

**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:

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

Maximum efficiency is obtained when the process is reversible, i.e.  $\Delta S = 0$  and the engines is Carnot. For a carnot engine, the temperatures satisfy:

$$\frac{T_2}{T_f} = \frac{T_f}{T_1}\tag{12}$$

which immediately gives  $T_f^2 = T_1 T_2$  for maximum efficiency.

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## A.3

The combustion heat of the fuel is given by:

$$\Delta Q = \rho V H_c\tag{13}$$

The total input heat has the additional potential energy term:

$$Q_{in} = \Delta Q + U_0 \quad (14)$$

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

$$W = Q_{in} - Q_{out} = \Delta Q + U_0 - U_f = \rho V [H_c + c_p(T_0 - T_f)] \quad (15)$$

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:

$$h = \frac{W}{mg} = 40.3 \text{ m} \quad (16)$$

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## A.4

The heat input happens during the isobaric expansion:

$$Q_{in} = C_p(T_3 - T_2) = \frac{1}{\gamma - 1} P_2(V_3 - V_2) \quad (17)$$

The heat output happens during the isochroic compression:

$$Q_{out} = C_v(T_4 - T_1) = \frac{\gamma}{\gamma - 1} V_1(p_4 - p_1) \quad (18)$$

The efficiency of the engine is:

$$\eta = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{C_v(T_4 - T_1)}{C_p(T_3 - T_2)} = 1 - \frac{\gamma}{\gamma - 1} \frac{V_1(p_4 - p_1)}{p_2(V_3 - V_2)} \quad (19)$$

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:

$$\begin{aligned} \frac{p_1}{p_2} &= \left( \frac{V_2}{V_1} \right)^\gamma \\ \frac{p_4}{p_2} &= \left( \frac{V_3}{V_1} \right)^\gamma \end{aligned} \quad (20)$$

Therefore, we can write:

$$\eta = 1 - \frac{\gamma}{\gamma - 1} \frac{(V_3/V_1)^\gamma - (V_2/V_1)^\gamma}{V_3/V_1 - V_2/V_1} \quad (21)$$

The heat input during the isobaric expansion is:

$$Q_{in} = C_p(T_3 - T_2) \quad (22)$$

The heat output during the isochoric compression is:

$$Q_{out} = C_v(T_4 - T_1) \quad (23)$$

Noting that  $C_p = \gamma C_v$ , the efficiency of the engine is:

$$\eta = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{C_v(T_4 - T_1)}{C_p(T_3 - T_2)} = 1 - \frac{1}{\gamma} \frac{V_1(p_4 - p_1)}{P_2(V_3 - V_2)} \quad (24)$$

With:

$$\begin{aligned} \frac{p_1}{p_2} &= \left( \frac{V_2}{V_1} \right)^\gamma \\ \frac{p_4}{p_2} &= \left( \frac{V_3}{V_1} \right)^\gamma \end{aligned} \quad (25)$$

we can write:

$$\eta = 1 - \frac{1}{\gamma} \frac{(V_3/V_1)^\gamma - (V_2/V_1)^\gamma}{V_3/V_1 - V_2/V_1} \quad (26)$$

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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:

$$n = V \frac{dp}{d\mu} = \frac{V}{d\mu/dp} = \frac{pV}{k_B T} \quad (27)$$

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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:

$$\Delta H = \int_{p_1}^{p_2} V dp = p_2 V_2 - p_1 V_1 - \int_{V_1}^{V_2} p dV = p_2 V_2 - p_1 V_1 + W \quad (28)$$

$p_2 V_2 - p_1 V_1$  is not known.

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:

$$\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial p}{\partial S} \right)_V \quad (29)$$

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

$$\left( \frac{\partial T}{\partial p} \right)_S = \left( \frac{\partial V}{\partial S} \right)_p \quad (30)$$

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

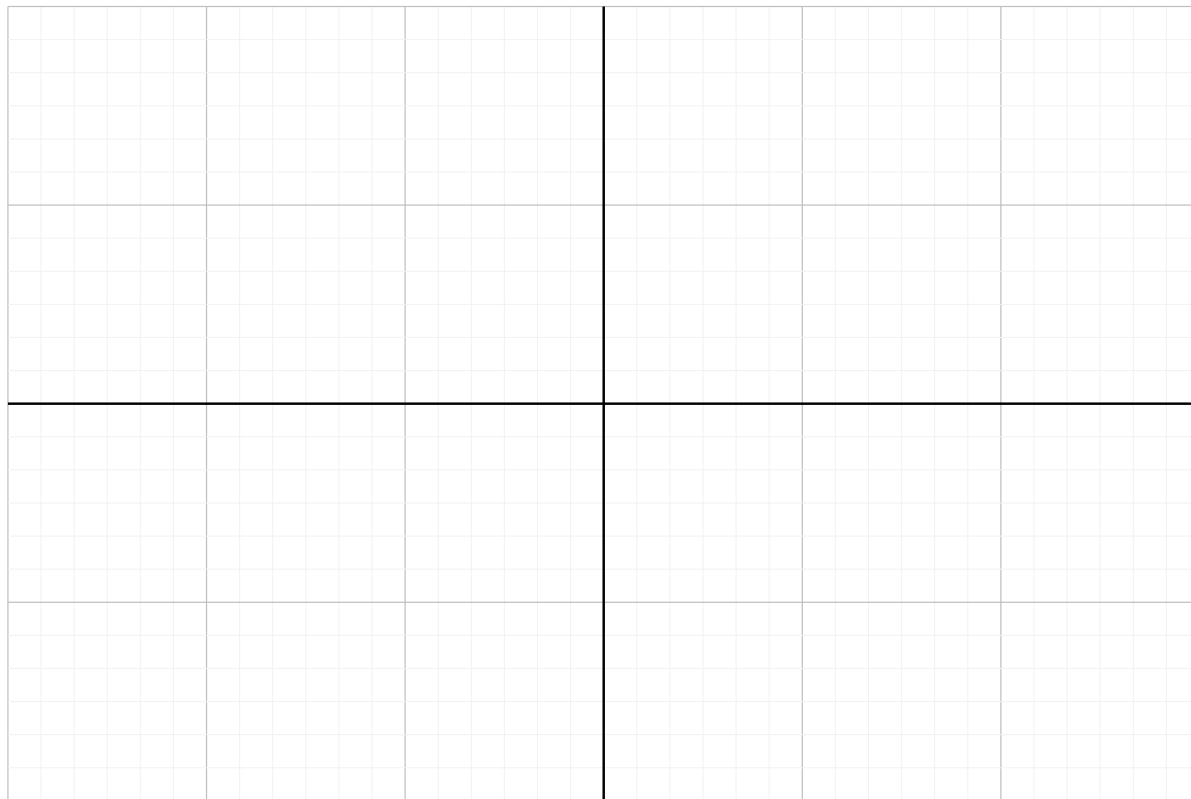
$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V \quad (31)$$

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

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad (32)$$

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## B.4



For an isotherm,  $p = T/V$  where  $T$  is constant. For an adiabat,  $p = C/V^\gamma$  where  $C$  is constant. The two curves intersect at some  $(p_0, V_0)$ . The area under graph for the isotherm is apparently larger than that for the adiabat. The extra work done comes from the heat transfer from the hot reservoir.

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## B.5

A chemical reaction that happens slowly and exposed to the atmosphere (e.g. rusting) is isobaric and isothermal. Since  $dG = Vdp - SdT$ , we have  $dG = 0$  and the Gibbs free energy is constant for this process.

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**B.6**

(i) Consider the ordinary internal energy  $dU = TdS - pdV$ . There is extra work done by the external force  $f$  on the rubber so that we modify the equation to:

$$dU = TdS - pdV + fdL \quad (33)$$

where the sign for  $f$  is positive as the external force is doing positive work.

(ii) Consider  $dU - d(fL)$ , which we define as  $dX$ :

$$dX = TdS - pdV - Ldf \quad (34)$$

Next, consider  $dX + d(pV)$ , which we define as  $dY$ :

$$dY = TdS + Vdp - Ldf \quad (35)$$

(ii) Let us further define  $dZ = dU - d(TS) + d(pV)$ :

$$dZ = -SdT + Vdp + f dL \quad (36)$$

Since  $dZ$  is an exact differential, we must have  $Z_{T,L} = Z_{L,T}$ . Noting this, we have:

$$\begin{aligned} \left( \frac{\partial S}{\partial L} \right)_{T,p} &= -\frac{\partial}{\partial L} \left( \frac{\partial Z}{\partial T} \right) \\ &= -\frac{\partial}{\partial T} \left( \frac{\partial Z}{\partial L} \right) \\ &= -\left( \frac{\partial f}{\partial T} \right)_{p,L} \end{aligned} \quad (37)$$

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## Applications (Rod, Surface, Magnetization, Solid)

### C.1

For an elastic rod, we have the expression for the internal energy:

$$dU = TdS + fdL \quad (38)$$

The heat capacity at constant length is defined as:

$$C_L = T \left( \frac{\partial S}{\partial T} \right)_L \quad (39)$$

Let us define the ‘Helmholtz free energy’ as  $d\tilde{F} = -SdT + fdL$ . We have the Maxwell relation:

$$\left( \frac{\partial S}{\partial L} \right)_T = - \left( \frac{\partial f}{\partial T} \right)_L \quad (40)$$

This implies:

$$\begin{aligned} \left( \frac{\partial C_L}{\partial L} \right)_T &= T \left( \frac{\partial^2 S}{\partial L \partial T} \right)_L \\ &= -T \left( \frac{\partial^2 f}{\partial T^2} \right)_L \end{aligned} \quad (41)$$

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### C.2

For a liquid, we have:

$$dU = TdS + \sigma dA \quad (42)$$

where  $\sigma$  is surface tension as a function of temperature.

Consider the quantity:

$$dX = TdS - Ad\sigma \quad (43)$$

where  $d\sigma/dT = -1.28\sigma_0(1 - T/T_c)^{0.28}/T_0$

Consider the free energy:

$$dF = -SdT + \sigma dA \quad (44)$$

The Maxwell relation reads:

$$\left(\frac{\partial S}{\partial A}\right)_T = -\left(\frac{\partial \sigma}{\partial T}\right)_A = 1.28 \frac{\sigma_0}{T_0} \left(1 - \frac{T}{T_c}\right)^{0.28} \quad (45)$$

Substituting the values yields the entropy per unit area:

$$\left(\frac{\partial S}{\partial A}\right)_T = 2.58 \times 10^{-4} \text{ JK}^{-1} \text{ m}^{-2} \quad (46)$$

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### C.3

Given the free energy  $dF = -SdT - m dB$ , we consider the change in  $F$  under constant temperature:

$$\begin{aligned} F(T, B) - F(T, 0) &= \int_0^B \left(\frac{\partial F}{\partial B}\right)_T dB \\ &= -mB \\ &= -\frac{1}{\mu_0} \chi V B^2 \\ &= -\frac{a}{\mu_0} \frac{1}{T - T_c} V B^2 \end{aligned} \quad (47)$$

On the other hand, note that  $S = -(\partial F / \partial T)_B$  so that:

$$\begin{aligned} S(T, B) - S(T, 0) &= -\frac{\partial}{\partial T} [F(T, B) - F(T, 0)] \\ &= -\frac{aV}{\mu_0} \frac{B^2}{(T - T_c)^2} \end{aligned} \quad (48)$$

For an adiabatic process, we have  $dS = 0$  so that:

$$\frac{B_0^2}{(T_f - T_c)^2} = \frac{B^2}{(T_i - T_c)^2} \quad (49)$$

which gives:

$$\frac{T_f - T_c}{T_i - T_c} = \frac{B_0}{B} \quad (50)$$

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**C.4**