

1.1

(a) (13 pt)

Final Temperature T_f is

$$0 = C_V(T_f - T_0) + C_V(T_f - 3T_0) \Rightarrow T_f = 2T_0 \quad (1)$$

Entropy change in each subvolume

$$\begin{aligned} \delta S_1 &= \int \frac{dQ}{T} = \int_{T_0}^{T_f} \frac{C_V dT}{T} = C_V \log\left(\frac{T_f}{T_0}\right) = C_V \log 2 \\ \delta S_2 &= \int \frac{dQ}{T} = \int_{3T_0}^{T_f} \frac{C_V dT}{T} = C_V \log\left(\frac{T_f}{3T_0}\right) = C_V \log \frac{2}{3} \end{aligned} \quad (2)$$

and the total entropy change $\delta S = C_V \log \frac{4}{3} > 0$ as it should be.

(b) (13 pt)

Solve for final pressure P_f is

$$P_f = \frac{(N + 3N)T}{V + V} = \frac{4NT}{2V} = 2P_0 \quad (3)$$

Since the internal energy of the ideal gas depends only on its temperature, the final temperature $T_f = T_{1i} = T_{2i} = \frac{P_0 V_0}{N}$. The process is irreversible, but the change of entropy can be calculated in a reversible process that brings the system to the same final state: e.g. slowly moving the partition until the pressures $P_{1f} = P_{2f} = P_f$ and removing it afterwards. Since the final temperature $T_f = T_0$ in both parts, the process can be isothermal with $\delta Q = P dV$:

$$\begin{aligned} V_0 \rightarrow V_1 &= \frac{P_0 V_0}{P_f} = \frac{1}{2} V_0, & \delta S_1 &= \int \frac{dQ}{T} = \int \frac{P dV}{T} = \int_{V_0}^{V_1} N \frac{dV}{V} = N \log \frac{1}{2} \\ V_0 \rightarrow V_2 &= \frac{3P_0 V_0}{P_f} = \frac{3}{2} V_0, & \delta S_2 &= \int \frac{dQ}{T} = \int \frac{P dV}{T} = \int_{V_0}^{V_2} 3N \frac{dV}{V} = 3N \log \frac{3}{2} \\ & & \Rightarrow \delta S &= \delta S_1 + \delta S_2 = N \log \frac{27}{16} \end{aligned} \quad (4)$$

1.2

(a) (6 pt)

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = \frac{\partial(P, V)}{\partial(T, S)} = \frac{\partial(P, V)}{\partial(T, V)} \frac{\partial(T, V)}{\partial(T, S)} = \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial S}\right)_T = 1 \quad (5)$$

The last equality follows from $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial^2 F(T, V)}{\partial T \partial V}$.

Be careful when using $\frac{\partial(A, B)}{\partial(C, D)}$. This expression means C and D are independent variable, while A and B are functions of C and D .

(b) (6 pt)

$$dH = TdS + Vdp \Rightarrow \left(\frac{\partial H}{\partial p}\right)_T = V + T \left(\frac{\partial S}{\partial p}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_p \quad (6)$$

(c) (6 pt)

Assume equation of state is of the form $p = p(T, V)$

$$\begin{aligned} \left(\frac{\partial C_P}{\partial P}\right)_T &= \left(\frac{\partial}{\partial P}\right)_T \left(\frac{\partial H}{\partial T}\right)_P \\ &= \left(\frac{\partial}{\partial T}\right)_P \left(\frac{\partial H}{\partial P}\right)_T \\ &= \left(\frac{\partial}{\partial T}\right)_P \left[T \left(-\frac{\partial V}{\partial T}\right)_P + V \right] \\ &= -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P \end{aligned} \quad (7)$$

(d) (6 pt)

Considering conditions

$$\begin{aligned} 0 &= \left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p, \Rightarrow \left(\frac{\partial p}{\partial T}\right)_V = \frac{p}{T} \\ 0 &= \left(\frac{\partial H}{\partial p}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p + V, \Rightarrow \left(\frac{\partial V}{\partial T}\right)_p = \frac{V}{T} \\ &\Rightarrow T = PV \times const \end{aligned} \quad (8)$$

The last equality follows from e.g. $dT = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV = \frac{T}{P}dP + \frac{T}{V}dV = T d \log(PV)$.
The system is an ideal gas.

1.3

(25 pt) Constant volume heat capacity

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V = aT e^{bT} \quad (9)$$

Find equation of state

$$\begin{aligned} \delta W &= cT \log \frac{V_2}{V_1}, \Rightarrow p = \frac{\partial W}{\partial V} = \frac{cT}{V} \\ \left(\frac{\partial E}{\partial V}\right)_T &= T \left(\frac{\partial p}{\partial T}\right)_V - p = 0 \end{aligned} \quad (10)$$

$$\begin{aligned} E &= \int \frac{dE}{dT} dT = \int aT e^{bT} dT \\ &= \frac{bT - 1}{b^2} a e^{bT} + const \end{aligned} \quad (11)$$

$$\begin{aligned} H &= E + pV \\ &= \frac{bT - 1}{b^2} a e^{bT} + cT + const \end{aligned}$$

Now to find $S = S(V, T)$

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V = \frac{c}{V}, \quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial Q}{\partial T}\right)_V = \frac{C_V}{T} \\ \Rightarrow S &= \int \frac{C_V}{T} dT + \frac{c}{V} dV = \frac{a}{b} e^{bT} + c \log(V) + \text{const} \\ F &= E - TS \\ G &= E - TS + PV = E - TS + cT \end{aligned} \quad (12)$$

1.4

(25 pt) Van der Waals gas has equation of state

$$\left(p + \frac{a}{v^2}\right)(v - b) = T, \quad \Rightarrow \quad p(T, v) = \frac{T}{v - b} - \frac{a}{v^2} \quad (13)$$

thus it is convenient to express the answer using derivatives of the pressure

$$(k_T)^{-1} = -v \left(\frac{\partial p}{\partial v}\right)_T = \frac{Tv}{(v - b)^2} - \frac{2a}{v^2}, \quad (14)$$

$$\left(\frac{\alpha}{k_T}\right) = - \left(\frac{\partial p}{\partial v}\right)_T \cdot \left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial p}{\partial T}\right)_v = \frac{1}{v - b} \quad (15)$$

(a)

$$\left(\frac{\partial \varepsilon}{\partial v}\right)_T = T \left(\frac{\partial s}{\partial v}\right)_T - P = \left(\frac{\partial p}{\partial T}\right)_v - P = \frac{a}{v^2}, \quad (16)$$

where $\varepsilon = E/N$, $s = S/N$ are the internal energy and the entropy per molecule.

(b) In an expansion process (Joule Expansion),

$$\left(\frac{\partial T}{\partial v}\right)_E = - \left(\frac{\partial T}{\partial \varepsilon}\right)_v \left(\frac{\partial \varepsilon}{\partial v}\right)_T = - \frac{1}{c_V} \frac{a}{v^2} \quad (17)$$

The temperature decreases so that $\left(\frac{\partial T}{\partial v}\right)_E < 0$.