_{vib} = \frac{hc\tilde{\nu}_0}{k_B} \qquad \Theta_{rot} = \frac{hc\tilde{B}_0}{k_B}$$

to find $\Theta_{vib} = 5696$ K and $\Theta_{rot} = 29.58$ K, and then solve for entropy as we did in the previous problems.

As in Problem 21–30,

$$\frac{\overline{S}}{R} = \frac{7}{2} + \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} \frac{\overline{V}}{N_A}\right] + \ln\frac{T}{\sigma\Theta_{rot}} - \ln(1 - e^{-\Theta_{vib}/T}) + \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} + \ln g_{e1}$$

Substitute in to find the values of the various components of entropy. Note that $\sigma = 1$ and $g_{e1} = 1$.

$$\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(3.322 \times 10^{-26}\text{ kg})(1.381 \times 10^{-23}\text{ J·K}^{-1})(298.15\text{ K})}{(6.626 \times 10^{34}\text{ J·s})^2}\right]^{3/2} = 8.658 \times 10^{31}\text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314\text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298.15\text{ K})}{(6.022 \times 10^{23}\text{ mol}^{-1})(1\text{ bar})} = 4.116 \times 10^{-26}\text{ m}^3$$

$$\ln\left(\frac{T}{\sigma\Theta_{rot}}\right) = 2.310$$

$$\ln(1 - e^{-\Theta_{vib}/T}) = -5.046 \times 10^{-9}$$

$$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} = 9.639 \times 10^{-8}$$

$$\frac{\overline{S}}{R} = 3.5 + 15.09 + 2.310 + 5.046 \times 10^{-9} + 9.639 \times 10^{-8} = 20.90$$

The standard molar entropy is 173.7 J·K^{-1}·mol^{-1}, which is very close to the value in Table 21.3.

21–35. Calculate the standard molar entropy of H$_2$(g) and D$_2$(g) at 298.15 K given that the bond length of both diatomic molecules is 74.16 pm and the vibrational temperatures of H$_2$(g) and D$_2$(g) are 6215 K and 4394 K, respectively. Calculate the standard molar entropy of HD(g) at 298.15 K ($R_e = 74.13$ pm and $\Theta_{vib} = 5496$ K).

We can use the relation $\Theta_{rot} = \hbar^2/2Ik_B$ (Equation 18.32) to find Θ_{rot} for HD, H$_2$, and D$_2$. Then we can solve for molar entropy as in Problem 21–30. For both H$_2$ and D$_2$, $\sigma = 2$ and $g_{e1} = 1$; for HD, $\sigma = 1$ and $g_{e1} = 1$. For H$_2$,

$$\Theta_{rot} = \frac{\hbar^2}{2\mu R_e^2 k_B} = \frac{\hbar^2}{2(8.368 \times 10^{-28}\text{ kg})(74.16 \times 10^{-12}\text{ m})^2 k_B} = 87.51\text{ K}$$

and

$$\frac{\overline{S}}{R} = \frac{7}{2} + \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} \frac{\overline{V}}{N_A}\right] + \ln\frac{T}{\sigma\Theta_{rot}} - \ln(1 - e^{-\Theta_{vib}/T}) + \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} + \ln g_{e1}$$

Substitute in to find the values of the various components of entropy.

$$\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(3.348 \times 10^{-27}\text{ kg})(1.381 \times 10^{-23}\text{ J·K}^{-1})(298.15\text{ K})}{(6.626 \times 10^{34}\text{ J·s})^2}\right]^{3/2} = 2.769 \times 10^{30}\text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314\text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298.15\text{ K})}{(6.022 \times 10^{23}\text{ mol}^{-1})(1\text{ bar})} = 4.116 \times 10^{-26}\text{ m}^3$$

$$\ln\left(\frac{T}{\sigma\Theta_{rot}}\right) = 0.533$$

$$\ln(1 - e^{-\Theta_{vib}/T}) = -8.852 \times 10^{-10}$$

$$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} = 1.845 \times 10^{-8}$$

$$\frac{\overline{S}}{R} = 3.5 + 11.64 + 0.533 + 8.852 \times 10^{-10} + 1.845 \times 10^{-8} = 15.68$$

The standard molar entropy of H$_2$(g) at 298.15 K is 130.3 J·K^{-1}·mol^{-1}.

For D$_2$,

$$\Theta_{rot} = \frac{\hbar^2}{2\mu R_e^2 k_B} = \frac{\hbar^2}{2(1.672 \times 10^{-27}\text{ kg})(74.16 \times 10^{-12}\text{ m})^2 k_B} = 43.79\text{ K}$$

and

$$\frac{\overline{S}}{R} = \frac{7}{2} + \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} \frac{\overline{V}}{N_A}\right] + \ln\frac{T}{\sigma\Theta_{rot}} - \ln(1 - e^{-\Theta_{vib}/T}) + \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} + \ln g_{e1}$$

Substitute in to find the values of the various components of entropy.

$$\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(6.689 \times 10^{-27}\text{ kg})(1.381 \times 10^{-23}\text{ J·K}^{-1})(298.15\text{ K})}{(6.626 \times 10^{34}\text{ J·s})^2}\right]^{3/2} = 7.822 \times 10^{30}\text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314\text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298.15\text{ K})}{(6.022 \times 10^{23}\text{ mol}^{-1})(1\text{ bar})} = 4.116 \times 10^{-26}\text{ m}^3$$

$$\ln\left(\frac{T}{\sigma\Theta_{rot}}\right) = 1.225$$

$$\ln(1 - e^{-\Theta_{vib}/T}) = -3.977 \times 10^{-7}$$

$$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} = 5.861 \times 10^{-6}$$

$$\frac{\overline{S}}{R} = 3.5 + 12.682 + 1.226 + 3.977 \times 10^{-7} + 5.861 \times 10^{-6} = 17.41$$

The standard molar entropy of D$_2$(g) at 298.15 K is 144.7 J·K^{-1}·mol^{-1}.

For HD,

$$\Theta_{\text{rot}} = \frac{\hbar^2}{2\mu R_e^2 k_B} = \frac{\hbar^2}{2(1.115 \times 10^{-27}\text{ kg})(74.13 \times 10^{-12}\text{ m})^2 k_B} = 65.71\text{ K}$$

and

$$\frac{\overline{S}}{R} = \frac{7}{2} + \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} \frac{\overline{V}}{N_A}\right] + \ln\frac{T}{\sigma\Theta_{\text{rot}}} - \ln(1 - e^{-\Theta_{\text{vib}}/T}) + \frac{\Theta_{\text{vib}}/T}{e^{\Theta_{\text{vib}}/T} - 1} + \ln g_{e1}$$

Substitute in to find the values of the various components of entropy.

$$\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(5.018 \times 10^{-27}\text{ kg})(1.381 \times 10^{-23}\text{ J·K}^{-1})(298.15\text{ K})}{(6.626 \times 10^{34}\text{ J·s})^2}\right]^{3/2} = 5.082 \times 10^{30}\text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314\text{ dm}^3\text{·bar·mol}^{-1}\text{·K}^{-1})(298.15\text{ K})}{(6.022 \times 10^{23}\text{ mol}^{-1})(1\text{ bar})} = 4.116 \times 10^{-26}\text{ m}^3$$

$$\ln\left(\frac{T}{\sigma\Theta_{\text{rot}}}\right) = 1.512$$

$$\ln(1 - e^{-\Theta_{\text{vib}}/T}) = -9.871 \times 10^{-9}$$

$$\frac{\Theta_{\text{vib}}/T}{e^{\Theta_{\text{vib}}/T} - 1} = 1.820 \times 10^{-7}$$

$$\frac{\overline{S}}{R} = 3.5 + 12.251 + 1.512 + 9.871 \times 10^{-9} + 1.820 \times 10^{-7} = 17.26$$

The standard molar entropy of HD(g) at 298.15 K is 143.5 J·K^{-1}·mol^{-1}.

21–36. Calculate the standard molar entropy of HCN(g) at 1000 K given that $I = 1.8816 \times 10^{-46}$ kg·m^2, $\tilde{v}_1 = 2096.70$ cm^{-1}, $\tilde{v}_2 = 713.46$ cm^{-1}, and $\tilde{v}_3 = 3311.47$ cm^{-1}. Recall that HCN(g) is a linear triatomic molecule and therefore the bending mode, v_2, is doubly degenerate.

In Problem 18–24, we found $\Theta_{\text{vib},j}$ and Θ_{rot} of HCN to be

$$\Theta_{\text{vib},1} = 3016\text{ K} \qquad \Theta_{\text{vib},4} = 4764\text{ K}$$
$$\Theta_{\text{vib},2,3} = 1026\text{ K} \qquad \Theta_{\text{rot}} = 2.135\text{ K}$$

For a linear polyatomic ideal gas having three atoms,

$$q = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V \frac{T}{\sigma\Theta_{\text{rot}}} \left(\prod_{j=1}^{4} \frac{e^{-\Theta_{\text{vib},j}/2T}}{1 - e^{-\Theta_{\text{vib},j}/T}}\right) g_{e1} e^{D_e/k_B T} \qquad (21.25)$$

Substituting into Equation 21.27, we find

$$\frac{\overline{S}}{R} = \frac{7}{2} + \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} \frac{\overline{V}}{N_A}\right] + \ln\frac{T}{\sigma\Theta_{\text{rot}}} - \sum_{j=1}^{4}\ln(1 - e^{-\Theta_{\text{vib},j}/T}) + \sum_{j=1}^{4}\left[\frac{(\Theta_{\text{vib},j}/T)e^{-\Theta_{\text{vib},j}/T}}{1 - e^{-\Theta_{\text{vib},j}/T}}\right] + \ln g_{e1}$$

Because HCN is asymmetrical, its symmetry number is unity. Then

$$\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(4.488 \times 10^{-26}\text{ kg})(1.381 \times 10^{-23}\text{ J·K}^{-1})(1000\text{ K})}{(6.626 \times 10^{34}\text{ J·s})^2}\right]^{3/2} = 8.350 \times 10^{32}\text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314\text{ dm}^3\text{·bar·mol}^{-1}\text{·K}^{-1})(1000\text{ K})}{(6.022 \times 10^{23}\text{ mol}^{-1})(1\text{ bar})} = 1.381 \times 10^{-25}\text{ m}^3$$

$$\ln\left(\frac{T}{\sigma\Theta_{\text{rot}}}\right) = \ln\left[\frac{1000\text{ K}}{(2.135\text{ K})}\right] = 6.149$$

$$\sum_{j=1}^{4}\ln(1 - e^{-\Theta_{\text{vib},j}/T}) = -0.9465$$

$$\sum_{j=1}^{4}\frac{\Theta_{\text{vib},j}}{T}\left(\frac{e^{-\Theta_{\text{vib},j}/T}}{1 - e^{-\Theta_{\text{vib},j}/T}}\right) = 1.343$$

The standard molar entropy is then

$$\frac{\overline{S}}{R} = 3.5 + 18.563 + 6.149 + 0.9465 + 1.343 = 30.5$$

The standard molar entropy of HCN(g) at 1000 K is 253.6 J·K^{-1}·mol^{-1}. The experimentally observed value is 253.7 J·K^{-1}·mol^{-1}.

21–37. Given that $\tilde{v}_1 = 1321.3$ cm^{-1}, $\tilde{v}_2 = 750.8$ cm^{-1}, $\tilde{v}_3 = 1620.3$ cm^{-1}, $\tilde{A}_0 = 7.9971$ cm^{-1}, $\tilde{B}_0 = 0.4339$ cm^{-1}, and $\tilde{C}_0 = 0.4103$ cm^{-1}, calculate the standard molar entropy of NO$_2$(g) at 298.15 K. (Note that NO$_2$(g) is a bent triatomic molecule.) How does your value compare with that in Table 21.2?

In Problem 18–29, we found that

$$\Theta_{\text{vib},1} = 1898.7\text{ K} \qquad \Theta_{\text{rot},A} = 11.512\text{ K}$$
$$\Theta_{\text{vib},2} = 1078.8\text{ K} \qquad \Theta_{\text{rot},B} = 0.62304\text{ K}$$
$$\Theta_{\text{vib},3} = 2327.6\text{ K} \qquad \Theta_{\text{rot},C} = 0.59047\text{ K}$$

For a nonlinear polyatomic ideal gas having three atoms,

$$q = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_{\text{rot},A}\Theta_{\text{rot},B}\Theta_{\text{rot},C}}\right)^{1/2}\left(\prod_{j=1}^{3}\frac{e^{-\Theta_{\text{vib},j}/2T}}{1 - e^{-\Theta_{\text{vib},j}/T}}\right) g_{e1} e^{D_e/k_B T} \qquad (21.26)$$

Substituting into Equation 21.27, we find

$$\frac{\overline{S}}{R} = 4 + \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} \frac{\overline{V}}{N_A}\right] + \ln\left(\frac{\pi^{1/2}}{\sigma}\right) + \frac{1}{2}\ln\frac{T^3}{\Theta_{\text{rot},A}\Theta_{\text{rot},B}\Theta_{\text{rot},C}}$$
$$- \sum_{j=1}^{3}\ln(1 - e^{-\Theta_{\text{vib},j}/T}) + \sum_{j=1}^{3}\left[\frac{(\Theta_{\text{vib},j}/T)e^{-\Theta_{\text{vib},j}/T}}{1 - e^{-\Theta_{\text{vib},j}/T}}\right] + \ln g_{e1}$$

From Table 18.4, $\sigma = 2$, and $g_{e1} = 1$. Then

$$\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(7.639 \times 10^{-26}\text{ kg})(1.381 \times 10^{-23}\text{ J·K}^{-1})(298.15\text{ K})}{(6.626 \times 10^{34}\text{ J·s})^2}\right]^{3/2} = 3.019 \times 10^{32}\text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314\text{ dm}^3\text{·bar·mol}^{-1}\text{·K}^{-1})(298.15\text{ K})}{(6.022 \times 10^{23}\text{ mol}^{-1})(1\text{ bar})} = 4.116 \times 10^{-26}\text{ m}^3$$

$$\frac{1}{2}\ln\left(\frac{T^3}{\Theta_{rot,A}\Theta_{rot,B}\Theta_{rot,C}}\right) = 7.825$$

$$\sum_{j=1}^{3}\ln(1 - e^{-\Theta_{vib,j}/T}) = -0.0293$$

$$\sum_{j=1}^{3}\frac{\Theta_{vib,j}}{T}\left(\frac{e^{-\Theta_{vib,j}/T}}{1 - e^{-\Theta_{vib,j}/T}}\right) = 0.114$$

The standard molar entropy is then

$$\frac{\overline{S}}{R} = 4 + 16.335 - 0.121 + 7.825 + 0.0293 + 0.114 = 28.18$$

This is 234.3 J·K^{-1}·mol^{-1}.

21–38. In Problem 21–48, you are asked to calculate the value of $\Delta_r S°$ at 298.15 K using the data in Table 21.2 for the reaction described by

$$2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$$
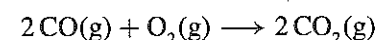
Use the data in Table 18.2 to calculate the standard molar entropy of each of the substances in this reaction [see Example 21–5 for the calculation of the standard molar entropy of $CO_2(g)$]. Then use these results to calculate the standard entropy change for the above reaction. How does your answer compare with what you obtained in Problem 21–48?

From Example 21–5, $S°[CO_2(g)] = 213.8$ J·K^{-1}·mol^{-1}. Because both CO and O_2 are diatomic molecules, we can write (as in Problem 21–30)

$$\frac{\overline{S}}{R} = \frac{7}{2} + \ln\left[\left(\frac{2\pi Mk_B T}{h^2}\right)^{3/2}\frac{\overline{V}}{N_A}\right] + \ln\frac{T}{\sigma\Theta_{rot}} - \ln(1 - e^{-\Theta_{vib}/T}) + \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} + \ln g_{e1}$$

Because CO is a heteronuclear diatomic molecule, $\sigma = 1$; because O_2 is homonuclear, $\sigma = 2$. For CO $\Theta_{vib} = 3103$ K and $\Theta_{rot} = 2.77$ K. Then

$$\left(\frac{2\pi Mk_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(4.651 \times 10^{-26}\text{ kg})(1.381 \times 10^{-23}\text{ J·K}^{-1})(298.15\text{ K})}{(6.626 \times 10^{34}\text{ J·s})^2}\right]^{3/2} = 1.434 \times 10^{32}\text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314\text{ dm}^3\cdot\text{bar·mol}^{-1}\cdot\text{K}^{-1})(298.15\text{ K})}{(6.022 \times 10^{23}\text{ mol}^{-1})(1\text{ bar})} = 4.116 \times 10^{-26}\text{ m}^3$$

$$\ln\left(\frac{T}{\sigma\Theta_{rot}}\right) = 4.679$$

$$\ln(1 - e^{-\Theta_{vib}/T}) = -3.02 \times 10^{-5}$$

$$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} = 3.14 \times 10^{-4}$$

$$\frac{\overline{S}}{R} = 3.5 + 15.591 + 4.679 + 3.02 \times 10^{-5} + 3.14 \times 10^{-4} = 23.77$$

The standard molar entropy of CO(g) at 298.15 K is 197.6 J·K^{-1}·mol^{-1}.

We follow the same procedure for O_2, with $\Theta_{vib} = 2256$ K and $\Theta_{rot} = 2.07$ K. Note that $g_{e1} = 3$ for O_2, so we cannot neglect the $\ln g_{e1}$ term!

$$\left(\frac{2\pi Mk_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(5.313 \times 10^{-26}\text{ kg})(1.381 \times 10^{-23}\text{ J·K}^{-1})(298.15\text{ K})}{(6.626 \times 10^{34}\text{ J·s})^2}\right]^{3/2} = 1.751 \times 10^{32}\text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314\text{ dm}^3\cdot\text{bar·mol}^{-1}\cdot\text{K}^{-1})(298.15\text{ K})}{(6.022 \times 10^{23}\text{ mol}^{-1})(1\text{ bar})} = 4.116 \times 10^{-26}\text{ m}^3$$

$$\ln\left(\frac{T}{\sigma\Theta_{rot}}\right) = 4.277$$

$$\ln(1 - e^{-\Theta_{vib}/T}) = -5.18 \times 10^{-4}$$

$$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} = 3.92 \times 10^{-3}$$

$$\ln g_{e1} = \ln 3 = 1.099$$

$$\frac{\overline{S}}{R} = 3.5 + 15.79 + 4.277 + 5.18 \times 10^{-4} + 3.92 \times 10^{-3} + 1.099 = 24.67$$

The standard molar entropy of $O_2(g)$ at 298.15 K is 205.1 J·K^{-1}·mol^{-1}.

We can calculate the entropy change for the above reaction easily using the method described in Section 21–9:

$$\Delta_r S° = 2S°[CO_2] - S°[O_2] - 2S°[CO]$$
$$= 2(213.8\text{ J·K}^{-1}\cdot\text{mol}^{-1}) - (205.1\text{ J·K}^{-1}\cdot\text{mol}^{-1}) - 2(197.6\text{ J·K}^{-1}\cdot\text{mol}^{-1})$$
$$= -172.7\text{ J·K}^{-1}\cdot\text{mol}^{-1}$$

This value is very close to that found in Problem 21–48.

21–39. Calculate the value of $\Delta_r S°$ for the reaction described by

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g)$$
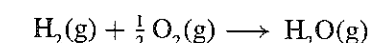
at 500 K using the data in Tables 18.2 and 18.4.

Because both H_2 and O_2 are diatomic molecules, we can write (as in the previous problem)

$$\frac{\overline{S}}{R} = \frac{7}{2} + \ln\left[\left(\frac{2\pi Mk_B T}{h^2}\right)^{3/2}\frac{\overline{V}}{N_A}\right] + \ln\frac{T}{\sigma\Theta_{rot}} - \ln(1 - e^{-\Theta_{vib}/T}) + \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} + \ln g_{e1}$$

Because both are homonuclear, $\sigma = 2$ for both H_2 and O_2. For H_2 $\Theta_{vib} = 6215$ K and $\Theta_{rot} = 85.3$ K. Then

$$\left(\frac{2\pi Mk_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(3.347 \times 10^{-27}\text{ kg})(1.381 \times 10^{-23}\text{ J·K}^{-1})(500\text{ K})}{(6.626 \times 10^{34}\text{ J·s})^2}\right]^{3/2} = 6.014 \times 10^{30}\text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314\text{ dm}^3\cdot\text{bar·mol}^{-1}\cdot\text{K}^{-1})(500\text{ K})}{(6.022 \times 10^{23}\text{ mol}^{-1})(1\text{ bar})} = 6.903 \times 10^{-26}\text{ m}^3$$

$$\ln\left(\frac{T}{\sigma\Theta_{rot}}\right) = 1.08$$

$$\ln(1 - e^{-\Theta_{vib}/T}) = -4.00 \times 10^{-6}$$

$$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} = 4.97 \times 10^{-5}$$

$$\frac{\overline{S}}{R} = 3.5 + 12.94 + 1.08 + 4.00 \times 10^{-6} + 4.97 \times 10^{-5} = 17.51$$

The standard molar entropy of H_2 at 500 K is 145.6 J·K^{-1}·mol^{-1}.

We can do the same for O_2 (with $\Theta_{vib} = 2256$ K and $\Theta_{rot} = 2.07$ K), keeping in mind that $g_{e1} = 3$:

$$\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(5.313 \times 10^{-26}\text{ kg})(1.381 \times 10^{-23}\text{ J·K}^{-1})(500\text{ K})}{(6.626 \times 10^{34}\text{ J·s})^2}\right]^{3/2} = 3.803 \times 10^{32}\text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314\text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(500\text{ K})}{(6.022 \times 10^{23}\text{ mol}^{-1})(1\text{ bar})} = 6.903 \times 10^{-26}\text{ m}^3$$

$$\ln\left(\frac{T}{\sigma\Theta_{rot}}\right) = 4.79$$

$$\ln(1 - e^{-\Theta_{vib}/T}) = -0.0110$$

$$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} = 0.0501$$

$$\ln g_{e1} = \ln 3 = 1.099$$

$$\frac{\overline{S}}{R} = 3.5 + 17.08 + 4.79 + 0.0110 + 0.0501 + 1.099 = 26.54$$

The standard molar entropy of O_2 at 500 K is 220.6 J·K^{-1}·mol^{-1}.

Because H_2O is a bent polyatomic molecule, we treat it as we did NO_2 in Problem 21–37. From Table 18.4, $\sigma = 2$, $\Theta_{rot,A} = 40.1$ K, $\Theta_{rot,B} = 20.9$ K, $\Theta_{rot,C} = 13.4$ K, $\Theta_{vib,1} = 5360$ K, $\Theta_{vib,2} = 5160$ K, and $\Theta_{vib,3} = 2290$ K. Then

$$\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi(2.991 \times 10^{-26}\text{ kg})(1.381 \times 10^{-23}\text{ J·K}^{-1})(500\text{ K})}{(6.626 \times 10^{34}\text{ J·s})^2}\right]^{3/2} = 1.607 \times 10^{32}\text{ m}^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314\text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(500\text{ K})}{(6.022 \times 10^{23}\text{ mol}^{-1})(1\text{ bar})} = 6.903 \times 10^{-26}\text{ m}^3$$

$$\frac{1}{2}\ln\left(\frac{T^3}{\Theta_{rot,A}\Theta_{rot,B}\Theta_{rot,C}}\right) = 4.66$$

$$\sum_{j=1}^{6}\ln(1 - e^{-\Theta_{vib,j}/T}) = -0.0104$$

$$\sum_{j=1}^{6}\frac{\Theta_{vib,j}}{T}\left(\frac{e^{-\Theta_{vib,j}/T}}{1 - e^{-\Theta_{vib,j}/T}}\right) = 0.048$$

The standard molar entropy is then

$$\frac{\overline{S}}{R} = 4 + \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}\frac{\overline{V}}{N_A}\right] + \ln\left(\frac{\pi^{1/2}}{\sigma}\right) + \frac{1}{2}\ln\frac{T^3}{\Theta_{rot,A}\Theta_{rot,B}\Theta_{rot,C}}$$

$$- \sum_{j=1}^{3}\ln(1 - e^{-\Theta_{vib,j}/T}) + \sum_{j=1}^{3}\left[\frac{(\Theta_{vib,j}/T)e^{-\Theta_{vib,j}/T}}{1 - e^{-\Theta_{vib,j}/T}}\right] + \ln g_{e1}$$

$$= 4 + 16.22 - 0.121 + 4.66 + 0.0104 + 0.048 = 24.82$$

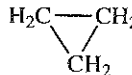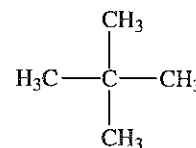which gives a value of $\overline{S} = 206.3$ J·K^{-1}·mol^{-1}.

Finally, we can calculate the value of $\Delta_r S°$ for the reaction above, as we did in the previous problem.

$$\Delta_r S° = S°[H_2O] - \tfrac{1}{2}S°[O_2] - S°[H_2]$$
$$= (206.3\text{ J·K}^{-1}\cdot\text{mol}^{-1}) - \tfrac{1}{2}(220.6\text{ J·K}^{-1}\cdot\text{mol}^{-1}) - (145.6\text{ J·K}^{-1}\cdot\text{mol}^{-1})$$
$$= -49.6\text{ J·K}^{-1}\cdot\text{mol}^{-1}$$

21–40. In each case below, predict which molecule of the pair has the greater molar entropy under the same conditions (assume gaseous species).
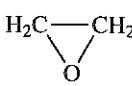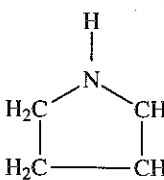
a. CO CO_2

b. $CH_3CH_2CH_3$ H_2C——CH_2 / CH_2

c. $CH_3CH_2CH_2CH_2CH_3$ H_3C—$C(CH_3)_2$—CH_3 (neopentane structure with central C bonded to four CH_3)

a. CO_2 (more atoms)

b. $CH_3CH_2CH_3$ (more flexibility)

c. $CH_3CH_2CH_2CH_2CH_3$ (more flexibility)

21–41. In each case below, predict which molecule of the pair has the greater molar entropy under the same conditions (assume gaseous species).

a. H_2O D_2O

b. CH_3CH_2OH H_2C——CH_2 / O

c. $CH_3CH_2CH_2CH_2NH_2$ pyrrolidine ring (H_2C, CH_2, H_2C, CH_2 with N—H)

a. D_2O (larger mass)

b. CH_3CH_2OH (more flexibility)

c. $CH_3CH_2CH_2CH_2NH_2$ (more flexibility)

21–42. Arrange the following reactions according to increasing values of $\Delta_r S°$ (do not consult any references).

a. $S(s) + O_2(g) \longrightarrow SO_2(g)$

b. $H_2(g) + O_2(g) \longrightarrow H_2O_2(l)$

c. $CO(g) + 3H_2(g) \longrightarrow CH_4(g) + H_2O(l)$

d. $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$

Recall that molar entropies of solids and liquids are much smaller than those of gases, so we can ignore the contribution of the solids and liquids to $\Delta_r S°$ when we order these reactions. Considering only the gaseous products and reactants, we can find Δn for each reaction to be

  a. $\Delta n = 0$ b. $\Delta n = -2$ c. $\Delta n = -3$ d. $\Delta n = +1$
The correct ordering of the reactions is therefore $\mathbf{d} > \mathbf{a} > \mathbf{b} > \mathbf{c}$.

21–43. Arrange the following reactions according to increasing values of $\Delta_r S°$ (do not consult any references).

  a. $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$
  b. $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$
  c. $K(s) + O_2(g) \longrightarrow KO_2(s)$
  d. $N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$

Again, calculating Δn for each reaction for the gaseous products and reactants gives

  a. $\Delta n = -3$ b. $\Delta n = -2$ c. $\Delta n = -1$ d. $\Delta n = -2$
The correct ordering of the reactions is therefore $\mathbf{c} > \mathbf{b} \approx \mathbf{d} > \mathbf{a}$.

21–44. In Problem 21–40, you are asked to predict which molecule, $CO(g)$ or $CO_2(g)$, has the greater molar entropy. Use the data in Tables 18.2 and 18.4 to calculate the standard molar entropy of $CO(g)$ and $CO_2(g)$ at 298.15 K. Does this calculation confirm your intuition? Which degree of freedom makes the dominant contribution to the molar entropy of CO? Of CO_2?

In Problem 21–38 and Example 21–5, we used the data in Tables 18.2 and 18.4 to find that the standard molar entropy of $CO(g)$ is $197.6\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ and that of $CO_2(g)$ is $213.8\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. In both cases, the translational degrees of freedom make the dominant contribution to the molar entropy.

21–45. Table 21.2 gives $\overline{S}°[CH_3OH(l)] = 126.8\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ at 298.15 K. Given that $T_{\mathrm{vap}} = 337.7$ K, $\Delta_{\mathrm{vap}}\overline{H}(T_b) = 36.5\ \mathrm{kJ\cdot mol^{-1}}$, $\overline{C}_P[CH_3OH(l)] = 81.12\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, and $\overline{C}_P[CH_3OH(g)] = 43.8\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, calculate the value of $\overline{S}°[CH_3OH(g)]$ at 298.15 K and compare your answer with the experimental value of $239.8\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

This is done in the same way as $\overline{S}°[Br_2(g)]$ was found in Section 21–7. First, we heat the methanol to its boiling point:

$$\Delta\overline{S}_1 = \overline{S}^l(337.7\ \mathrm{K}) - \overline{S}^l(298.15\ \mathrm{K}) = \overline{C}_P^l \ln\frac{T_2}{T_1}$$

$$= (81.12\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}) \ln\frac{337.7}{298.15} = 10.10\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

Then vaporize the methanol at its normal boiling point:

$$\Delta\overline{S}_2 = \overline{S}^g(337.7\ \mathrm{K}) - \overline{S}^l(337.7\ \mathrm{K}) = \frac{\Delta_{\mathrm{vap}}\overline{H}}{T_{\mathrm{vap}}}$$

$$= \frac{36\,500\ \mathrm{J\cdot mol^{-1}}}{337.7\ \mathrm{K}} = 108.1\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

Finally, cool the gas back down to 298.15 K:

$$\Delta\overline{S}_3 = \overline{S}^g(298.15\ \mathrm{K}) - \overline{S}^g(337.7\ \mathrm{K}) = \overline{C}_P^g \ln\frac{T_2}{T_1}$$

$$= (43.8\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}) \ln\frac{298.15}{337.7} = -5.456\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

The sum of these three steps plus $\overline{S}_{298}°[CH_3OH(l)] = 126.8\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ will be the desired value:

$$\overline{S}_{298}°[CH_3OH(g)] = \overline{S}_{298}°[CH_3OH(l)] + \Delta\overline{S}_1 + \Delta\overline{S}_2 + \Delta\overline{S}_3$$
$$= 239.5\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

which is within 0.1% of the experimental value.

21–46. Given the following data, $T_{\mathrm{vap}} = 373.15$ K, $\Delta\overline{H}_{\mathrm{vap}}(T_{\mathrm{vap}}) = 40.65\ \mathrm{kJ\cdot mol^{-1}}$, $\overline{C}_P[H_2O(l)] = 75.3\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, and $\overline{C}_P[H_2O(g)] = 33.8\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, show that the values of $\overline{S}°[H_2O(l)]$ and $\overline{S}°[H_2O(g)]$ in Table 21.2 are consistent.

This is done in the same way as Problem 21–45. First, we heat the water to its boiling point:

$$\Delta\overline{S}_1 = \overline{S}^l(373.15\ \mathrm{K}) - \overline{S}^l(298.15\ \mathrm{K}) = \overline{C}_P^l \ln\frac{T_2}{T_1}$$

$$= (75.3\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}) \ln\frac{373.15}{298.15} = 16.90\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

Then vaporize the water at its normal boiling point:

$$\Delta\overline{S}_2 = \overline{S}^g(373.15\ \mathrm{K}) - \overline{S}^l(373.15\ \mathrm{K}) = \frac{\Delta_{\mathrm{vap}}\overline{H}}{T_{\mathrm{vap}}}$$

$$= \frac{40\,650\ \mathrm{J\cdot mol^{-1}}}{373.15\ \mathrm{K}} = 108.9\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

Finally, cool the gas back down to 298.15 K:

$$\Delta\overline{S}_3 = \overline{S}^g(298.15\ \mathrm{K}) - \overline{S}^g(373.15\ \mathrm{K}) = \overline{C}_P^g \ln\frac{T_2}{T_1}$$

$$= (33.8\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}) \ln\frac{298.15}{373.15} = -7.584\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

The sum of these three steps plus $S_{298}°[H_2O(l)] = 70.0\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ will be the desired value:

$$\overline{S}_{298}°[H_2O(g)] = \overline{S}_{298}°[H_2O(l)] + \Delta\overline{S}_1 + \Delta\overline{S}_2 + \Delta\overline{S}_3$$
$$= 188.2\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

which is within 0.4% of the value in Table 21.2.

21–47. Use the data in Table 21.2 to calculate the value of $\Delta_r S°$ for the following reactions at 25°C and one bar.

  a. $C(s, \text{graphite}) + O_2(g) \longrightarrow CO_2(g)$
  b. $CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$
  c. $C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g)$

  a. $\Delta_r S° = S°[\text{products}] - S°[\text{reactants}]$
    $= 213.8\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}} - 205.2\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}} - 5.74\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$
    $= 2.86\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$

b. $\Delta_r S^\circ = S^\circ[\text{products}] - S^\circ[\text{reactants}]$

$= 2(70.0\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) + 213.8\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 2(205.2\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) - 186.3\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

$= -242.9\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

c. $\Delta_r S^\circ = S^\circ[\text{products}] - S^\circ[\text{reactants}]$

$= 219.6\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 130.7\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 200.9\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

$= -112.0\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

21–48. Use the data in Table 21.2 to calculate the value of $\Delta_r S^\circ$ for the following reactions at 25°C and one bar.

a. $CO(g) + 2\,H_2(g) \longrightarrow CH_3OH(l)$

b. $C(s, \text{graphite}) + H_2O(l) \longrightarrow CO(g) + H_2(g)$

c. $2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$

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a. $\Delta_r S^\circ = S^\circ[\text{products}] - S^\circ[\text{reactants}]$

$= 126.8\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 197.7\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 2(130.7\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$

$= -332.3\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

b. $\Delta_r S^\circ = S^\circ[\text{products}] - S^\circ[\text{reactants}]$

$= 130.7\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 197.7\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 70.0\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 5.74\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

$= 252.66\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

c. $\Delta_r S^\circ = S^\circ[\text{products}] - S^\circ[\text{reactants}]$

$= 2(213.8\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) - 205.2\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 2(197.7\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$

$= -173.0\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

Helmholtz and Gibbs Energies

PROBLEMS AND SOLUTIONS

22–1. The molar enthalpy of vaporization of benzene at its normal boiling point (80.09°C) is 30.72 kJ·mol^{-1}. Assuming that $\Delta_{vap}\overline{H}$ and $\Delta_{vap}\overline{S}$ stay constant at their values at 80.09°C, calculate the value of $\Delta_{vap}\overline{G}$ at 75.0°C, 80.09°C, and 85.0°C. Interpret these results physically.

We can write (as in Section 22–2)

$$\Delta_{vap}\overline{G} = \Delta_{vap}\overline{H} - T\Delta_{vap}\overline{S}$$

At the boiling point of benzene, the liquid and vapor phases are in equilibrium, so $\Delta_{vap}\overline{G} = 0$. Thus, at 80.09°C,

$$0 = 30.72\,\text{kJ}\cdot\text{mol}^{-1} - (353.24\,\text{K})\Delta_{vap}\overline{S}$$

$$\Delta_{vap}\overline{S} = 86.97\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Since $\Delta_{vap}\overline{H}$ and $\Delta_{vap}\overline{S}$ are assumed to stay constant at their boiling-point values, we know their numerical values and can substitute into our first equation:

$$\Delta_{vap}\overline{G}(75.0°C) = 30.72\,\text{kJ}\cdot\text{mol}^{-1} - (348.15\,\text{K})(86.97\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 441.4\,\text{J}\cdot\text{mol}^{-1}$$

$$\Delta_{vap}\overline{G}(85.0°C) = 30.72\,\text{kJ}\cdot\text{mol}^{-1} - (358.15\,\text{K})(86.97\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = -428.3\,\text{J}\cdot\text{mol}^{-1}$$

From these values, we can see that at 75.0°C benzene will spontaneously condense, whereas at 85.0°C it will spontaneously evaporate (just as we would expect).

22–2. Redo Problem 22–1 without assuming that $\Delta_{vap}\overline{H}$ and $\Delta_{vap}\overline{S}$ do not vary with temperature. Take the molar heat capacities of liquid and gaseous benzene to be 136.3 J·K^{-1}·mol^{-1} and 82.4 J·K^{-1}·mol^{-1}, respectively. Compare your results with those you obtained in Problem 22–1. Are any of your physical interpretations different?

We wish to consider the temperature variation of $\Delta_{vap}\overline{G}$, so we must use Equation 22.31a,

$$\left(\frac{\partial \Delta_{vap}\overline{G}}{\partial T}\right)_P = -\Delta_{vap}\overline{S}(T)$$