

Chapter 1

Review of Thermodynamics

1.1.

We assume that the energy is a function of N and T and refer to Figure 1.1 in the text. Then

$$Q_1 = \int_{V_A}^{V_B} P dV = Nk_B T_1 \ln \frac{V_B}{V_A}$$

$$Q_2 = Nk_B T_2 \ln \frac{V_D}{V_C} .$$

Along an adiabat $TV^{\gamma-1} = \text{const.}$, with $\gamma = C_P/C_V$. It follows that

$$\ln V_A - \ln V_D = \ln V_B - \ln V_C$$

$$\ln \frac{V_D}{V_C} = -\ln \frac{V_B}{V_A}$$

and we get the desired result

$$\eta = \frac{Q_1 + Q_2}{Q_1} = 1 - \frac{T_2}{T_1} .$$

1.2

(a)

For a reversible process in a magnetic system we have $dQ = TdS = dE - HdM$ and $A = E - TS$ with $dA = -SdT + HdM$. Therefore

$$\left(\frac{\partial S}{\partial M}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_M = -\frac{H}{T}$$

where the last step follows from the equation of state. Differentiation of $E = A + TS$ with respect to M yields

$$\left(\frac{\partial E}{\partial M}\right)_T = T\left(\frac{\partial S}{\partial M}\right)_T + H = 0.$$

Therefore $E(M, T) = E(T)$.

Consider an adiabatic reversible process:

$$\begin{aligned} TdS = 0 &= \left(\frac{\partial E}{\partial T}\right)_M dT - HdM \\ &= C_M(T)dT - \frac{MT}{C}dM. \end{aligned}$$

Integrating, we find

$$\frac{M^2}{2C}\Big|_i^f = \int_{T_i}^{T_f} dT \left(\frac{C_M(T)}{T}\right).$$

To make further progress, we may assume that the specific heat C_M is constant.

With this we have

$$\frac{1}{T} \exp \frac{M^2}{2CC_M} = \text{const.}$$

along an adiabat.

(b)

Assume that the four end-points of the Carnot cycle are given by (H_1, T_1) , (H_2, T_1) , (H_3, T_2) , (H_4, T_2) . Along the isotherm at temperature T_1 we have

$$\Delta Q_{1 \rightarrow 2} = -\int_1^2 HdM = -C \frac{H_2^2 - H_1^2}{2T_1}.$$

Similarly,

$$\Delta Q_{3 \rightarrow 4} = -C \frac{H_4^2 - H_3^2}{2T_2}.$$

Therefore,

$$\eta = 1 + \frac{T_1 (H_4^2 - H_3^2)}{T_2 (H_2^2 - H_1^2)}$$

Along the adiabat connecting points 2 and 3, e.g. we have, since the energy is a function of T only

$$\int_2^3 \frac{dE(T)}{T} = \phi(T_2, T_1) = \frac{1}{C} \int dMM = \frac{C}{2} \left(\frac{H_3^2}{T_2^2} - \frac{H_2^2}{T_1^2} \right).$$

Similarly,

$$\int_4^1 \frac{dE(T)}{T} = -\phi(T_2, T_1) = \frac{C}{2} \left(\frac{H_1^2}{T_1^2} - \frac{H_4^2}{T_2^2} \right)$$

where ϕ is an unknown function. Adding, we obtain

$$0 = \frac{C}{2} \left[\frac{H_3^2 - H_4^2}{T_2^2} + \frac{H_1^2 - H_2^2}{T_1^2} \right].$$

Substituting into the expression for η we obtain

$$\eta = 1 - \frac{T_2}{T_1}.$$

Notice that in this derivation we did not need to assume that C_M is independent of T .

1.3.

Consider a system of fixed volume in contact with a reservoir at fixed temperature T_0 and chemical potential μ_0 . This system can exchange energy and particles with the reservoir. Fluctuations in S and N can only increase the grand potential

$$\Omega(\mu, V, T) = E(S, V, N) - T_0 S - \mu_0 N.$$

Thus

$$\delta\Omega = \delta S \left[\left(\frac{\partial E}{\partial S} \right)_{V,N} - T_0 \right] + \delta N \left[\left(\frac{\partial E}{\partial N} \right)_{V,S} - \mu_0 \right]$$

$$+\frac{1}{2}\delta S^2\frac{\partial^2 E}{\partial S^2} + \delta S\delta N\frac{\partial^2 E}{\partial S\partial N} + \frac{1}{2}\delta N^2\frac{\partial^2 E}{\partial N^2} + \dots \geq 0.$$

At equilibrium the first order terms are zero, requiring the second order terms to be positive semi-definite yields

$$\begin{aligned}\frac{\partial^2 E}{\partial S^2} &= \frac{\partial T}{\partial S} \geq 0 && \rightarrow C_{V,N} \geq 0 \\ \frac{\partial^2 E}{\partial N^2} &= \frac{\partial \mu}{\partial N} \geq 0 && \rightarrow \left(\frac{\partial N}{\partial \mu}\right)_{V,S} \geq 0 \\ \frac{\partial^2 E}{\partial S^2} \frac{\partial^2 E}{\partial N^2} - \left(\frac{\partial^2 E}{\partial S\partial N}\right)^2 &\geq 0 && \rightarrow \frac{C_{V,N}}{T} \frac{\partial N}{\partial \mu} \leq \left(\frac{\partial S}{\partial \mu}\right)^2.\end{aligned}$$

1.4.

The definitions

$$\begin{aligned}C_M &= T \left(\frac{\partial S}{\partial T}\right)_M \\ C_H &= T \left(\frac{\partial S}{\partial T}\right)_H \\ \chi_T &= T \left(\frac{\partial M}{\partial H}\right)_T \\ \chi_S &= T \left(\frac{\partial M}{\partial H}\right)_S\end{aligned}$$

together with the Maxwell relation

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H$$

when substituted into the chain rule formula

$$\left(\frac{\partial S}{\partial T}\right)_H = \left(\frac{\partial S}{\partial T}\right)_M + \left(\frac{\partial S}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_H$$

gives the desired result

$$C_H - C_M = \frac{T}{\chi_T} \left(\frac{\partial M}{\partial T}\right)_H^2. \quad (1.1)$$

To obtain the second formula we apply the chain rule expression

$$\left(\frac{\partial M}{\partial H}\right)_T = \left(\frac{\partial M}{\partial H}\right)_S + \left(\frac{\partial M}{\partial S}\right)_H \left(\frac{\partial S}{\partial H}\right)_T$$

to obtain

$$C_H(\chi_T - \chi_S) = T \left(\frac{\partial S}{\partial T}\right)_H \left(\frac{\partial M}{\partial S}\right)_H \left(\frac{\partial S}{\partial H}\right)_T =$$

$$-T \left(\frac{\partial M}{\partial T} \right)_H \frac{\partial^2 G}{\partial H \partial T} = T \left(\frac{\partial M}{\partial T} \right)_H^2$$

from which we find

$$\chi_T - \chi_S = \frac{T}{C_H} \left(\frac{\partial M}{\partial T} \right)_H^2. \quad (1.2)$$

Finally, by combining (1.1) with (1.2) we find

$$\chi_T(C_H - C_M) = C_H(\chi_T - \chi_H)$$

or

$$\frac{\chi_T}{\chi_H} = \frac{C_H}{C_M}.$$

1.5.

(a)

Along part of the straight line segment the system will absorb heat, while the system will expell heat during the remaining part of the segment. The resolution of the apparent paradox is that while

$$\begin{aligned} \text{work} &= \text{absorbed heat} - |\text{expelled heat}| = Q_{12} \\ \eta &= \text{work}/\text{absorbed heat} < 1. \end{aligned}$$

(b)

We have $C_V = \frac{3}{2}Nk_B$, $\gamma = C_P/C_V = \frac{5}{3}$. Along the straight line segment

$$P = P_1 + (V - V_1) \frac{P_2 - P_1}{V_2 - V_1}$$

and

$$dQ = PdV + C_V dT.$$

We define

$$v = \frac{V}{V_1}; \quad r = \frac{V_2}{V_1}; \quad p = \frac{P}{P_1}; \quad t = \frac{T}{T_1}; \quad q = \frac{Q}{P_1 V_1}; \quad c = \frac{C_V}{Nk_B}$$

and introduce

$$z = \frac{dq}{dv} = (1+c)p + cv \frac{dp}{dv}.$$

If $z = 0$ for $v = x$ we find

$$\eta = \frac{\int_1^r z dv}{\int_1^x z dv}.$$

Numerically we find $x = 1.537$ and $\eta = 0.259$

1.6.

The heat absorbed by the working substance in the step $B \rightarrow C$ is $Q_{B \rightarrow C} = C_P(T_C - T_B)$ and during $D \rightarrow A$ it is $Q_{D \rightarrow A} = C_P(T_A - T_D)$. The efficiency of the cycle is thus

$$\eta = 1 + \frac{T_A - T_D}{T_C - T_B}. \quad (1.3)$$

Along an adiabat $P^{1/\gamma-1}T = \text{const.}$ where $\gamma = C_P/C_V$. Therefore

$$\begin{aligned} T_B &= T_A \left(\frac{P_B}{P_A} \right)^{\frac{\gamma-1}{\gamma}} \\ T_C &= T_D \left(\frac{P_B}{P_A} \right)^{\frac{\gamma-1}{\gamma}}. \end{aligned} \quad (1.4)$$

If we substitute (1.4) into (1.3) we get the desired result.

1.7.

We have

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left(\frac{\partial}{\partial T} \frac{Nk_B T}{P} \right)_P = \frac{1}{T} \quad (1.5)$$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left(\frac{\partial}{\partial P} \frac{Nk_B T}{P} \right)_T = \frac{1}{P}. \quad (1.6)$$

Combining (1.5) and (1.6) gives

$$C_P - C_V = \frac{TV}{\kappa_T} \alpha^2 = Nk_B.$$

1.8.

Since the added gas is inert, we can take the Gibbs free energy in the gas phase to be equal to the sum of the Gibbs free energies of the two components,

evaluated at their respective partial pressures. At constant temperature small changes in the Gibbs free energy can be written $\Delta g = v\Delta P$ where v is the volume per particle. For the system to remain in equilibrium, the change in chemical potential in the gas and liquid phases must remain the same. Thus

$$\Delta\mu_L = v_L(P_i + \delta P) = \Delta\mu_g = v_g\delta P.$$

Assuming that $\delta P \ll P_i \ll P$ and $v_G = k_B T/P$ we get the desired result

$$\frac{\delta P}{P} = \frac{P_i v_L}{k_B T}.$$

1.9.

Connect the two thermodynamic states by a reversible process, i.e. for gas A consider an isothermal expansion. Thus

$$\Delta S_A = \int_{V_A}^{V_A+V_B} dV \frac{N_A k_B T}{V} = N_A k_B \ln \frac{V_A + V_B}{V_A}.$$

A similar expression is obtained for gas B and we find for the entropy of mixing

$$\Delta S = \frac{P}{T} \left(V_A \ln \frac{V}{V_A} + V_B \ln \frac{V}{V_B} \right).$$

1.10

(a)

To show that in equilibrium the energy must be a minimum, consider the following argument. Suppose that we have an equilibrium state at volume V and entropy S in which the energy E is greater than E_{\min} , the minimum value of the energy compatible with the given values of the parameters. Extract $E - E_{\min}$ from the system by doing work on some other system. We can then return this energy in the form of heat. This will raise the entropy, implying that the initial state with E and V was not the state of maximum entropy and therefore not an equilibrium state.

Another way of at least partially demonstrating that E is a concave function is the following argument. The relation $S(E+\Delta E)+S(E-\Delta E)-2S(E, V) \leq 0$ implies that any straight line connecting $S(E_1)$ and $S(E_2)$ lies below the curve $S(E)$. By simply flipping the E and S axes one immediately sees that any straight line connecting $E(S_1)$ and $E(S_2)$ must lie *above* the curve $E(S)$. The local convexity conditions on the energy are then

$$\frac{\partial^2 E}{\partial S^2} \geq 0 \quad \frac{\partial^2 E}{\partial V^2} \geq 0 \quad \frac{\partial^2 E}{\partial S^2} \frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S \partial V} \right)^2 \geq 0.$$

(b)

We will prove that G is a concave function of P and T using the local conditions.

We have $A = E - TS$ and

$$\frac{\partial^2 A}{\partial T^2} = - \left(\frac{\partial S}{\partial T} \right)_V = - \left(\frac{\partial^2 E}{\partial S^2} \right)_V^{-1} \leq 0.$$

Similarly, $\partial^2 A / \partial V^2 \geq 0$. A further Legendre transformation yields the Gibbs potential $G = A + PV$ which has the properties

$$\left(\frac{\partial^2 G}{\partial P^2} \right)_T = \left(\frac{\partial P}{\partial V} \right)^{-1} = - \left(\frac{\partial^2 A}{\partial V^2} \right)_T^{-1} \leq 0$$

and

$$\left(\frac{\partial^2 G}{\partial T^2} \right)_P \leq 0$$

which shows that G is a concave function of P and T separately. To show that the cross-derivatives satisfy the appropriate inequality we proceed somewhat indirectly. From part **(a)** we have

$$\left(\frac{\partial^2 E}{\partial V^2} \right)_S = - \left(\frac{\partial P}{\partial V} \right)_S \geq 0.$$

Let $V = V(P, T)$. Then

$$\begin{aligned} \left(\frac{\partial V}{\partial P} \right)_S &= \left(\frac{\partial V}{\partial P} \right)_T + \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_S \\ &= \left(\frac{\partial^2 G}{\partial P^2} \right)_T + \left(\frac{\partial^2 G}{\partial P \partial T} \right) \left(\frac{\partial T}{\partial P} \right)_S. \end{aligned}$$

From the enthalpic Maxwell relations we have

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

and

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial S}{\partial T}\right)_P^{-1} = -\frac{\partial^2 G}{\partial T \partial P} \left(\frac{\partial^2 G}{\partial T^2}\right)^{-1}.$$

Therefore

$$-\left(\frac{\partial V}{\partial P}\right)_S = \frac{G_{PP}G_{TT} - G_{TP}^2}{G_{TT}} \geq 0$$

where the subscripts indicate partial differentiation with respect to those variables. Since $G_{TT} \leq 0$ we obtain

$$G_{PP}G_{TT} - G_{TP}^2 \leq 0$$

which completes the proof that G is a concave function of P and T .

1.11.

(a)

We combine

$$T = \left(\frac{\partial E}{\partial S}\right)_{NV} = \frac{Ed}{Nk_B}$$

and

$$P = -\left(\frac{\partial E}{\partial V}\right)_{SN} = \frac{Ed}{V} \quad (1.7)$$

to get $PV = Nk_B T$.

(b)

Using (1.7) we find

$$P(S, V, N) = \text{const } d \left(\frac{N}{V}\right)^{d+1} \exp\left[\frac{dS}{Nk_B}\right]$$

and find that $\gamma = d + 1$. Also, from $E = Nk_B T/d$ we find $C_V = Nk_B/d$ and $C_P = \gamma C_V = Nk_B(d + 1)/d$.