

2.1 Heat and work

Use Carnot engine to generate work, $dW = \eta dQ$, $dQ = C_H dT$

$$W = \int \eta C_H dT = -C_H \int_{T_H}^{T_C} \left(1 - \frac{T_C}{T}\right) dT = C_H \left(T_H - T_C + T_C \log \frac{T_C}{T_H}\right) \quad (1)$$

Having 10 tons of boiling water (373.15K) and heat reservoir at 5°C = 278.15K.

$$W = 10 \times 10^6 \times 4.2 \times \left(95 - 278.15 \times \log \frac{373.15}{278.15}\right) = 55.75 \times 10^7 J = 5.58 \times 10^8 J \quad (2)$$

If you use short tons/ U.S. ton (1T=2000lb=907kg) instead of metric tons (1T=1000kg), you will obtain $W = 5.06 \times 10^8 J$. Both answers receive full credits.

2.2 Speed of Sound

For 1-dimensional wave propagation, small non-uniform displacements $\xi(t, x) \ll \lambda$ result in compression(rarefaction) of distance L by $\Delta L = \left(\frac{\partial \xi}{\partial x}\right) L$. Due to conservation of matter (continuity equation) $L\rho(x) = \text{const}$, the local density is changed by $\Delta\rho/\rho = -\Delta L/L$, causing local changes in the pressure, $\Delta p = \left(\frac{\partial p}{\partial \rho}\right)_S \Delta\rho$. The derivative is adiabatic because the wave travels faster than heat exchange. These changes in the pressure create net force

$$F = -A \cdot \left(\frac{\partial \Delta p}{\partial x}\right) \cdot L = -A \cdot \left(\frac{\partial p}{\partial \rho}\right)_S \left(\frac{\partial}{\partial x}\right) \left(-\rho \frac{\Delta L}{L}\right) \cdot L \approx AL\rho \left(\frac{\partial p}{\partial \rho}\right)_S \left(\frac{\partial^2 \xi}{\partial x^2}\right) \quad (3)$$

acting on the air inside the volume AL with mass $AL\rho$, where A is the area perpendicular to the wave direction. Note that we neglected the second-order term $\propto \left(\frac{\partial \xi}{\partial x}\right)^2$.

This force creates acceleration

$$\left(\frac{\partial^2 \xi}{\partial t^2}\right) = \frac{F}{AL\rho} = \left(\frac{\partial p}{\partial \rho}\right)_S \left(\frac{\partial^2 \xi}{\partial x^2}\right) \quad (4)$$

which is a wave equation with phase velocity $u^2 = \left(\frac{\partial p}{\partial \rho}\right)_S$.

More generally, define $\vec{\xi}(\vec{r}, t)$ as small displacement of small volume of gas from its equilibrium position under small pressure variation δp . By Newton's law

$$\rho \frac{\partial^2 \vec{\xi}}{\partial t^2} = -\vec{\nabla} \delta p \quad (5)$$

Consider a cubic region at origin with edges length Δx , Δy , Δz . When origin shifts $\vec{0} \rightarrow \vec{\xi}$, its edges become (in first order in $\vec{\xi}$)

$$\begin{aligned} X : \Delta x \hat{i} &\rightarrow \Delta x \hat{i} + \frac{\partial \vec{\xi}}{\partial x} \Delta x + \vec{\xi}(\vec{0}) \\ Y : \Delta x \hat{j} &\rightarrow \Delta y \hat{j} + \frac{\partial \vec{\xi}}{\partial y} \Delta y + \vec{\xi}(\vec{0}) \\ Z : \Delta x \hat{k} &\rightarrow \Delta z \hat{k} + \frac{\partial \vec{\xi}}{\partial z} \Delta z + \vec{\xi}(\vec{0}) \end{aligned} \quad (6)$$

$$\frac{V + \delta V}{V} = \left(\hat{i} + \frac{\partial \vec{\xi}}{\partial x}\right) \times \left(\hat{j} + \frac{\partial \vec{\xi}}{\partial y}\right) \cdot \left(\hat{k} + \frac{\partial \vec{\xi}}{\partial z}\right) = 1 + \vec{\nabla} \cdot \vec{\xi} \Rightarrow \frac{\delta V}{V} = \vec{\nabla} \cdot \vec{\xi} \quad (7)$$

By definition of compressibility under adiabatic reservable process

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S = V \left(\frac{\partial}{\partial p} \frac{1}{V} \right)_S = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_S \quad (8)$$

Also

$$\begin{aligned} \delta p &= -\frac{1}{\kappa_S} \frac{\delta V}{V} = -\frac{1}{\kappa_S} \vec{\nabla} \cdot \vec{\xi} \\ \rho \frac{\partial^2 \vec{\xi}}{\partial t^2} &= -\vec{\nabla} \delta p = \frac{1}{\kappa_S} \vec{\nabla} (\vec{\nabla} \cdot \vec{\xi}) \end{aligned} \quad (9)$$

It's wave equation for longitudinal wave. Read out

$$u^2 = \frac{1}{\rho \kappa_S} = \frac{-v}{\rho} \left(\frac{\partial p}{\partial v} \right)_S = \frac{-v}{\rho} \frac{d\rho}{dv} \left(\frac{\partial p}{\partial \rho} \right)_S = \frac{\rho}{\rho} \left(\frac{\partial p}{\partial \rho} \right)_S = \left(\frac{\partial p}{\partial \rho} \right)_S \quad (10)$$

For ideal gas $pv = T$

$$\begin{aligned} \kappa_S &= \frac{\kappa_T}{\gamma} = \frac{-1}{\gamma} \frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T = \frac{T}{\gamma v p^2} = \frac{1}{\gamma p} \\ u^2 &= \frac{\gamma p}{\rho} = \frac{\gamma T}{m_0} = \frac{5T}{3m_0} \end{aligned} \quad (11)$$

For van der Waals gas $(p + \frac{a}{v^2})(v - b) = T$

$$u^2 = \frac{1}{\rho \kappa_S} = -\frac{\gamma v}{\rho} \left(\frac{\partial p}{\partial v} \right)_T = \frac{\gamma v}{\rho} \left[\frac{T}{(v-b)^2} - \frac{2a}{v^3} \right] \quad (12)$$

By homework 1.4 (a)

$$\begin{aligned} c_p - c_v &= \frac{1}{1 - \frac{2a(v-b)^2}{Tv^3}} \Rightarrow \gamma = \frac{c_p}{c_v} = 1 + \frac{2}{3} \frac{1}{1 - \frac{2a(v-b)^2}{Tv^3}} \\ \Rightarrow u^2 &= \frac{vT}{\rho(v-b)^2} \left[1 - \frac{2a(v-b)^2}{Tv^3} \right] \frac{\frac{5}{3} - \frac{2a(v-b)^2}{Tv^3}}{1 - \frac{2a(v-b)^2}{Tv^3}} = \frac{T}{m_0} \left[\frac{5v^2}{3(v-b)^2} - \frac{2a}{Tv} \right] \end{aligned} \quad (13)$$

In ideal gas limit $a, b \rightarrow 0$, $u_{\text{vanderWaals}}^2 \rightarrow u_{\text{ideal}}^2$

2.3 Thermodynamics of an electric battery

(a) Discharge current is equivalent to expanding volume of a gas, so $dV \leftrightarrow dq$, and the work done by the battery is equal to $\mathcal{E}dq$, so the e.m.f. \mathcal{E} is equivalent to gas pressure.

(b) When battery discharges, it does work $\delta W = \mathcal{E}dq$ (neglecting battery volume change), hence

$$\Rightarrow TdS = dU + \mathcal{E}(T)dq \quad \Rightarrow \quad dU = TdS - \mathcal{E}(T)dq. \quad (14)$$

It's important we have (+) in front of \mathcal{E} . With (-) sign, one would have $dU = TdS + \mathcal{E}dq$ and the battery would gain energy when discharging.

(c) The internal energy of the battery is reduced by the amount of work done *by the battery* ($\mathcal{E}\Delta q$) and increased by the heat absorbed from the environment:

$$(\Delta U)_T = -w(T)\Delta q = -\mathcal{E}\Delta q + T\Delta S \quad \Rightarrow \quad -w(T) = -\mathcal{E}(T) + T \left(\frac{\partial S}{\partial q} \right)_T. \quad (15)$$

Equivalently, the work done by the battery at $T = \text{const}$ reduces its free energy $F = U - TS$, and

$$dF = -SdT - \mathcal{E}dq \quad (16)$$

(d) Since the free energy is a function of state, there is a relation between entropy and e.m.f derivatives

$$\left(\frac{\partial S}{\partial q}\right)_T = \left(\frac{\partial \mathcal{E}}{\partial T}\right)_q \quad (17)$$

One can express the change of the internal energy at constant temperature $w(T)$ through its change at constant entropy,

$$-\mathcal{E}(T)\Delta q = \Delta(U - TS) = (\Delta U)_T - T\Delta S = -w(T) - T\Delta S \Rightarrow -\mathcal{E}(T) = -w(T) - T\left(\frac{dS}{dq}\right)_T. \quad (18)$$

Note that the change of the internal energy of the battery $(\Delta U)_T$ discussed above is related *only* to the chemical energy stored in the battery; the thermal energy is not changed because the temperature is constant.

(e) From the differential of the free energy $dF = d(U - TS) = -SdT - \mathcal{E}(T)dq$, the derivatives are related as $\left(\frac{\partial S}{\partial q}\right)_T = \left(\frac{\partial \mathcal{E}}{\partial T}\right)_q$ and

$$T\left(\frac{\partial \mathcal{E}}{\partial T}\right)_q = T\left(\frac{\partial S}{\partial q}\right)_T = -w(T) + \mathcal{E}(T) \Rightarrow w(T) = \mathcal{E}(T) - T\frac{d\mathcal{E}}{dT} \quad (19)$$

Now suppose $\frac{d\mathcal{E}}{dT} < 0$, then $\mathcal{E}(T) - w(T) = T\frac{d\mathcal{E}}{dT} < 0$. The chemical energy of the battery is reduced by $w(T)\Delta q$ to do work $\mathcal{E}(T)\Delta q < w(T)\Delta q$ while moving charge $\Delta q > 0$. The excess energy has to be released as heat $\Delta Q = (w(T) - \mathcal{E}(T))\Delta q > 0$, therefore the battery will become hotter, increasing its temperature by $\Delta T = \Delta Q/C$, where C is the heat capacity of the battery. If the battery is in contact with a heatbath at T_{HB} , the temperature will increase temporarily to $T > T_{HB}$ to transfer heat from the battery to the heatbath.

2.4 Paramagnetic medium

N non-interacting magnetic dipoles $\mu_z^{(k)} = \pm\mu$. Under external magnetic field H , $E = -H\sum_k \mu_z^{(k)}$

(a) If $N_{\uparrow\downarrow}$ is the number of dipoles pointing upward(downward), then

$$N = N_{\uparrow} + N_{\downarrow}, \quad E = -H\mu N_{\uparrow} + H\mu N_{\downarrow} = -H\mu(N_{\uparrow} - N_{\downarrow}) = -HM, \quad (20)$$

$$N_{\uparrow\downarrow} = \frac{1}{2} \left(N \pm \frac{-E}{H\mu} \right) = \frac{1}{2} \left(N \mp \frac{E}{H\mu} \right)$$

(When flipping one dipole, it generates -2μ to M). The statistical weight is equal to the possible number of combinations $\binom{N}{N_{\uparrow}} = \binom{N}{N_{\downarrow}} = \frac{N!}{N_{\uparrow}!N_{\downarrow}!}$

$$S = \log \frac{N!}{N_{\uparrow}!N_{\downarrow}!} \simeq N \log N - \frac{1}{2} \left(N + \frac{E}{H\mu} \right) \log \frac{1}{2} \left(N + \frac{E}{H\mu} \right) - \frac{1}{2} \left(N - \frac{E}{H\mu} \right) \log \frac{1}{2} \left(N - \frac{E}{H\mu} \right) \quad (21)$$

One may check the result by $E = \pm H\mu$ (all dipole pointing in same direction), giving $S = 0$.

(b) Find T from its definition

$$\frac{1}{T} = \beta = \left(\frac{\partial S}{\partial E}\right)_H = \frac{1}{2H\mu} \log \frac{NH\mu - E}{NH\mu + E} \quad (22)$$

(note that $E < 0$) and solve for $E(T, H)$

$$\frac{NH\mu - E}{NH\mu + E} = e^{2H\mu/T} \Leftrightarrow E(T, H) = NH\mu \frac{1 - e^{2H\mu/T}}{1 + e^{2H\mu/T}} = -NH\mu \tanh \frac{H\mu}{T} = -NH\mu \tanh(\beta H\mu), \quad (23)$$

and the magnetization can be computed from the energy directly

$$M(T, H) = -\frac{E}{H} = N\mu \tanh \frac{H\mu}{T} = N\mu \tanh(\beta H\mu) \quad (24)$$

with $\beta = \frac{1}{T}$. One may check at $T = 0$, $\beta \rightarrow \infty$, one gets $E = -NH\mu$, $M = N\mu$, and when $H \rightarrow 0$, $E, M \rightarrow 0$ as expected.

(c) Susceptibility

$$\chi = \left(\frac{\partial M}{\partial H} \right)_T = \frac{\partial}{\partial H} N\mu \tanh \beta H\mu = \frac{N\beta\mu^2}{\cosh^2 \beta H\mu} \quad (25)$$

One may check as $T \rightarrow 0$, $\beta \rightarrow \infty$, $\Rightarrow \chi \rightarrow 0$ as expected. No matter how large H is, dipoles will always point in the same direction up to thermal fluctuations. With increasing temperature, magnetization decreases:

$$\left(\frac{\partial M}{\partial T} \right)_H = \frac{d\beta}{dT} \left(\frac{\partial M}{\partial \beta} \right)_H = (-\beta^2) \frac{NH\mu^2}{\cosh^2 \beta H\mu} \quad (26)$$