

Thermodynamics

Problem Set 3

Thermodynamic Potentials and Methods

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More Practice

A.1

(a) The entropy change of the water is:

$$\Delta S_w = \int_{T_1}^{T_2} \frac{C}{T} dT = C \ln \frac{T_2}{T_1} \quad (1)$$

The entropy change of the 100 °C reservoir is:

$$\Delta S_r = \frac{Q}{T_2} = C \frac{T_1 - T_2}{T_2} \quad (2)$$

The total entropy change is:

$$\Delta S_{uni} = \Delta S_w + \Delta S_r \quad (3)$$

(b) The entropy change of the water is unchanged while the entropy change of the reservoirs is:

$$\Delta S_r = C \frac{T_3 - T_1}{T_3} + C \frac{T_2 - T_3}{T_2} \quad (4)$$

The total entropy change is:

$$\Delta S_{uni} = \Delta S_w + \Delta S_r \quad (5)$$

(c) For a reversible process, the total entropy change is zero. The water obtains a heat $Q = C(T_2 - T_1)$ from the reservoir. The entropy change of the reservoir is:

$$\Delta S_r = -\frac{Q}{T_2} = -C \frac{T_2 - T_1}{T_2} \quad (6)$$

and to have a total entropy change of zero, the entropy change of the water must be:

$$\Delta S_w = -\Delta S_r = C \frac{T_2 - T_1}{T_2} \quad (7)$$

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A.2

Assume without loss of generality that $T_2 > T_1$. Let Q_2 be the heat drawn from the hot reservoir and Q_1 be the heat released to the cold reservoir. The work done by the engine is $W = Q_2 - Q_1$. At final common temperature T_f , the changes of internal energy of the two reservoirs are:

$$\begin{aligned}\Delta U_1 &= C_p(T_f - T_1) \\ \Delta U_2 &= C_p(T_f - T_2)\end{aligned}\tag{8}$$

By first law, we have $Q_1 = \Delta U_1$ and $Q_2 = -\Delta U_2$. The work done by the engine is:

$$W = Q_2 - Q_1 = -\Delta U_2 - \Delta U_1 = C_p(T_1 + T_2 - 2T_f)\tag{9}$$

The efficiency of the engine is:

$$\eta = \frac{W}{Q_2} = \frac{T_1 + T_2 - 2T_f}{T_2 - T_f}\tag{10}$$

Maximising the efficiency with respect to T_f , we need:

$$\frac{(T_2 - T_f)(-2) - (T_1 + T_2 - 2T_f)(-1)}{(T_2 - T_f)^2} = 0\tag{11}$$

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A.3

The combustion heat of the fuel is given by:

$$\Delta Q = \rho V H_c\tag{12}$$

The total input heat has the additional potential energy term:

$$Q_{in} = \Delta Q + U_0\tag{13}$$

By first law, the work done by the engine is:

$$W = Q_{in} - Q_{out} = \Delta Q + U_0 - U_f = \rho V [H_c + c_p(T_0 - T_f)]\tag{14}$$

Using a specific heat capacity $c_p = 2.22 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$ for air, we have $W = 3.96 \times 10^6 \text{ J}$. The maximum height is thus:

$$h = \frac{W}{mg} = 40.3 \text{ m} \quad (15)$$

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A.4

The heat input happens during the isobaric expansion:

$$Q_{in} = C_p(T_3 - T_2) = \frac{1}{\gamma - 1} P_2(V_3 - V_2) \quad (16)$$

The heat output happens during the isochroic compression:

$$Q_{out} = C_v(T_4 - T_1) = \frac{\gamma}{\gamma - 1} V_1(p_4 - p_1) \quad (17)$$

The efficiency of the engine is:

$$\eta = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{C_v(T_4 - T_1)}{C_p(T_3 - T_2)} = 1 - \frac{\gamma}{\gamma - 1} \frac{V_1(p_4 - p_1)}{p_2(V_3 - V_2)} \quad (18)$$

Since the pairs (p_1, V_1) , (p_2, V_2) and (p_2, V_3) , (p_4, V_1) are on the same reversible adiabat, we have:

$$\begin{aligned} \frac{p_1}{p_2} &= \left(\frac{V_2}{V_1} \right)^\gamma \\ \frac{p_4}{p_2} &= \left(\frac{V_3}{V_1} \right)^\gamma \end{aligned} \quad (19)$$

Therefore, we can write:

$$\eta = 1 - \frac{\gamma}{\gamma - 1} \frac{(V_3/V_1)^\gamma - (V_2/V_1)^\gamma}{V_3/V_1 - V_2/V_1} \quad (20)$$

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Potentials and Maxwell Relations

B.1

We know from Gibbs-Duhem equation that $SdT - Vdp + nd\mu = 0$. Given that dT is zero, we have:

$$n = V \frac{dp}{d\mu} = \frac{V}{d\mu/dp} = \frac{pV}{k_B T} \quad (21)$$

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B.2

The change in internal energy is just $\Delta U = W$. Since the process is reversible and adiabatic, we have $Q = 0$ and $\Delta S = 0$. We will be able to know the change in enthalpy as $dH = TdS + Vdp$ and dS is zero so the change in enthalpy is:

$$\Delta H = \int_{p_1}^{p_2} V dp = p_2 V_2 - p_1 V_1 - \int_{V_1}^{V_2} p dV = p_2 V_2 - p_1 V_1 + W \quad (22)$$

We cannot tell the change in F or G since we do not know the temperature. If we do know that the temperature is kept constant, we will have $\Delta F = W$ and $\Delta G = \Delta H$.

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B.3

Consider the equation $dU = TdS - pdV$. We have $T = (\partial U / \partial S)_V$ and $p = -(\partial U / \partial V)_S$. Therefore, we can write:

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V \quad (23)$$

Next consider $dH = TdS + Vdp$. We have $T = (\partial H / \partial S)_p$ and $V = (\partial H / \partial p)_S$. Therefore:

$$\left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p \quad (24)$$

Then consider $dF = -SdT - pdV$. We have $S = -(\partial F / \partial T)_V$ and $p = -(\partial F / \partial V)_T$ and:

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V \quad (25)$$

Finally consider $dG = -SdT + Vdp$. We have $S = -(\partial G / \partial T)_p$ and $V = (\partial G / \partial p)_T$. Thus:

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad (26)$$

Applications (Rod, Surface, Magnetization, Solid)