Thermodynamics

Problem Set 3

Thermodynamic Potentials and Methods

Xin, Wenkang

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More Practice

A.1

(a)   The entropy change of the water is:

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

The entropy change of the $100\,^\circ\text{C}$ reservoir is:

$$\Delta S_r = \frac{Q}{T_2} = C \frac{T_1 - T_2}{T_2} \tag{2}$$

The total entropy change is:

$$\Delta S_{uni} = \Delta S_w + \Delta S_r \tag{3}$$

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

$$\Delta S_r = C \frac{T_3 - T_1}{T_3} + C \frac{T_2 - T_3}{T_2} \tag{4}$$

The total entropy change is:

$$\Delta S_{uni} = \Delta S_w + \Delta S_r \tag{5}$$

(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:

$$\Delta S_r = -\frac{Q}{T_2} = -C \frac{T_2 - T_1}{T_2} \tag{6}$$

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

$$\Delta S_w = -\Delta S_r = C \frac{T_2 - T_1}{T_2} \tag{7}$$

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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:

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

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:

$$Q_{in} = \Delta Q + U_0 \tag{14}$$

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

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

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

$$h = \frac{W}{mg} = 40.3 \, \mathrm{m} \tag{16}$$

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A.4

The heat input happens during the isobaric expansion:

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

The heat output happens during the isochroic compression:

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

The efficiency of the engine is:

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

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:

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

Therefore, we can write:

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

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The heat input during the isobaric expansion is:

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

The heat output during the isochoric compression is:

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

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

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

With:

$$\frac{p_1}{p_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$$
$$\frac{p_4}{p_2} = \left(\frac{V_3}{V_1}\right)^{\gamma} \tag{25}$$

we can write:

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

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Potentials and Maxwell Relations

B.1

We know from Gibbs-Duhem equation that $S\mathrm{d}T - V\mathrm{d}p + n\mathrm{d}\mu = 0$. Given that $\mathrm{d}T$ is zero, we have:

$$n = V\frac{\mathrm{d}p}{\mathrm{d}\mu} = \frac{V}{\mathrm{d}\mu/\mathrm{d}p} = \frac{pV}{k_B T} \tag{27}$$

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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 $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$ and $\mathrm{d}S$ is zero so the change in enthalpy is:

$$\Delta H = \int_{p_1}^{p_2} V\mathrm{d}p = p_2V_2 - p_1V_1 - \int_{V_1}^{V_2} p\mathrm{d}V = \textcolor{red}{p_2V_2 - p_1V_1} + W \tag{28}$$

$p_2V_2 - p_1V_1$ 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 $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$. We have $T = (\partial U/\partial S)_V$ and $p = -(\partial U/\partial V)_S$. Therefore, we can write:

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

Next consider $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$. We have $T = (\partial H/\partial S)_p$ and $V = (\partial H/\partial p)_S$. Therefore:

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

Then consider $\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V$. We have $S = -(\partial F/\partial T)_V$ and $p = -(\partial F/\partial V)_T$ and:
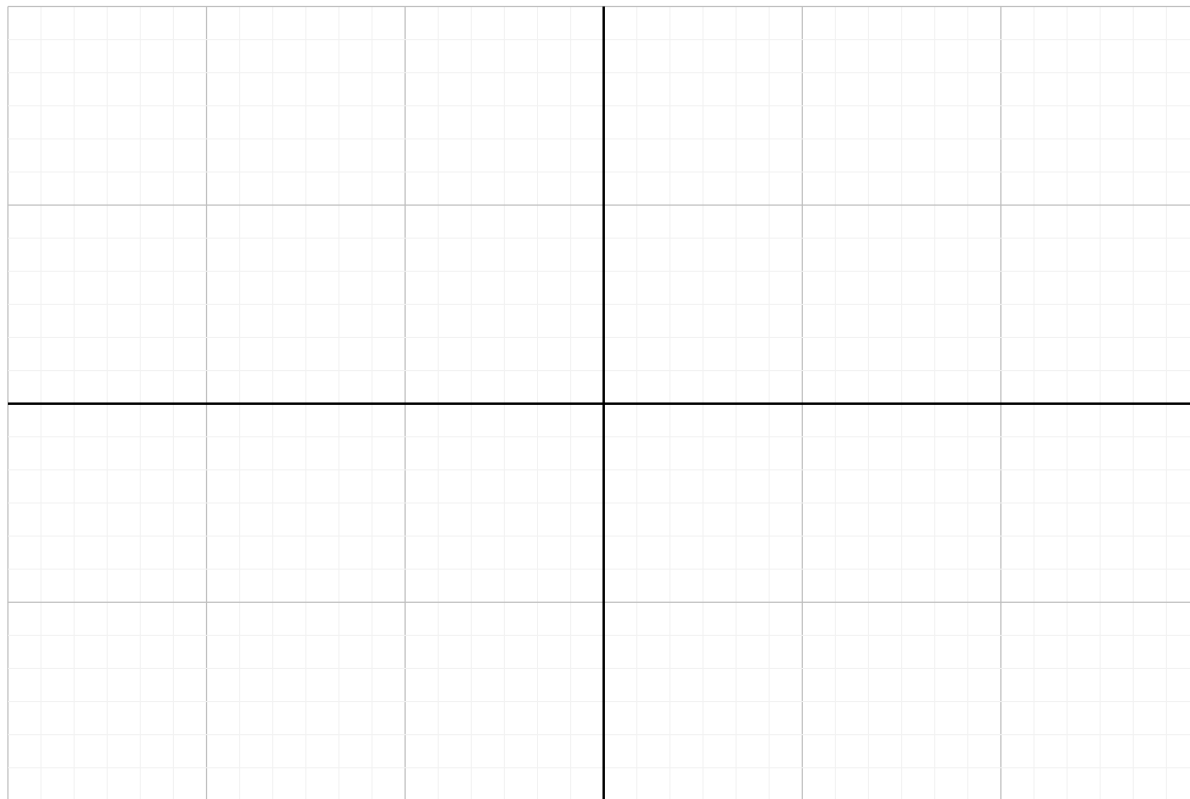
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{31}$$

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

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

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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 $dG = V\,dp - S\,dT$, 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:

$$dU = TdS - pdV + fdL \tag{33}$$

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:

$$dX = TdS - pdV - Ldf \tag{34}$$

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

$$dY = TdS + Vdp - Ldf \tag{35}$$

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

$$dZ = -SdT + Vdp + fdL \tag{36}$$

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

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

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Applications (Rod, Surface, Magnetization, Solid)

C.1

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

$$dU = TdS + fdL \tag{38}$$

The heat capacity at constant length is defined as:

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

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

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

This implies:

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

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C.2

For a liquid, we have:

$$dU = TdS + \sigma dA \tag{42}$$

where σ is surface tension as a function of temperature.

Consider the quantity:

$$dX = TdS - Ad\sigma \tag{43}$$

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

Consider the free energy:

$$\mathrm{d}F = -S\mathrm{d}T + \sigma\mathrm{d}A \tag{44}$$

The Maxwell relation reads:

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

Substituting the values yields the entropy per unit area:

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

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C.3

Given the free energy $\mathrm{d}F = -S\mathrm{d}T - m\mathrm{d}B$, we consider the change in F under constant temperature:

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

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

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

For an adiabatic process, we have $\mathrm{d}S = 0$ so that:

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

which gives:

$$\frac{T_f - T_c}{T_i - T_c} = \frac{B_0}{B} \tag{50}$$

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C.4

We define the isothermal bulk modulus as a partial derivative:

$$B_T = -V \left(\frac{\partial p}{\partial V} \right)_T \tag{51}$$

and the cubic expansion coefficient as:

$$\alpha = \left(\frac{\partial V}{\partial T} \right)_p \tag{52}$$

(i)   In the given isothermal compression, the argon gas satisfy the equation $pV = RT$. We may write the work done on the gas as:

$$
\begin{aligned}
W_g &= -\int_{V_{g0}}^{V_{g1}} p \, dV \\
&= -\int_{V_{g0}}^{V_{g1}} \frac{RT_0}{V} \, dV \\
&= -RT_0 \ln \left(\frac{V_{g1}}{V_{g0}} \right) \\
&= RT_0 \ln \left(\frac{p_1}{p_0} \right)
\end{aligned}
\tag{53}
$$

Let us assume that the isothermal bulk modulus of the sodium metal is approximately constant and the change in its volume is very small. The work done on the sodium is then:

$$
\begin{aligned}
W_s &= -\int p \, dV \\
&= -\int p \left(-\frac{V}{B_T} \right) dp \\
&\approx \frac{V_{s0}}{B_T} \int_{p_0}^{p_1} p \, dp \\
&= \frac{V_{s0}}{2B_T} (p_1^2 - p_0^2)
\end{aligned}
\tag{54}
$$

(ii)   In the given isobaric expansion, we may write the work done on the gas as:

$$
\begin{aligned}
W_g &= -\int_{V_{g0}}^{V_{g1}} p \, dV \\
&= -p_0(V_{g1} - V_{g0}) \\
&= R(T_0 - T_1)
\end{aligned}
\tag{55}
$$

Assuming an approximately constant cubic expansion coefficient, the work done on the sodium is:

$$
\begin{aligned}
W_s &= -\int p \, dV \\
&= -p_0 \Delta V_s \\
&\approx p_0 \alpha (T_0 - T_1)
\end{aligned}
\tag{56}
$$

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