We will need the following values from Table 19.2:

$$\Delta_f H^\circ[\mathrm{CO_2(g)}] = -393.509\ \mathrm{kJ\cdot mol^{-1}} \qquad \Delta_f H^\circ[\mathrm{H_2O(l)}] = -285.83\ \mathrm{kJ\cdot mol^{-1}}$$
$$\Delta_f H^\circ[\mathrm{N_2H_4(l)}] = +50.6\ \mathrm{kJ\cdot mol^{-1}} \qquad \Delta_f H^\circ[\mathrm{CH_3OH(l)}] = -239.1\ \mathrm{kJ\cdot mol^{-1}}$$
$$\Delta_f H^\circ[\mathrm{N_2(g)}] = 0$$

a. Using Hess's law,

$$\begin{aligned}\Delta_r H^\circ &= \sum \Delta_f H^\circ[\text{products}] - \sum \Delta_f H^\circ[\text{reactants}]\\ &= 2(-285.83\ \mathrm{kJ}) + (-393.5\ \mathrm{kJ}) - (-239.1\ \mathrm{kJ})\\ &= \left(\frac{-726.1\ \mathrm{kJ}}{\text{mol methanol}}\right)\left(\frac{1\ \mathrm{mol}}{32.042\ \mathrm{g}}\right) = -22.7\ \mathrm{kJ\cdot g^{-1}}\end{aligned}$$

b. Again, by Hess's law,

$$\begin{aligned}\Delta_r H^\circ &= \sum \Delta_f H^\circ[\text{products}] - \sum \Delta_f H^\circ[\text{reactants}]\\ &= 2(-285.83\ \mathrm{kJ}) - (+50.6\ \mathrm{kJ})\\ &= \left(\frac{-622.3\ \mathrm{kJ}}{\mathrm{mol\ N_2H_4}}\right)\left(\frac{1\ \mathrm{mol}}{32.046\ \mathrm{g}}\right) = -19.4\ \mathrm{kJ\cdot g^{-1}}\end{aligned}$$

More energy per gram is produced by combusting methanol.

19–40. Using Table 19.2, calculate the heat required to vaporize 1.00 mol of $\mathrm{CCl_4(l)}$ at 298 K.

$$\mathrm{CCl_4(l)} \longrightarrow \mathrm{CCl_4(g)}$$

We can subtract $\Delta_f H^\circ[\mathrm{CCl_4(l)}]$ from $\Delta_f H^\circ[\mathrm{CCl_4(g)}]$ to find the heat required to vaporize $\mathrm{CCl_4}$:

$$\Delta_{\text{vap}} H^\circ = -102.9\ \mathrm{kJ} + 135.44\ \mathrm{kJ} = 32.5\ \mathrm{kJ}$$

19–41. Using the $\Delta_f H^\circ$ data in Table 19.2, calculate the values of $\Delta_r H^\circ$ for the following:

a. $\mathrm{C_2H_4(g) + H_2O(l) \longrightarrow C_2H_5OH(l)}$

b. $\mathrm{CH_4(g) + 4\,Cl_2(g) \longrightarrow CCl_4(l) + 4\,HCl(g)}$

In each case, state whether the reaction is endothermic or exothermic.

a. Using Hess's law,

$$\Delta_r H^\circ = -277.69\ \mathrm{kJ} - (-285.83\ \mathrm{kJ} + 52.28\ \mathrm{kJ}) = -44.14\ \mathrm{kJ}$$

This reaction is exothermic.

b. Again, by Hess's law,

$$\Delta_r H^\circ = 4(-92.31\ \mathrm{kJ}) - 135.44\ \mathrm{kJ} - (-74.81\ \mathrm{kJ}) = -429.87\ \mathrm{kJ}$$

This reaction is also exothermic.

19–42. Use the following data to calculate the value of $\Delta_{\text{vap}} H^\circ$ of water at 298 K and compare your answer to the one you obtain from Table 19.2: $\Delta_{\text{vap}} H^\circ$ at 373 K $= 40.7\ \mathrm{kJ\cdot mol^{-1}}$; $\overline{C}_P(\mathrm{l}) = 75.2\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$; $\overline{C}_P(\mathrm{g}) = 33.6\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$.

We can create a figure similar to Figure 19.10 to illustrate this reaction:

$$\begin{tikzcd}
H_2O(l) \arrow[r, "\Delta_{vap}H^\circ{,}373\text{ K}"] & H_2O(g) \arrow[d, "\Delta H_3"] \\
H_2O(l) \arrow[u, "\Delta H_2"] \arrow[r, "\Delta_{vap}H^\circ{,}298\text{ K}"] & H_2O(g)
\end{tikzcd}$$

Now we use Hess's Law to determine the enthalpy of vaporization.

$$\begin{aligned}
\Delta_{vap}H^\circ_{298\text{ K}} &= \Delta H_2 + \Delta H_3 + \Delta_{vap}H^\circ_{373\text{ K}} \\
&= (75\text{ K})(75.2\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) + (-75\text{ K})(33.6\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) + 40.7\text{ kJ}\cdot\text{mol}^{-1} \\
&= 43.8\text{ kJ}\cdot\text{mol}^{-1}
\end{aligned}$$

Using Table 19.2, we find

$$\begin{aligned}
\Delta_{vap}H^\circ &= \Delta_f H^\circ[H_2O(g)] - \Delta_f H^\circ[H_2O(l)] \\
&= -241.8\text{ kJ}\cdot\text{mol}^{-1} + 285.83\text{ kJ}\cdot\text{mol}^{-1} = 44.0\text{ kJ}\cdot\text{mol}^{-1}
\end{aligned}$$

These values are fairly close. (Using values of $\overline{C}_P$ which include temperature-dependent terms may further improve the agreement.)

19–43. Use the following data and the data in Table 19.2 to calculate the standard reaction enthalpy of the water-gas reaction at 1273 K. Assume that the gases behave ideally under these conditions.

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

$$\begin{aligned}
C^\circ_P[CO(g)]/R &= 3.231 + (8.379 \times 10^{-4}\text{ K}^{-1})T - (9.86 \times 10^{-8}\text{ K}^{-2})T^2 \\
C^\circ_P[H_2(g)]/R &= 3.496 + (1.006 \times 10^{-4}\text{ K}^{-1})T + (2.42 \times 10^{-7}\text{ K}^{-2})T^2 \\
C^\circ_P[H_2O(g)]/R &= 3.652 + (1.156 \times 10^{-3}\text{ K}^{-1})T + (1.42 \times 10^{-7}\text{ K}^{-2})T^2 \\
C^\circ_P[C(s)]/R &= -0.6366 + (7.049 \times 10^{-3}\text{ K}^{-1})T - (5.20 \times 10^{-6}\text{ K}^{-2})T^2 \\
&\quad + (1.38 \times 10^{-9}\text{ K}^{-3})T^3
\end{aligned}$$

We can create a figure similar to Figure 19.10 to illustrate this reaction.

$$\begin{tikzcd}
C(s) + H_2O(g) \arrow[r, "\Delta_r H^\circ{,}1273\text{ K}"] \arrow[d, "\Delta H_1"] & CO(g) + H_2(g) \\
C(s) + H_2O(g) \arrow[r, "\Delta_r H^\circ{,}298\text{ K}"] & CO(g) + H_2(g) \arrow[u, "\Delta H_2"]
\end{tikzcd}$$

Now use Hess's Law to calculate the standard reaction enthalpy at 1273 K. To do the integrals, it is helpful to use a program like *Excel* or *Mathematica* (I used *Mathematica*), so that the tedium of adding and multiplying can be avoided.

$$\begin{aligned}
\Delta_r H^\circ_{1273} &= \Delta_r H^\circ_{298} + \Delta H_1 + \Delta H_2 \\
&= (-110.5\text{ kJ}\cdot\text{mol}^{-1} + 241.8\text{ kJ}\cdot\text{mol}^{-1}) \\
&\qquad + R\int_{298}^{1273}\left\{\overline{C}_P[CO(g)] + \overline{C}_P[H_2(g)] - \overline{C}_P[H_2O(g)] - \overline{C}_P[C(s)]\right\}dT \\
&= 131.3\text{ kJ}\cdot\text{mol}^{-1} + R[3725.01\text{ K} + 3649.92\text{ K} - 4542.43\text{ K} - 2151.29\text{ K}] \\
&= 131.3\text{ kJ}\cdot\text{mol}^{-1} + 5.664\text{ kJ}\cdot\text{mol}^{-1} = 136.964\text{ kJ}\cdot\text{mol}^{-1}
\end{aligned}$$

20–8. Calculate the value of ΔS if one mole of an ideal gas is expanded reversibly and isothermally from 10.0 dm^3 to 20.0 dm^3. Explain the sign of ΔS.

For an isothermal reaction of an ideal gas, $\delta w = -\delta q$, so $\delta q = P dV$. Then

$$\Delta S = \int \frac{\delta q_{\text{rev}}}{T} = \int \frac{P}{T} dV$$

Using T from the ideal gas equation gives

$$\Delta S = \int \frac{nR}{V} dV = nR \ln 2.00 = 5.76\ \text{J}\cdot\text{K}^{-1}$$

The value of ΔS is positive because the gas is expanding.

20–9. Calculate the value of ΔS if one mole of an ideal gas is expanded reversibly and isothermally from 1.00 bar to 0.100 bar. Explain the sign of ΔS.

As in the previous problem, because the reaction is isothermal, $\delta q = P dV$. For an ideal gas,

$$dV = -\frac{nRT}{P^2} dP = -\frac{V}{P} dP$$

so we write ΔS as

$$\Delta S = \int \frac{P}{T} dV = \int -\frac{V}{T} dP = \int -\frac{nR}{P} dP = -nR \ln 0.1 = 19.1\ \text{J}\cdot\text{K}^{-1}$$

The value of ΔS is positive because the gas expands.

20–10. Calculate the values of q_{rev} and ΔS along the path D + E in Figure 20.3 for one mole of a gas whose equation of state is given in Example 20–2. Compare your result with that obtained in Example 20–2.

Path D + E is the path described by $(P_1, V_1, T_1) \rightarrow (P_1, V_2, T_3) \rightarrow (P_2, V_2, T_1)$. For the first step,

$$\delta q_{\text{rev}} = dU - \delta w = C_V(T) dT - P dV$$

and for the second step (because the volume remains constant)

$$\delta q_{\text{rev}} = dU = C_V(T) dT$$

Then

$$\begin{aligned}\int \delta q_{\text{rev,D+E}} &= \int_{T_1}^{T_3} C_V(T) dT - \int_{V_1}^{V_2} P_1 dV + \int_{T_3}^{T_1} C_V(T) dT \\ &= -\int_{V_1}^{V_2} P_1 dV = -P_1(V_2 - V_1)\end{aligned}$$

and

$$\Delta S_{\text{rev,D+E}} = -\int_{V_1}^{V_2} \frac{P_1}{T} dV$$

This is (by no coincidence) the same value as that found for ΔS_A, ΔS_{B+C}, and ΔS_{D+E}.

20–13. Show that

$$\Delta S = C_P \ln \frac{T_2}{T_1}$$

for a constant-pressure process if C_P is independent of temperature. Calculate the change in entropy of 2.00 moles of $H_2O(l)$ ($\overline{C}_P = 75.2 \text{ J·K}^{-1}\text{·mol}^{-1}$) if it is heated from 10°C to 90°C.

Because ΔS is a state function, we can calculate it using a reversible process. For a constant-pressure reversible process (Equation 19.37), $\delta q_{\text{rev}} = dH = C_P dT$, and so

$$\Delta S = \frac{q_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{C_P}{T} dT = n\overline{C}_P \ln\left(\frac{T_2}{T_1}\right)$$

For 2.00 mol of H_2O,

$$\Delta S = (2.00 \text{ mol})(75.2 \text{ J·K}^{-1}\text{·mol}^{-1}) \ln \frac{363}{283} = 37.4 \text{ J·K}^{-1}$$

20–14. Show that

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

if one mole of an ideal gas is taken from T_1, V_1 to T_2, V_2, assuming that $\overline{C}_V$ is independent of temperature. Calculate the value of $\Delta\overline{S}$ if one mole of $N_2(g)$ is expanded from 20.0 dm^3 at 273 K to 300 dm^3 at 400 K. Take $\overline{C}_P = 29.4 \text{ J·K}^{-1}\text{·mol}^{-1}$.

For the path $(T_1, V_1) \rightarrow (T_2, V_2)$, $\delta w = -PdV$ and $\delta q = dU - \delta w = C_V dT + PdV$. We can then write $\Delta\overline{S}$ as

$$\begin{aligned}\Delta\overline{S} &= \frac{1}{n}\left(\int \frac{C_V}{T} dT + \int \frac{P}{T} dV\right)\\ &= \int \frac{\overline{C}_V}{T} dT + \int \frac{R}{V} dV\\ &= \overline{C}_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}\end{aligned}$$

Because $\overline{C}_P - \overline{C}_V = R$ for an ideal gas, we can write this as

$$\Delta\overline{S} = (\overline{C}_P - R) \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

For N_2,

$$\begin{aligned}\Delta\overline{S} &= (29.4 \text{ J·mol}^{-1}\text{·K}^{-1} - 8.314 \text{ J·K}^{-1}\text{·mol}^{-1}) \ln \frac{400}{273} + 8.314 \text{ J·K}^{-1}\text{·mol}^{-1} \ln \frac{300}{20.0}\\ &= 30.6 \text{ J·K}^{-1}\text{·mol}^{-1}\end{aligned}$$

for an isothermal process. What does this equation say about the sign of ΔS? Can ΔS decrease in a reversible isothermal process? Calculate the entropy change when one mole of an ideal gas is compressed reversibly and isothermally from a volume of 100 dm^3 to 50.0 dm^3 at 300 K.

We defined ΔS as (Equation 20.22)

$$\Delta S \geq \int \frac{\delta q}{T}$$

For an isothermal process T is constant, so we can write this expression as

$$\Delta S \geq \frac{1}{T} \int \delta q$$

and integrate over δq to write

$$\Delta S \geq \frac{q}{T}$$

We know that q can be positive or negative, while T is always positive; therefore, ΔS can be positive or negative for an isothermal process. For one mole of an ideal gas compressed reversibly and isothermally, $dU = 0$, so $\delta q_{\text{rev}} = -\delta w = P dV$. Then

$$\delta q_{\text{rev}} = P dV = \frac{nRT}{V} dV$$

$$q_{\text{rev}} = nRT \ln \frac{V_2}{V_1}$$

and the change in entropy is given by

$$\Delta S = nR \ln \frac{V_2}{V_1} = (1 \text{ mol})(8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) \ln 0.5 = -5.76 \text{ J}\cdot\text{K}^{-1}$$

The quantity ΔS is equal to q/T, rather than greater than it, because this is a reversible process.

20–18. Vaporization at the normal boiling point (T_{vap}) of a substance (the boiling point at one atm) can be regarded as a reversible process because if the temperature is decreased infinitesimally below T_{vap}, all the vapor will condense to liquid, whereas if it is increased infinitesimally above T_{vap}, all the liquid will vaporize. Calculate the entropy change when two moles of water vaporize at 100.0°C. The value of $\Delta_{\text{vap}}\overline{H}$ is 40.65 kJ·mol^{-1}. Comment on the sign of $\Delta_{\text{vap}}S$.

At constant pressure and temperature, $q_{\text{rev}} = n\Delta\overline{H}_{\text{rev}}$ (Equation 19.37). We know from the previous problem that, for a reversible isothermal process,

$$\Delta S = \frac{q}{T} = \frac{(2 \text{ mol})(40.65 \text{ kJ}\cdot\text{mol}^{-1})}{373.15 \text{ K}} = 217.9 \text{ J}\cdot\text{K}^{-1}$$

As the water becomes more disordered, changing from liquid to gas, the entropy increases.

20–19. Melting at the normal melting point (T_{fus}) of a substance (the melting point at one atm) can be regarded as a reversible process because if the temperature is changed infinitesimally from exactly T_{fus}, then the substance will either melt or freeze. Calculate the change in entropy when two moles of water melt at 0°C. The value of $\Delta_{\text{fus}}\overline{H}$ is 6.01 kJ·mol^{-1}. Compare your answer with the one you obtained in Problem 20–18. Why is $\Delta_{\text{vap}}S$ much larger than $\Delta_{\text{fus}}S$?

Because this is an isothermal reversible expansion, $\delta q = -\delta w = PdV$. We then use the ideal gas equation to write

$$\Delta S_{\text{sys}} = \int \frac{\delta q_{\text{rev}}}{T} = \int \frac{P}{T} dV = \int \frac{nR}{V} dV = nR \ln \frac{V_2}{V_1}$$

For an isothermal expansion of an ideal gas, $P_1 V_1 = P_2 V_2$. We can then write the change of entropy of the gas as

$$\Delta S_{\text{sys}} = (1 \text{ mol})(8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \ln 5.00 = +13.4 \text{ J}\cdot\text{K}^{-1}$$

For a reversible expansion, $\Delta S_{\text{tot}} = 0$, so $\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} = -13.4 \text{ J}\cdot\text{K}^{-1}$.

20–26. Redo Problem 20–25 for an expansion into a vacuum, with an initial pressure of 10.0 bar and a final pressure of 2.00 bar.

As in Problem 20–25, $\Delta S_{\text{sys}} = 13.4 \text{ J}\cdot\text{K}^{-1}$. However, because this is an irreversible expansion into a vacuum, $\Delta S_{\text{surr}} = 0$, so $\Delta S_{\text{tot}} = 13.4 \text{ J}\cdot\text{K}^{-1}$.

20–27. The molar heat capacity of 1-butene can be expressed as

$$\overline{C}_P(T)/R = 0.05641 + (0.04635 \text{ K}^{-1})T - (2.392 \times 10^{-5} \text{ K}^{-2})T^2 + (4.80 \times 10^{-9} \text{ K}^{-3})T^3$$

over the temperature range $300 \text{ K} < T < 1500 \text{ K}$. Calculate the change in entropy when one mole of 1-butene is heated from 300 K to 1000 K at constant pressure.

At constant pressure, $\delta q = dH = n\overline{C}_P dT$. Then Equation 20.22 becomes (assuming a reversible process)

$$\begin{aligned}\Delta S &= n \int_{300}^{1000} \frac{\overline{C}_P}{T} dT \\ &= (1 \text{ mol}) R \int_{300}^{1000} \left[0.05641 T^{-1} + (0.04635 \text{ K}^{-1}) - (2.392 \times 10^{-5} \text{ K}^{-2})T \right. \\ &\qquad \left. + (4.80 \times 10^{-9} \text{ K}^{-3})T^2\right] dT \\ &= 192.78 \text{ J}\cdot\text{K}^{-1}\end{aligned}$$

20–28. Plot $\Delta_{\text{mix}}\overline{S}$ against y_1 for the mixing of two ideal gases. At what value of y_1 is $\Delta_{\text{mix}}\overline{S}$ a maximum? Can you give a physical interpretation of this result?

We can use Equation 20.30 for two gases:

$$\Delta_{\text{mix}}\overline{S} = -R\left(y_1 \ln y_1 - y_2 \ln y_2\right)$$

Because $y_1 + y_2 = 1$, we can write this as

$$\Delta_{\text{mix}}\overline{S}/R = -y_1 \ln y_1 - (1 - y_1) \ln(1 - y_1)$$

20–38. Consider one mole of an ideal gas confined to a volume V. Calculate the probability that all the N_A molecules of this ideal gas will be found to occupy one half of this volume, leaving the other half empty.

From Problem 20–35, we can write the probability as

$$\left(\frac{\frac{1}{2}V}{V}\right)^{N_A} = \left(\frac{1}{2}\right)^{N_A} \approx 0$$

20–39. Show that S_{system} given by Equation 20.40 is a maximum when all the p_j are equal. Remember that $\sum p_j = 1$, so that

$$\begin{aligned}\sum_j p_j \ln p_j &= p_1 \ln p_1 + p_2 \ln p_2 + \cdots + p_{n-1} \ln p_{n-1}\\ &\quad + (1 - p_1 - p_2 - \cdots - p_{n-1}) \ln(1 - p_1 - p_2 - \cdots - p_{n-1})\end{aligned}$$

See also Problem J–10.

Begin with Equation 20.40,

$$S_{\text{system}} = -k_B \sum_j p_j \ln p_j$$

Substituting the expression given for $\sum_j p_j \ln p_j$, we find

$$\begin{aligned}S_{\text{system}} &= -k_B \left[p_1 \ln p_1 + p_2 \ln p_2 + \cdots + p_{n-1} \ln p_{n-1}\right.\\ &\quad \left.+ (1 - p_1 - p_2 - \cdots - p_{n-1}) \ln(1 - p_1 - p_2 - \cdots - p_{n-1})\right]\\ \frac{\partial S_{\text{system}}}{\partial p_j} &= \ln p_j + 1 - \ln(1 - p_1 - \cdots - p_{j-1} - p_{j+1} - \cdots - p_{n-1}) - 1\\ 0 &= \ln p_j - \ln(1 - p_1 - \cdots - p_{j-1} - p_{j+1} - \cdots - p_{n-1})\\ p_j &= 1 - p_1 - \cdots - p_{j-1} - p_{j+1} - \cdots - p_{n-1}\end{aligned}$$

Because p_j can be any of p_1 to p_{n-1}, and the above equality holds for all p_j, all the p_j must be equal.

20–40. Use Equation 20.45 to calculate the molar entropy of krypton at 298.2 K and one bar, and compare your result with the experimental value of $164.1\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

This problem is like Example 20–6. We use Equation 20.45,

$$\overline{S} = \frac{5}{2}R + R \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{\overline{V}}{N_A}\right]$$

Assuming ideal behavior, at 298.2 K and one bar

$$\begin{aligned}\frac{N_A}{\overline{V}} &= \frac{N_A P}{RT}\\ &= \frac{(6.022 \times 10^{23}\ \text{mol}^{-1})(1\ \text{bar})}{(0.08314\ \text{dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298.2\ \text{K})}\\ &= 2.429 \times 10^{22}\ \text{dm}^{-3} = 2.429 \times 10^{25}\ \text{m}^{-3}\end{aligned}$$

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 $\Delta_{\text{vap}}\overline{S} \approx 88\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ 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	$t_{\text{fus}}/^\circ\text{C}$	$t_{\text{vap}}/^\circ\text{C}$	$\Delta_{\text{fus}}\overline{H}/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{vap}}\overline{H}/\text{kJ}\cdot\text{mol}^{-1}$
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,

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

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

Substance	$\Delta_{\text{vap}}\overline{S}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
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 $\Delta_{\text{fus}}\overline{S}$ for each substance.

21–18. Use the following data to calculate the standard molar entropy of cyclopropane at 298.1 K.

$$C_P^\circ[\mathrm{C_3H_6(s)}]/R = -1.921 + (0.1508\ \mathrm{K^{-1}})T - (9.670\times10^{-4}\ \mathrm{K^{-2}})T^2 + (2.694\times10^{-6}\ \mathrm{K^{-3}})T^3$$

$$15\ \mathrm{K} \le T \le 145.5\ \mathrm{K}$$

$$C_P^\circ[\mathrm{C_3H_6(l)}]/R = 5.624 + (4.493\times10^{-2}\ \mathrm{K^{-1}})T - (1.340\times10^{-4}\ \mathrm{K^{-2}})T^2$$

$$145.5\ \mathrm{K} \le T \le 240.3\ \mathrm{K}$$

$$C_P^\circ[\mathrm{C_3H_6(g)}]/R = -1.793 + (3.277\times10^{-2}\ \mathrm{K^{-1}})T - (1.326\times10^{-5}\ \mathrm{K^{-2}})T^2$$

$$240.3\ \mathrm{K} \le T \le 1000\ \mathrm{K}$$

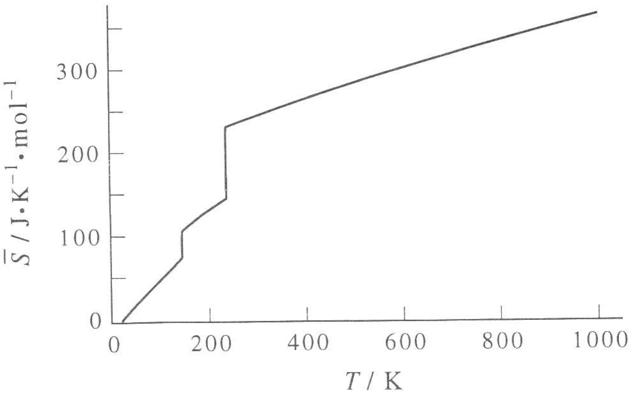
$T_{\mathrm{fus}} = 145.5$ K, $T_{\mathrm{vap}} = 240.3$ K, $\Delta_{\mathrm{fus}}\overline{H} = 5.44\ \mathrm{kJ\cdot mol^{-1}}$, $\Delta_{\mathrm{vap}}\overline{H} = 20.05\ \mathrm{kJ\cdot mol^{-1}}$, and $\Theta_{\mathrm{D}} =$ 130 K. The correction for nonideality $= 0.54\ \mathrm{J\cdot K^{-1}\cdot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

$$\begin{aligned}\overline{S}(T) = {} & \int_0^{15} \frac{12\pi^4}{5T} R\left(\frac{T}{\Theta_{\mathrm{D}}}\right)^3 dT + \int_{15}^{145.5} \frac{\overline{C}_P[\mathrm{C_3H_6(s)}]}{T} dT + \frac{\Delta_{\mathrm{fus}}\overline{H}}{145.5\ \mathrm{K}} \\ & + \int_{145.5}^{240.3} \frac{\overline{C}_P[\mathrm{C_3H_6(l)}]}{T} dT + \frac{\Delta_{\mathrm{vap}}\overline{H}}{240.3\ \mathrm{K}} + \int_{240.3}^{298.1} \frac{\overline{C}_P[\mathrm{C_3H_6(g)}]}{T} dT \\ & + \text{correction} \\ = {} & 0.995\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}} + 66.1\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}} + 37.4\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}} \\ & + 38.5\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}} + 83.4\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}} + 10.8\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}} \\ & + 0.54\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}} \\ = {} & 237.8\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}\end{aligned}$$

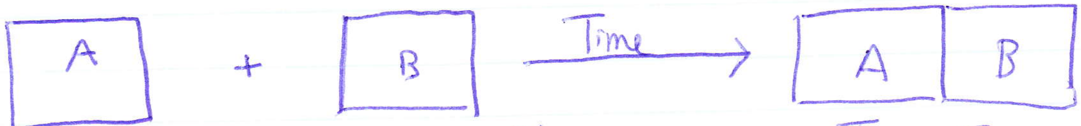
This compares very well with the literature value of $237.5\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

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.



①

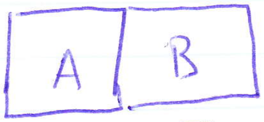


$C_A = 1000\ J/K$ $\quad$ $C_B = 500\ J/K$ $\quad$ $T_{f,A} = T_{f,B}$

$T_{i,A} = 10°C$ $\quad$ $T_{i,B} = 40°C$ $\quad$ "thermal equil"

same final T

Just after placing blocks together:



$T_{i,A} = 10°C$ $\quad$ $T_{i,B} = 40°C$

$T_{f,A} > T_{i,A}$ $\quad$ $T_{f,B} < T_{i,B}$

$\longleftarrow$

heat flow

In McQuarrie:

19: 41, 43

20: 8, 14, 18, 27, 38

21: 10, 18

So $-q_B = q_A$ ← A gains it.

↗ B loses heat

$$-q_B = q_A$$
$$-C_B \Delta T = +C_A \Delta T$$
$$-C_B(T_f - T_{i,B}) = +C_A(T_f - T_{i,A})$$
$$-C_B T_f + C_B T_{i,B} = C_A T_f - C_A T_{i,A}$$
$$T_f\ (C_A + C_B) = C_A T_{i,A} + C_B T_{i,B}$$

$$T_f = \frac{C_A T_{i,A} + C_B T_{i,B}}{(C_A + C_B)}$$

$$T_f = \frac{(1000\ J/K)(283.15\ K) + (500\ J/K)(313.15\ K)}{(1000 + 500)\ J/K}$$

$$\boxed{T_f = \underset{\uparrow\,K}{293.15} = 20°C}$$

Entropy:

$dS = \frac{\delta q_{rev}}{T}$ → No work done so $\delta q = C\,dT$

$$\int_{S_i}^{S_f} dS = \int_{T_i}^{T_f} \frac{C\,dT}{T} \longrightarrow \Delta S = C \ln(T_f/T_i)$$

$\Delta S_A = (1000\ J/K) \cdot \ln(293.15/283.15) = +34.7\ J/K$

$\Delta S_B = (500\ J/K) \cdot \ln(293.15/313.15) = -32.9\ J/K$

$\Delta S_{sys} = \Delta S_A + \Delta S_B$

$\Delta S_{sys} = 34.7\ J/K - 32.9\ J/K$

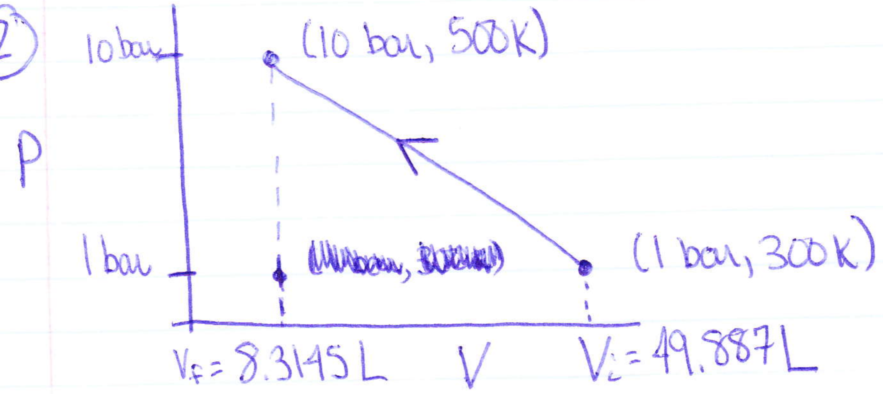
$\boxed{\Delta S_{sys} = 1.8\ J/K}$

$\Delta S_{Tot} = \cancel{\Delta S_{surr}}^{\,0} + \Delta S_{sys}$ (isolated from surrounding)

$\boxed{\Delta S_{Tot} = +1.8\ J/K}$

↑ ⊕ so process is spontaneous (it happened).

②



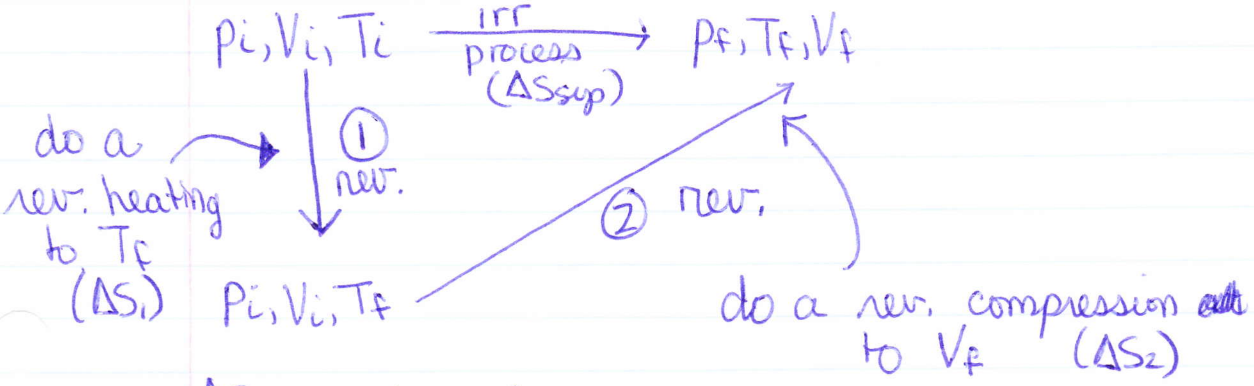
One Step → irreversibility

$p_i = 1$ bar
$T_i = 300K$
$V_i = 49.887L$

$\longrightarrow$

$p_f = 10$ bar
$T_f = 500K$
$V_f = 8.3145 L$

$dS_{sys} = \frac{\delta q_{rev}}{T}$. Since dS_{sys} is a state fxn, I can select path in order to compute ΔS_{sys}.



$\Delta S_{sys} = \Delta S_1 + \Delta S_2$
$\Delta S_{sys} = \int \frac{\delta q_{1,rev}}{T} + \int \frac{\delta q_{2,rev}}{T}$

In step 1, V doesn't change, so $dU = \delta q_1 = C_v dT$
In step 2, T doesn't change, so $dU = 0 = q_2 + w_2$,
$\delta q_2 = -\delta w_2$
$\downarrow$
rev. work: $-nRT \ln(V_f/V_i)$

$$\Delta S_{sys} = \int_{T_i}^{T_f} \frac{C_v dT}{T} + \int_{V_i}^{V_f} \frac{nR\cancel{T}}{\cancel{T}V} dV$$

$\Delta S_{sys} = C_v \ln(T_f/T_i) + nR \ln(V_f/V_i)$
$\Delta S_{sys} = n C_{v,m} \ln(T_f/T_i) + nR \ln(V_f/V_i)$
$\Delta S_{sys} = (2\text{ mol})(1.5R) \ln(500/300) + (2\text{ mol})(8.3145\text{ J/K·mol}) \ln(8.3145/49.887)$
$\Delta S_{sys} = 12.74\text{ J/K} - 29.8\text{ J/K}$
$\boxed{\Delta S_{sys} = -17.06\text{ J/K}}$

ΔS_{surr}: For process, $\Delta U = nC_{v,m}\Delta T = q + w$

$\Delta U = (2\text{ mol})(1.5R)(500\text{ K} - 300\text{ K})$

$\Delta U = 4{,}988.7\text{ J}$

$w_{irr} = -p_{ext}\Delta V$

$w_{irr} = -10\text{ bar}(8.3145L - 49.887L)$ J

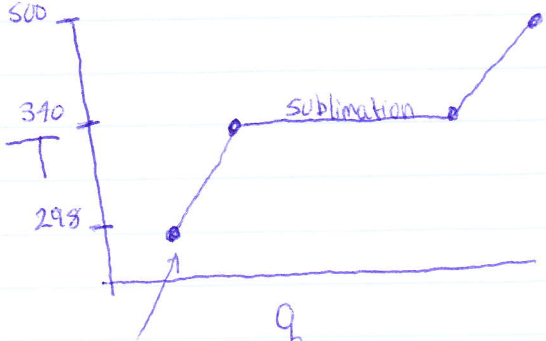
$w_{irr} = +415.725\text{ bar}\cdot L = +41{,}572.5\text{ J} \rightarrow q_{irr} =$ [illegible] J

-36583.8 ← for system!

$q_{surr} = -q_{sys} = +365838\text{ J}$

$\Delta S_{surr} = 36583.8\text{ J}/500\text{ K} = \boxed{+73.1\text{ J/K}}$ $\boxed{\Delta S_{tot} = +56.04\text{ J/K}}$

③



solid anthracene at 298K

$S^\circ_s = 208\text{ J/K}\cdot\text{mol}$

$208 \frac{J}{K\,mol}$ ⊕

$$S^\circ(500) = \int_{298}^{340} \frac{210\text{ J}\cdot K^{-1}\cdot mol^{-1}}{T}dT + \frac{\Delta_{sub}H^\circ}{T_{sub}} + \int_{340}^{500}\frac{C_{p,vap}(T)}{T}dT$$

linear variation → interpolate

(300, 186) and (500, 300)

$\frac{300-186}{500-300} = 0.57$

$186 = 0.57(300) + b$

$b = 15$

So $C_{p,vap} = 0.57T + 15$

$$S^\circ(500) = (210\text{ J/K}\cdot mol)\ln(340/298) + \frac{100{,}000\text{ J/mol}}{340\text{ K}} + \int_{340}^{500}\frac{0.57T+15}{T}dT$$

208 J/K·mol ⊕

$S^\circ(500) = 27.7\text{ J/K}\cdot mol + 294\text{ J/K}\cdot mol + 0.57(500-340) + 15\ln(500/340)$

$S°(SCO) = 208\ J/k,mol + 27.7\ J/k,mol + 294\ J/k,mol + 91.2\ J/k,mol + 5.8\ J/k,mol$

$\boxed{S°(SCO) = 626.7\ J/k,mol}$

④ A to B: process is reversible / isothermal.

$$\Delta S_{sys} = \frac{+10.37 \times 10^3\ J}{300K} = 34.57\ J/k$$

$$\Delta S_{surr} = -\frac{10.37 \times 10^3 J}{300K} = -34.57\ J/k$$

$\Delta S_{Tot} = \Delta S_{sys} + \Delta S_{surr}$

$\boxed{\Delta S_{Tot} = 0\ J/k}$

B to C: process is adiabatic + reversible

$$\downarrow$$

$$\delta q = 0!$$

$$\Delta S_{sys} = 0\ J/k$$
$$\Delta S_{surr} = 0\ J/k$$
$$\Delta S_{Tot} = 0\ J/k$$

C to A: unknown process, but $\Delta S_{surr} = 40\ J/k$.
Need to find ΔS_{sys}.

$\oint \Delta S_{sys} = 0$ (state fxn is zero around cycle)

$$\Delta S_{sys} = \Delta S_{A \to B} + \Delta S_{B \to C} + \Delta S_{C \to A}$$
$$0\ J/k = 34.57\ J/k + 0\ J/k + \Delta S_{C \to A}$$
$$\Delta S_{C \to A} = -34.57\ J/k$$

So $\Delta S_{Tot} = -34.57\ J/k + 40\ J/k$

$\boxed{\Delta S_{Tot} = 5.43\ J/k}$

⑤ Need data:

130.6 J/k·mol

	$\Delta_f^\circ H$	$\Delta_f^\circ G$	S_m°	$C_{p,m}$
$H_{2(g)}$	0 J/mol	0 J/mol	130.6 J/kmol	28.824 J/k·mol
$N_{2(g)}$	0 J/mol	0 J/mol	191.6 J/kmol	29.125 J/kmol
$NH_{3(g)}$	−46110 J/mol	−16450 J/mol	192.5 J/kmol	35.06 J/kmol

$\Delta^\circ H_R$ at 298:

$$\Delta^\circ H_R = 2(-46110\ \mathrm{J/mol}) - (0\ \mathrm{J/mol}(3) + 0\ \mathrm{J/mol}(1))$$

$$\boxed{\Delta^\circ H_R = -92220\ \mathrm{J}/\cancel{\mathrm{mol}}_{\mathrm{rxn}}}$$

$\Delta^\circ S_R$ at 298:

$$\Delta^\circ S_R = 2(192.5\ \mathrm{J/kmol}) - (130.6\ \mathrm{J/kmol}(3) + 191.6\ \mathrm{J/kmol}(1))$$

$$\boxed{\Delta S_R = -198.4\ \mathrm{J}/\mathrm{k}\cancel{\mathrm{mol}}_{\mathrm{rxn}}}$$

$\Delta^\circ G_R$ at 298:

Method 1: $\Delta^\circ G_R = \Delta H^\circ_R - T\Delta S^\circ_R$

$$\Delta^\circ G_R = -92220\ \mathrm{J/mol} - 298\,\mathrm{K}(-198.4\ \mathrm{J/kmol})$$

$$\boxed{\Delta^\circ G_R = -33099\ \mathrm{J}/\cancel{\mathrm{mol}}_{\mathrm{rxn}}}$$

Method 2:

$$\Delta^\circ G_R = 2(-16450\ \mathrm{J/mol}) - (0\ \mathrm{J/mol}(3) + 0\ \mathrm{J/mol}(1))$$

$$\boxed{\Delta^\circ G_R = -32900\ \mathrm{J}/\cancel{\mathrm{mol}}_{\mathrm{rxn}}}$$

should be close if done right.

Now at 500K:

ΔH°_R (500 K): Use Kirchoff's Law:

just use Hess' Law as shown for $\Delta H, \Delta S, \Delta G$ @ 298 above but with C_p!

$$\Delta H^\circ_R(500) = \Delta H^\circ_R(298) + \int_{298}^{500} \Delta C_p \, dT$$

$$\Delta H^\circ_R(500) = -92220 \, \text{J}/\cancel{\text{mol}}\,\text{rxn} + \int_{298}^{500} 35.06 \, \text{J/K mol}(2) - \left(28.824 \, \text{J/K mol}(3) + \overset{29.125}{\cancel{}} \, \text{J/K mol}(1)\right) dT$$

$$\Delta H^\circ_R(500) = -92220 \, \text{J/rxn} + \int_{298}^{500} \left(\overset{-45.477}{\cancel{}} \, \text{J/K mol}\right) dT$$

$$\Delta H^\circ_R(500) = -92220 \, \text{J}/\cancel{\text{mol}}\,\text{rxn} - \overset{45.477}{\cancel{}} \, \text{J/K}\,\cancel{\text{mol}}\,\text{rxn}\,(500\,\text{K} - 298\,\text{K})$$

$$\boxed{\Delta H^\circ_R(500) = -101{,}406 \, \text{J/rxn}}$$

$$\Delta S^\circ_R(500) = \Delta S^\circ_R(298) + \int_{298}^{500} \frac{\Delta C_p}{T} \, dT$$

$$\Delta S^\circ_R(500) = -198.4 \, \text{J/Rxn} + \int_{298}^{500} \frac{(-45.477)}{T} \, \text{J/K rxn} \, dT$$

$$\underline{\Delta S^\circ_R(500) = -198.4 \, \text{J/rxn}} - 45.477 \cdot \ln(500/298)$$

$$\boxed{\Delta S^\circ_R(500) = -221.9 \, \text{J/K rxn}}$$

$\Delta G^\circ_R(500)$: $\Delta G^\circ_R(500) = \Delta H^\circ_R(500) - T\Delta S^\circ_R(500)$

$$\underline{\Delta G^\circ_R(500) = -101{,}406 \, \text{J/rxn} - 500(-221.9 \, \text{J/K mol})}$$

$$\boxed{\Delta G^\circ_R(500) = 9561.5 \, \text{J/rxn}}$$