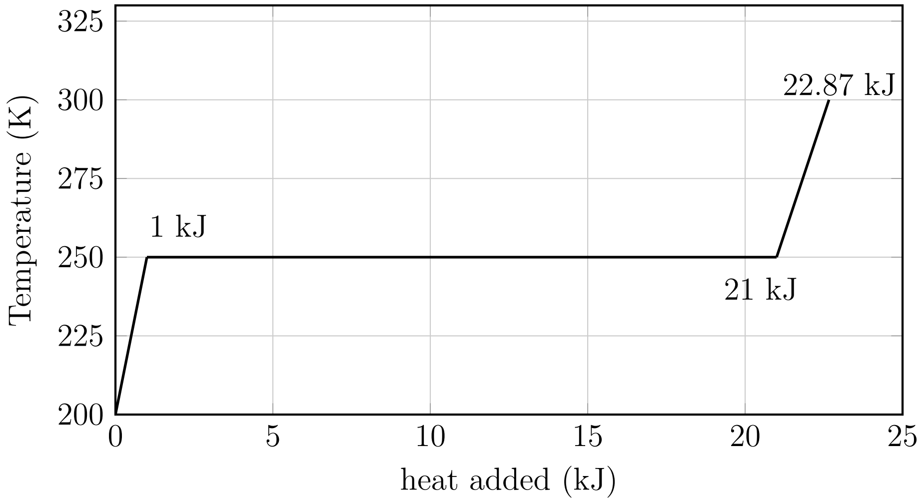
1. One mole of a fictitious element Hamiltonian is heated under constant pressure. Hamiltonian has mp = 200 K and bp = 250 K.



(a) What is ΔH_{vap} of Hamiltonian?

$$\frac{21\,\text{kJ} - 1\,\text{kJ}}{1\,\text{mol}} = 20\,\frac{\text{kJ}}{\text{mol}}$$

(b) Assume Hamiltonian acts as an ideal gas. What can you infer about the number of atoms and the molecular structure (linear vs non-linear)?

Equipartition $\overline{C_V}$ Monoatomic: $\frac{3}{2}R$
Linear diatomic: $\frac{3}{2}R + R + R = \frac{7}{2}R$
Linear triatomic: $\frac{3}{2}R + \frac{3}{2}R + 3R = 6R$
Non-linear triatomic: $\frac{3}{2}R + R + 4R = 6.5R$
$q = n\overline{C_p}\Delta T \implies \overline{C_p} = \frac{q}{n\Delta T} = \frac{22{,}870\,\text{J} - 21{,}000\,\text{J}}{1\,\text{mol}(300\,\text{K} - 250\,\text{K})} = 37.4\,\frac{\text{J}}{\text{mol}\cdot\text{K}} = 4.5R$
This corresponds to linear diatomic, since $\overline{C_p} = \overline{C_V} + R = \frac{7}{2}R + R = 4.5R$

(c) What is the entropy change associated with just the vaporization and heating to 300 K?

$$\begin{aligned}\Delta S &= \Delta S_{vap} + \Delta S_{\Delta T} \\ &= \frac{\Delta H}{T} + n\overline{C_V}\ln T_2 T_1 \\ &= \frac{20{,}000\,\text{J}}{250\,\text{K}} + (1\,\text{mol})(\frac{9}{2}8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}})\ln\frac{300\,\text{K}}{250\,\text{K}} \\ &= 86.8\,\frac{\text{J}}{\text{K}}\end{aligned}$$

2. The goal of this problem is to calculate S_m° of gaseous acetone.

Property	**Value**
$\overline{C}_p$ (acetone, liquid)	$125.5\,\frac{\text{J}}{\text{K}\cdot\text{mol}}$
$\overline{C}_p$ (acetone, gas)	$75\,\frac{\text{J}}{\text{K}\cdot\text{mol}}$
$\Delta H_{\text{vap}}^\circ$ (acetone)	$29.1\,\frac{\text{kJ}}{\text{mol}}$
S_m° (acetone, liquid)	$200\,\frac{\text{J}}{\text{K}\cdot\text{mol}}$
T_m (acetone)	178 K
T_b (acetone)	329.4 K

(a) Find the ΔS for heating 1 mol of liquid acetone from 298 K to 329.4 K.

$$\begin{aligned}\Delta S &= n\overline{C_p}\ln\frac{T_2}{T_1}\\ &= (1\text{ mol})\left(125.5\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}}\right)\ln\frac{329.4\,\text{K}}{298\,\text{K}}\\ &= 12.57\,\tfrac{\text{J}}{\text{K}}\end{aligned}$$

(b) Find the ΔS for vaporizing 1 mol of liquid acetone at 329.4 K.

$$\begin{aligned}\Delta S &= \frac{n\Delta H_{\text{vap}}}{T}\\ &= \frac{(1\text{ mol})(29{,}100\,\frac{\text{J}}{\text{mol}})}{329.4\,\text{K}}\\ &= 88.3\,\tfrac{\text{J}}{\text{K}}\end{aligned}$$

(c) Find the ΔS associated with cooling 1 mol of gaseous acetone from 329.4 K to 298 K, disregarding any phase changes.

$$\begin{aligned}\Delta S &= n\overline{C_p}\ln\frac{T_2}{T_1}\\ &= (1\text{ mol})\left(75\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}}\right)\ln\frac{298\,\text{K}}{329.4\,\text{K}}\\ &= -7.513\,\tfrac{\text{J}}{\text{K}}\end{aligned}$$

(d) Determine S_m° of gaseous acetone.

$$\begin{aligned}S_{m,\text{g}}^\circ &= 200\,\tfrac{\text{J}}{\text{K}} + 12.57\,\tfrac{\text{J}}{\text{K}} + 88.3\,\tfrac{\text{J}}{\text{K}} - 7.513\,\tfrac{\text{J}}{\text{K}}\\ &= 293.36\,\tfrac{\text{J}}{\text{K}}\end{aligned}$$

3. A closed, rigid 2.5 L flask contains a mixture of Ne(g) and F_2(g) with a total pressure of 3.32 atm at 0 °C. The system is heated to 15 °C. The change in entropy for this process is $0.345\,\frac{\text{J}}{\text{K}}$. What is the mole fraction of Ne in the flask, X_{Ne}?

$$
\begin{aligned}
n &= \frac{PV}{RT} = \frac{3.22\,\text{atm} \times 2.5\,\text{L}}{0.0821\,\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times 273\,\text{K}} = 0.3705\,\text{mol} \\
\Delta S &= \Delta S_{\text{Ne}} + \Delta S_{\text{F}_2} = 0.345\,\tfrac{\text{J}}{\text{K}} \\
&= n\overline{C_V}\ln\frac{T_2}{T_1} + n\overline{C_V}\ln\frac{T_2}{T_1} \quad (\text{for Ne and F}_2) \\
&= x\frac{3}{2}R\ln\frac{288\,\text{K}}{273\,\text{K}} + (0.3705\,\text{mol} - x)\frac{7}{2}R\ln\frac{288\,\text{K}}{273\,\text{K}} = 0.345\,\tfrac{\text{J}}{\text{K}} \\
0.345\tfrac{\text{J}}{\text{K}} &= 0.445\,\tfrac{\text{J}}{\text{K}\cdot\text{mol}} \cdot \left[\frac{3}{2}x + \frac{7}{2}(0.371\,\text{mol}) - \frac{7}{2}x\right] \\
&= 0.445\,\tfrac{\text{J}}{\text{K}\cdot\text{mol}} \cdot [1.297\,\text{mol} - 2x] \\
x &= 0.261\,\text{mol Ne} \\
X_{\text{Ne}} &= \frac{0.261\,\text{mol}}{0.371\,\text{mol}} = \boxed{0.703}
\end{aligned}
$$

Homework Problem 17

1. A 1 mol sample of CH_4 at 298 K and 24.5 atm is contained in a 1 L closed, flexible container. The gas undergoes expansion to 2 L. In order to maintain a zero change in entropy ($\Delta S = 0$) during the expansion, what must the final temperature and pressure of the sample be?