PHYS 5130 Problem Set 3 Solution

1.

Solution:

(a) By definition, the efficiency of a heat engine is

$$\eta = \frac{W_{by}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} \tag{1}$$

Moreover, as stated in the question, $Q_{out} = 750\,\mathrm{J}$ and $\eta = 0.25$, so

$$\frac{Q_{in} - 750}{Q_{in}} = 0.25 \tag{2}$$

$$\frac{750}{Q_{in}} = 0.75. \tag{3}$$

One then obtains $Q_{in} = 1000\,\mathrm{J}$.

(b) The Clausius inequality states that $\oint \frac{đQ}{T} \leq 0$. For this particular process,

$$\oint \frac{đQ}{T} = \frac{Q_{in}}{T_{Hot}} - \frac{Q_{out}}{T_{Cold}} \tag{4}$$

$$= \frac{1000}{300} - \frac{750}{150} \tag{5}$$

$$= -\frac{5}{3}\mathrm{JK}^{-1} \tag{6}$$

$$< 0. \tag{7}$$

2.

Solution: For heating under constant pressure,

$$\Delta S = \int \frac{đQ}{T} \tag{8}$$

$$= \int \frac{c_v dT}{T} \tag{9}$$

$$= c_v \ln\left(\frac{T_f}{T_i}\right) \tag{10}$$

For phase transition, the temperature is constant, so entropy change is simply given by

$$\Delta S = \frac{\Delta Q}{T} \tag{11}$$

$$= \frac{l}{T} \tag{12}$$

Therefore, one might separate the heating of ice at $200\,\mathrm{K}$ into steam at $400\,\mathrm{K}$ into 5 processes, and add up the entropy change for each part to obtain the total entropy change, which is given by

$$\Delta S = c_p^{(ice)} \ln\left(\frac{273}{200}\right) + \frac{l_{SL}}{273} + c_p^{(water)} \ln\left(\frac{373}{273}\right) + \frac{l_{LV}}{373} + c_p^{(steam)} \ln\left(\frac{400}{373}\right) \tag{13}$$

$$= 9.38\,\mathrm{kJK}^{-1} \tag{14}$$

3.

Solution:

(a) Using the equation of state $pV = nRT$, one could first obtain T_A, given by

$$\begin{aligned} T_A &= \frac{P_A V_A}{1000R} && (15) \\ &= 240.5\,\mathrm{K} && (16) \end{aligned}$$

As state A, B are linked by an adiabat,

$$P_A V_A^{\gamma} = P_B V_B^{\gamma}, \qquad (17)$$

where $\gamma = \frac{5}{3}$ for monatomic gas. Therefore,

$$\begin{aligned} P_B &= \frac{P_A V_A^{\frac{5}{3}}}{V_B^{\frac{5}{3}}} && (18) \\ &= 3.15 \times 10^5\,\mathrm{Pa} && (19) \end{aligned}$$

With both V_B, P_B known, T_B can be computed from the equation of state, given by $T_B = 151.5\,\mathrm{K}$.

As state C and state B are linked by an isobaric process, $P_C = P_B$. Therefore, making use of the equation of state again, one obtains $T_C = 75.8\,\mathrm{K}$.

(b) As path AB is an adiabat, $Q_{AB} = 0$, and with no heat exchange, $\Delta S_{AB} = 0$ as well. Work done on the system W_{AB} is given by

$$\begin{aligned} W_{AB} &= -\int p dV && (20) \\ &= -C \int_{V_A}^{V_B} V^{-\gamma} dV && (21) \\ &= -\frac{C}{1-\gamma}(V_B^{1-\gamma} - V_A^{1-\gamma}) && (22) \\ &= \frac{3}{2} P_A V_A^{\frac{5}{3}} (V_B^{-\frac{2}{3}} - V_A^{-\frac{2}{3}}) && (23) \\ &= -1110\,\mathrm{kJ} && (24) \end{aligned}$$

(c) As the process is isobaric,

$$\begin{aligned} Q_{BC} &= C_p \Delta T && (25) \\ &= 1000 * \left(\frac{5}{2}R\right)(T_C - T_B) && (26) \\ &= -1575\,\mathrm{kJ} && (27) \end{aligned}$$

$$\begin{aligned} \Delta S_{BC} &= \int \frac{đQ}{T} dT && (28) \\ &= C_p \int_{T_B}^{T_C} \frac{dT}{T} && (29) \\ &= C_p \ln\left(\frac{T_C}{T_B}\right) && (30) \\ &= -14.4\,\mathrm{kJK^{-1}} && (31) \end{aligned}$$

Work done is simply given by

$$\begin{aligned} W_{BC} &= -P_B(V_C - V_B) && (32) \\ &= 630\,\mathrm{kJ} && (33) \end{aligned}$$

(d) As the path CA represents an isochoric process, $\Delta V = 0$, so $W_{CA} = 0$.

$$\begin{aligned} Q_{CA} &= C_v \Delta T && (34) \\ &= 1000 \left(\frac{3}{2}R\right)(T_A - T_C) && (35) \\ &= 2055\,\mathrm{kJ} && (36) \end{aligned}$$

$$\Delta S_{CA} = \int \frac{đQ}{T} \tag{37}$$

$$= C_V \int_{T_C}^{T_A} \frac{dT}{T} \tag{38}$$

$$= 1000 \left(\frac{3}{2} R\right) \ln\left(\frac{T_A}{T_C}\right) \tag{39}$$

$$= 14.4\,\mathrm{kJK^{-1}} \tag{40}$$

(e) Efficiency is defined by

$$\eta = \frac{W_{by}}{Q_{in}}, \tag{41}$$

where W_{by} is net work done by the system ($-W_{tot}$), and Q_{in} is the amount of heat input into the system (Sum of all positive Q terms). Therefore,

$$\eta = \frac{-(W_{AB} + W_{BC})}{Q_{CA}} \tag{42}$$

$$= 0.234 \tag{43}$$

Moreover, $W_{by} = Q_{in} - Q_{out}$.

4.

Solution:

(a) From $\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$, one could obtain

$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}. \tag{44}$$

Then,

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V - nb}. \tag{45}$$

Substituting back p and $\left(\frac{\partial p}{\partial T}\right)_V$ back into the expression for $\left(\frac{\partial U}{\partial V}\right)_T$, one obtains

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{nR}{V - nb} - \frac{nRT}{V - nb} + \frac{n^2 a}{V^2} \tag{46}$$

$$= \frac{n^2 a}{V^2} \tag{47}$$

$$= \frac{a}{v^2}. \tag{48}$$

which depends on a only. Under constant temperature, as volume increases, the intermolecular attraction between molecules (characterized by a) decreases, leading to higher U.

For an ideal gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{49}$$

$$= p - p \tag{50}$$

$$= 0, \tag{51}$$

as expected.

(b) For $u(T, V)$, one could write the total differential as

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dV \tag{52}$$

$$= c_v dT + \left(\frac{\partial u}{\partial v}\right)_T dV. \tag{53}$$

Using the result from part a, one obtains

$$du = c_v dT + \left(T\left(\frac{\partial p}{\partial T}\right)_v - p\right) dv. \tag{54}$$

As shown in part a, $\left(\frac{\partial u}{\partial v}\right)_T = \left(T\left(\frac{\partial p}{\partial T}\right)_v - p\right) \neq 0$, so u cannot be written as a function of T only, therefore $u = u(v, T)$.

(c) Reusing the results from problem set 1, one could obtain

$$\begin{aligned}
\beta &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p && (55)\\
&= \frac{1}{V}\frac{nR}{p + \frac{n^2 a}{V^2} - \frac{2n^2 a}{V^3}(V - nb)} && (56)\\
&= \frac{nR}{\frac{nRTV}{V-nb} - \frac{2n^2 a}{V^2}(V - nb)} && (57)\\
&= \frac{R}{\frac{RTv}{v-b} - \frac{2a}{v^2}(v - b)} && (58)
\end{aligned}$$

$$\begin{aligned}
\kappa &= -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T && (59)\\
&= -\frac{1}{V}\frac{nb - V}{p + \frac{n^2 a}{V^2} - \frac{2n^2 a}{V^3}(V - nb)} && (60)\\
&= \frac{V - nb}{\frac{nRTV}{V-nb} - \frac{2n^2 a}{V^2}(V - nb)} && (61)\\
&= \frac{v - b}{\frac{RTv}{v-b} - \frac{2a}{v^2}(v - b)} && (62)
\end{aligned}$$

From the lecture notes,

$$c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p = Tv\frac{\beta^2}{\kappa} \tag{63}$$

Then,

$$\begin{aligned}
c_p - c_v &= Tv\frac{\beta^2}{\kappa} && (64)\\
&= Tv\frac{R^2}{v - b}\left(pv + \frac{a}{v} - \frac{2a}{v^2}(v - b)\right)^{-1} && (65)\\
&= \frac{TR^2}{v - b}\left(\frac{RT}{v - b} - \frac{2a}{v^3}(v - b)\right)^{-1} && (66)\\
&= R\left(1 - \frac{2a(v - b)^2}{RTv^3}\right)^{-1} && (67)
\end{aligned}$$

5.

Solution: As $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$ and $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$.

$$\frac{C_p}{C_V} = \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial S}\right)_V \tag{68}$$

Using the cyclic rule, one could write

$$\left(\frac{\partial S}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_S \tag{69}$$

and also

$$\left(\frac{\partial T}{\partial S}\right)_V = -\left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial T}{\partial V}\right)_S. \tag{70}$$

Then,

$$\frac{C_p}{C_V} = \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial S}\right)_V \tag{71}$$
$$= \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial T}{\partial V}\right)_S \tag{72}$$
$$= \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial p}{\partial T}\right)_S \left(\frac{\partial T}{\partial V}\right)_S \tag{73}$$
$$= \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_S \tag{74}$$
$$= \frac{-V^{-1}\left(\frac{\partial V}{\partial p}\right)_T}{-V^{-1}\left(\frac{\partial V}{\partial p}\right)_S} \tag{75}$$
$$= \frac{\kappa_T}{\kappa_S}. \tag{76}$$

As an illustration, one could apply the obtained result to an ideal gas. For an ideal gas,

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{77}$$
$$= -\frac{1}{V}\left(-\frac{nRT}{p^2}\right) \tag{78}$$
$$= \frac{1}{p}. \tag{79}$$

For κ_S, one needs to find partial derivative under constraint of constant entropy. One therefore could use the equation for an adiabat $PV^\gamma = C$. Performing partial derivative on both sides, one obtain

$$V^\gamma + \gamma p V^{\gamma-1}\left(\frac{\partial V}{\partial p}\right)_S = 0 \tag{80}$$
$$\left(\frac{\partial V}{\partial p}\right)_S = -\frac{V}{\gamma p}. \tag{81}$$

Therefore, $\kappa_S = \frac{1}{\gamma p}$. One could then obtain $\frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S} = \gamma$ as expected.

6.

Solution:

(a) To check that the proposed expression for entropy is indeed extensive, one could scale the extensive variables by α and see whether $S(\alpha U, \alpha V, \alpha N) = \alpha S(U, V, N)$.

$$S(\alpha U, \alpha V, \alpha N) = \alpha N k \ln\left(\frac{\alpha V}{\alpha N}\left(\frac{m\alpha U}{3\pi\alpha N\hbar^2}\right)^{\frac{3}{2}}\right) + \frac{5}{2}\alpha N k \tag{82}$$
$$= \alpha S(U, V, N) \tag{83}$$

So the proposed expression for entropy is indeed extensive.

(b) From the given exact differential, one could identify

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}. \tag{84}$$

Therefore,

$$\frac{1}{T} = \frac{3}{2}NkU^{-1} \tag{85}$$
$$T = \frac{U}{\frac{3}{2}Nk} \tag{86}$$

Similarly, one could identify $\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}$, and so

$$p = T\left(\frac{\partial S}{\partial V}\right)_{U,N} \tag{87}$$
$$= T\frac{Nk}{V} \tag{88}$$

(c) From part b, one obtains $pV = NkT$ and $U = \frac{3}{2}NkT$, therefore the system is just a system of monatomic ideal gas.

(d) One could identify $\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$. Explicitly, one obtains

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} \tag{89}$$
$$= -T\left(k\ln\left(\frac{V}{N}\left(\frac{mU}{3\pi N\hbar^2}\right)^{\frac{3}{2}}\right) - \frac{5}{2}\frac{Nk}{N} + \frac{5}{2}k\right) \tag{90}$$
$$= -kT\ln\left(\frac{V}{N}\left(\frac{mU}{3\pi N\hbar^2}\right)^{\frac{3}{2}}\right) \tag{91}$$