

Solutions to exercises week 40

FYS2160

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November 7, 2017

Schroeder 4.1

a)

Net work done by gas during one cycle: $|W| = 2P_1V_1$

Heat absorbed (steps where $Q > 0$): $Q_h = \frac{33}{2}P_1V_1$

Efficiency: $e = \frac{|W|}{Q_h} = \frac{4}{33} = 12\%$

b)

Efficiency of heat engine: $e \leq 1 - \frac{T_c}{T_h}$

Use the ideal gas law, $PV = NkT$, to find the ratio of T_c to T_h . Lower left corner has the lowest temperature, $T = T_c$. Step A: P increases by a factor 2 $\Rightarrow T$ increases by the same factor 2. Step B: V increases by a factor 3 $\Rightarrow T$ increases by a factor 3. The highest temperature is then found in the upper right corner of the rectangular cycle in the PV -diagram, and is $T_h = 2 \cdot 3T_c = 6T_c$.

Maximal efficiency: $e_{\max} = 1 - \frac{T_c}{6T_c} = 5/6 = 83\%$

Schroeder 5.2

Look up $\Delta_f H$ and S for N_2 , H_2 and NH_3 at the back of the book, calculate $\Delta G = \Delta H - T\Delta S$ for the reaction $N_2 + 3H_2 \rightarrow 2NH_3$ and check with the tabulated value of $\Delta G(NH_3)$. The change in Gibbs free energy in this process is $2\Delta G(NH_3) = -32.90$ kJ.

Schroeder 5.23

a)

Writing $\Phi = U - TS - \mu N$ in terms of infinitesimal changes of the quantities involved:

$$d\Phi = dU - TdS - SdT - \mu dN - Nd\mu.$$

Inserting the thermodynamic identity for dU gives

$$d\Phi = -PdV - SdT - Nd\mu.$$

The partial derivatives of Φ wrt. T , V or μ is obtained by holding the two other quantities fixed:

$$\left(\frac{\partial\Phi}{\partial T}\right)_{V,\mu} = -S, \quad \left(\frac{\partial\Phi}{\partial V}\right)_{T,\mu} = -P, \quad \left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V} = -N.$$

b)

As was done for F and G in chapter 5.2 in Schroeder, express an infinitesimal change in the total entropy S_{total} as a sum of changes in the entropy S of the system and the entropy S_R of the reservoir it is in contact with:

$$dS_{\text{total}} = dS + dS_R.$$

Assuming V fixed, apply the thermodynamic identity to dS_R (solve the expression for dU_R in terms of dS_R), and use the fact that $dU_R = -dU$ and $dN_R = -dN$ to write dS_R in terms of system variables. The total entropy of the system plus reservoir (expressed in terms of system variables) is then

$$dS_{\text{total}} = -\frac{1}{T}(dU - TdS - \mu dN) = -\frac{1}{T}d\Phi.$$

The tendency of the total entropy to increase therefore means that the grand free energy tends to decrease (since dS_{total} is positive, $d\Phi$ must be negative in order to make $-d\Phi/T$ positive).

c)

$$\begin{aligned}\Phi &= U - TS - \mu N \\ &= U - TS + PV - PV - \mu N \\ &= G - PV - \mu N \\ &= -PV,\end{aligned}$$

where we in the last step use that $G = \mu N$ when T and P are constant (from the thermodynamic identity of G , $dG = -SdT + VdP + \mu dN$ with $dN = 1$).

d)

For the unoccupied state: $U = S = N = 0 \Rightarrow \Phi = 0$.

For the occupied state: $U = U_0 = -13.6 \text{ eV}$, $S = 0$, $N = 1$

$$\begin{aligned}\Phi_{\text{occupied}} &= U_0 - \mu \\ &= U_0 + kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right],\end{aligned}$$

where eq. 3.63 in Schroeder is used for the chemical potential of an ideal gas. Here m is the electron mass, and the electron concentration is given as $N/V = 2 \times 10^{19} \text{ m}^{-3}$. Putting in numbers gives us (the logarithm is calculated to be equal to 17.8)

$$\begin{aligned}\Phi_{\text{occupied}} &= -13.6 \text{ eV} + 8.62 \times 10^{-5} \text{ eV/K} \times 5800 \text{ K} \times 17.8 \\ &\approx -4.7 \text{ eV} < \Phi_{\text{unoccupied}} = 0 \text{ eV}.\end{aligned}$$

To find the temperature at which the occupied and unoccupied states are equally likely, we set their grand free energies to be equal and solve for T (neglecting the $\ln T^{3/2}$ dependence, which is insignificant compared to the factor T outside the logarithm, when T is varied):

$$\begin{aligned}\Phi_{\text{occupied}} &= \Phi_{\text{unoccupied}} \\ U_0 - 17.8kT &= 0 \\ T &= -\frac{U_0}{17.8k} \approx 8800 \text{ K}\end{aligned}$$

Schroeder 5.32

a)

The Clausius-Clapeyron relation: $\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}$.

When ice melts to water, the entropy increases (ΔS , $L > 0$), while the volume decreases ($\Delta V < 0$); therefore, $dP/dT < 0$.

b)

Latent heat for converting ice into water: $L = 333 \text{ J/g}$

Density of ice: $\rho_{\text{ice}} = 917 \text{ kg/m}^3 = 0.917 \times 10^6 \text{ g/m}^3$

Density of water: $\rho_{\text{water}} = 1000 \text{ kg/m}^3 = 1.000 \times 10^6 \text{ g/m}^3$

Volume of 1 g of ice: $V_{\text{ice}} = \frac{1 \text{ g}}{0.917 \times 10^6 \text{ g/m}^3} = 1.091 \times 10^{-6} \text{ m}^3$

Volume of 1 g of water: $V_{\text{water}} = 1.000 \times 10^{-6} \text{ m}^3$

$$\Delta V = V_{\text{water}} - V_{\text{ice}} = -0.091 \times 10^{-6} \text{ m}^3$$

Ice melts at -1°C if the pressure is at least

$$\begin{aligned} \frac{dP}{dT} &= \frac{L}{T\Delta V} = \frac{333 \text{ J}}{273 \text{ K} \times (-0.091 \times 10^{-6} \text{ m}^3)} \\ &\approx -1.35 \times 10^7 \text{ Pa/K} = -135 \text{ bar/K}. \end{aligned}$$

c)

The pressure P (force per area) under an ice column of height z and density ρ is $P = \rho gz$. Therefore, the depth corresponding to a pressure of 135 bar is

$$z = \frac{P}{\rho g} = \frac{135 \times 10^5 \text{ N/m}^2}{917 \text{ kg/m}^3 \times 9.81 \text{ N/m}^2} \approx 1500 \text{ m}.$$

d)

As a crude approximation, take the area under the ice skate that's in contact with the ice to be $\sim 1 \text{ mm}$ in width and $\sim 10 \text{ cm}$ in length, that is $\sim 10^{-4} \text{ m}^2$. An ice skater weighing 50 kg would exert a force of $\sim 500 \text{ N}$ on the ice. This amounts to a pressure on the ice of $P = 500 \text{ N}/10^{-4} \text{ m}^2 = 5 \times 10^6 \text{ Pa} = 50 \text{ bar}$. Under this pressure the melting point only drops by $\sim (50 \text{ bar})/(135 \text{ bar}/^\circ\text{C}) \approx 0.4^\circ\text{C}$. So the temperature needs to be within half a degree from the melting point in the first place, in order for this to have any effect.

Schroeder 6.5

a)

Consider a particle with three energy levels: $\epsilon_1 = -0.05 \text{ eV}$, $\epsilon_2 = 0 \text{ eV}$ and $\epsilon_3 = 0.05 \text{ eV}$. At 300 K, $kT \approx 0.026 \text{ eV}$. The partition function is then

$$Z = e^{-(-0.05/0.026)} + e^0 + e^{-(0.05/0.026)} \approx 6.84 + 1 + 0.15 = 7.99.$$

b)

The probability of an energy state ϵ_i is equal to

$$P(\epsilon_i) = \frac{e^{-\epsilon_i/kT}}{Z},$$

giving

$$P(\epsilon_1 = -0.05 \text{ eV}) \approx 0.86$$

$$P(\epsilon_2 = 0 \text{ eV}) \approx 0.13$$

$$P(\epsilon_3 = 0.05 \text{ eV}) \approx 0.02$$

c)

We now shift the zero point of energy so that: $\epsilon_1 = 0 \text{ eV}$, $\epsilon_2 = 0.05 \text{ eV}$ and $\epsilon_3 = 0.10 \text{ eV}$. In this case the partition function becomes

$$Z = e^0 + e^{-(0.05/0.026)} + e^{-(0.10/0.026)} \approx 1 + 0.15 + 0.02 = 1.17,$$

with corresponding probabilities

$$P(\epsilon_1 = 0 \text{ eV}) \approx 0.86$$

$$P(\epsilon_2 = 0.05 \text{ eV}) \approx 0.13$$

$$P(\epsilon_3 = 0.10 \text{ eV}) \approx 0.02$$

The choice of zero-point of energy is arbitrary. Shifting the zero-point changes the values of the Boltzmann factors and the sum of these. However, the probability of the energy states ($P_i = e^{-\epsilon_i/kT}/Z$, that is, the ratio of individual Boltzmann factors to the sum) are not dependent on this choice.

Schroeder 6.6

Hydrogen atom in the ground state ($n = 1$): $E_1 = -13.6$ eV.

Hydrogen atom in the first excited state ($n = 2$): $E_2 = -3.4$ eV.

$$\Delta E = E_2 - E_1 = 10.2 \text{ eV}$$

Probability of finding a Hydrogen atom in one of its first excited states compared to the ground state:

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}}$$

Degeneracy of energy levels: $d(n) = \sum_{l=0}^{n-1} (2l + 1) = n^2$

There are four states with energy E_2 , hence finding a Hydrogen atom at room temperature (300 K) in a state with energy E_2 compared to the ground state becomes

$$\frac{P(E_2)}{P(E_1)} = 4e^{-(E_2-E_1)/kT} \approx 4e^{-10.2/0.026} \approx 10^{-171}.$$

Hence, you will never find a Hydrogen atom in its first excited state at room temperature.

Now, doing the same calculation for a Hydrogen atom in the atmosphere of the star γ UMa, with surface temperature $T = 9500$ K:

$$\frac{P(E_2)}{P(E_1)} = 4e^{-10.2 \text{ eV}/(k \times 9500 \text{ K})} \approx 1.6 \times 10^{-5}.$$

In the atmosphere of γ UMa approximately 1 in 64 000 Hydrogen atoms will be found in one of their first excited states.

Compendium 8.1

a)

First law of thermodynamics: $\Delta U = Q + W$

Adiabatic process: $Q = 0 \Rightarrow \Delta U = Q \Rightarrow \Delta U - W = 0$

Finding expressions for ΔU and W :

Equipartition theorem: $U = \frac{1}{2}fnRT \Rightarrow \Delta U = \frac{1}{2}fnR\Delta T$

Work: $W = -P\Delta V = -\frac{nRT}{V}\Delta V$ (the ideal gas law has been used in the last step)

Inserting the expressions for ΔU and W :

$$\begin{aligned}\Delta U - W &= 0 \\ \frac{1}{2}fnR\Delta T - \left(-\frac{nRT}{V}\Delta V\right) &= 0 \\ \frac{fR}{2}\frac{\Delta T}{T} + R\frac{\Delta V}{V} &= 0\end{aligned}$$

Now, what remains is to show that $c_{V,m} = fR/2$. In general the heat capacity can be expressed as

$$C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T} = \frac{\Delta U + P\Delta V}{\Delta T}.$$

Heat capacity at constant volume is then

$$C_V = \left(\frac{\Delta U}{\Delta T}\right)_V = \frac{fnR\Delta T/2}{\Delta T} = \frac{fnR}{2},$$

which for 1 mole of gas ($n = 1$) becomes

$$c_{V,m} = \frac{fR}{2}.$$

Inserting this last relation, we end up with the expression we were asked to show:

$$c_{V,m}\frac{\Delta T}{T} + R\frac{\Delta V}{V} = 0$$

b)

Let $\Delta T \rightarrow dT$ and $\Delta V \rightarrow dV$, and integrate the expression in a) over T and V between two states, 1 and 2:

$$\begin{aligned}c_{V,m} \int_{T_1}^{T_2} \frac{dT}{T} &= -R \int_{V_1}^{V_2} \frac{dV}{V} \\c_{V,m} \ln \frac{T_2}{T_1} &= -R \ln \frac{V_2}{V_1} = R \ln \frac{V_1}{V_2} \\ \ln \left(\frac{T_2}{T_1} \right)^{c_{V,m}} &= \ln \left(\frac{V_1}{V_2} \right)^R \\ \left(\frac{T_2}{T_1} \right)^{c_{V,m}} &= \left(\frac{V_1}{V_2} \right)^R \quad (\text{exponentiating both sides}) \\ T_2^{c_{V,m}} V_2^R &= T_1^{c_{V,m}} V_1^R \\ T_2 V_2^{R/c_{V,m}} &= T_1 V_1^{R/c_{V,m}} \quad (\text{taking the } c_{V,m}\text{-root of both sides}) \\ T_2 V_2^\alpha &= T_1 V_1^\alpha,\end{aligned}$$

where $\alpha = R/c_{V,m}$.

c)

Using the ideal gas law to insert $T = \frac{PV}{nR}$:

$$TV^\alpha = \frac{PV}{nR} V^\alpha = \frac{P}{nR} V^{\alpha+1}.$$

The heat capacity at constant pressure is

$$\begin{aligned}
 C_P &= \left(\frac{Q}{\Delta T} \right)_P = \left(\frac{\Delta U - W}{\Delta T} \right)_P \\
 &= \left(\frac{fnR\Delta T/2 + P\Delta V}{\Delta T} \right)_P \\
 &= \frac{fnR}{2} + P \left(\frac{\Delta V}{\Delta T} \right)_P \\
 &= \frac{fnR}{2} + P \frac{\Delta(nRT/P)_P}{\Delta T} \\
 &= \frac{fnR}{2} + P \frac{nR\Delta T/P}{\Delta T} \\
 &= \frac{fnR}{2} + nR.
 \end{aligned}$$

The specific heat capacity for one mole at constant pressure, is then

$$\begin{aligned}
 c_{P,m} &= \frac{fR}{2} + R \\
 &= c_{V,m} + R \\
 \Rightarrow \frac{c_{P,m}}{c_{V,m}} &= 1 + \frac{R}{c_{V,m}} = 1 + \alpha \equiv \gamma
 \end{aligned}$$

This gives us

$$TV^\alpha = \frac{P}{nR}V^{\alpha+1} = \frac{P}{nR}V^\gamma.$$

For one mole

$$\begin{aligned}
 T_1V_1^\alpha &= T_2V_2^\alpha \\
 \frac{P_1}{R}V_1^\gamma &= \frac{P_2}{R}V_2^\gamma \\
 P_1V_1^\gamma &= P_2V_2^\gamma.
 \end{aligned}$$

Inserting $V = RT/P$ in the equation above, we can in a similar manner rewrite it on the following form

$$T_1P_1^\beta = T_2P_2^\beta,$$

where $\beta \equiv (1 - \gamma)/\gamma$.

Compendium 8.2

a)

Isentropic = adiabatic + quasistatic. A quasistatic process means a change in volume that is sufficiently slow so that the gas has time to equilibrate to the changing conditions, and therefore maintains a uniform pressure. In order to compress the gas non-quasistatically, one would need to compress the gas faster than it is able to respond. This corresponds to a speed at least as fast as the speed of sound in the gas, and so quasistatic compression is often a reasonable assumption.

b)

For an ideal gas undergoing an adiabatic process, we know that $PV^\gamma = C$, where C is some constant. Solved for V , this becomes $V = (C/P)^{1/\gamma}$. The isentropic compressibility (with constant entropy S) is then

$$\begin{aligned}\kappa_S &= -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S = -\frac{1}{V} \frac{\partial}{\partial P} \left(\frac{C}{P} \right)^{1/\gamma} \\ &= -\frac{C^{1/\gamma}}{V} \left(-\frac{1/\gamma}{P^{1/\gamma+1}} \right) = \frac{C^{1/\gamma}}{V} \left(\frac{1/\gamma}{PP^{1/\gamma}} \right) \\ &= \frac{1}{\gamma PV} \left(\frac{C}{P} \right)^{1/\gamma} = \frac{1}{\gamma PV} V \\ &= \frac{1}{\gamma P}.\end{aligned}$$

For an isothermal process (T is constant) we use the ideal gas law to find an expression for V in terms of P : $V = (nRT)/P$. The isothermal compress-

ibility is then

$$\begin{aligned}
 \kappa_T &= -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \frac{\partial}{\partial P} \left(\frac{nRT}{P} \right) \\
 &= -\frac{1}{V} \left(-\frac{nRT}{P^2} \right) = \frac{nRT}{P^2 V} \\
 &= \frac{1}{P^2} \frac{nRT}{V} = \frac{P}{P^2} \\
 &= \frac{1}{P}.
 \end{aligned}$$

The ratio

$$\frac{\kappa_T}{\kappa_S} = \frac{1/P}{1/(\gamma P)} = \frac{\gamma P}{P} = \gamma,$$

therefore tells us that κ_S is smaller than κ_T by a factor γ , as we wanted to show.

c)

The speed of sound in air can be expressed as $v = (\kappa_S \rho)^{-1/2}$, where $\kappa_S = 1/(\gamma P)$ is the isentropic compressibility and $\rho = nM/V$, with n equal to the number of moles, M the mass of one mole and V the total volume of the gas.

Using this information we can write

$$\begin{aligned}
 v &= (\kappa_S \rho)^{-1/2} = \left(\frac{1}{\gamma P} \frac{nM}{V} \right)^{-1/2} \\
 &= \left(\frac{nM}{\gamma nRT} \right)^{-1/2} \quad (\text{using } PV = nRT) \\
 &= \sqrt{\frac{\gamma RT}{M}}.
 \end{aligned}$$

d)

Using that $\gamma = (f + 2)/f$, where the number of active degrees of freedom f in air at room temperature ($T = 300$ K) is assumed to be 5 (3 translational

and 2 rotational), the speed of sound in air is calculated to be

$$v = \sqrt{\frac{[(5 + 2)/5] \times 8.315 \text{ J/mol}\cdot\text{K} \times 300 \text{ K}}{2.9 \times 10^{-2} \text{ kg/mol}}} \approx 347 \text{ m/s.}$$

e)

The average translational kinetic energy per molecule is

$$\bar{K}_{\text{trans,molecule}} = \frac{1}{2}m\bar{v}^2 = \frac{1}{2}m(\bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2) = \frac{3}{2}kT.$$

For n moles of air, with molar mass M , this amounts to

$$\bar{K}_{\text{trans}} = \frac{1}{2}nM\bar{v}^2 = \frac{3}{2}nRT.$$

Solving for \bar{v}^2 gives

$$\bar{v}^2 = \frac{3RT}{M}.$$

Taking the square root on both sides does not give us the average speed, but the root-mean-square (rms), which is a close approximation to the average:

$$v_{\text{rms}} \equiv \sqrt{\bar{v}^2} = \sqrt{\frac{3RT}{M}} \approx 508 \text{ m/s.}$$