HW8 —Solutions

Problem 1: Adiabatic compression

Problem statement (summary). For an ideal gas undergoing a reversible adiabatic process, derive relations between P, V, T and compute numerical results for two gases ($\gamma = 5/3$ and $\gamma = 7/5$) compressed from V_0 to $V_0/2$. Compare final pressures and the work done.

Solution

Key relations

For a reversible adiabatic process for an ideal gas

$$PV^\gamma = \text{const.} \tag{1}$$

The ideal gas law is

$$PV = nRT. \tag{2}$$

Substitute $P = nRT/V$ into Eq. (1):

$$\left(\frac{nRT}{V}\right) V^\gamma = nRT\, V^{\gamma-1} = \text{const} \quad \Rightarrow \quad TV^{\gamma-1} = \text{const.} \tag{3}$$

Thus

$$T \propto V^{1-\gamma}.$$

Also eliminate V to get P vs T:

$$V \propto T^{-1/(\gamma-1)}, \qquad P \propto V^{-\gamma} \propto T^{\gamma/(\gamma-1)}.$$

Final pressure after compression $V_0 \to V_0/2$

From Eq. (1):

$$P_f = P_0 \left(\frac{V_0}{V_f}\right)^\gamma = P_0 (2)^\gamma. \tag{4}$$

Therefore

$$P_A = P_0\, 2^{5/3} \approx 3.1748\, P_0,$$
$$P_B = P_0\, 2^{7/5} \approx 2.6390\, P_0.$$

Work done during reversible adiabatic compression

For a reversible process, the work done *on* the gas (positive for compression) from V_1 to V_2 is

$$W_{\text{on}} = -\int_{V_1}^{V_2} P\, dV. \tag{5}$$

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Using $P = \text{const} \cdot V^{-\gamma}$, integrate:

$$W_{\text{on}} = -P_1 V_1^{\gamma} \int_{V_1}^{V_2} V^{-\gamma}\, dV = -P_1 V_1^{\gamma} \left[\frac{V^{1-\gamma}}{1-\gamma} \right]_{V_1}^{V_2} \tag{6}$$

$$= \frac{P_1 V_1}{\gamma - 1} \left[\left(\frac{V_2}{V_1} \right)^{1-\gamma} - 1 \right]. \tag{7}$$

With $V_2/V_1 = 1/2$ this becomes

$$W_{\text{on}} = \frac{P_0 V_0}{\gamma - 1} \left(2^{\gamma - 1} - 1 \right). \tag{8}$$

Since $P_0 V_0$ is the same for both gases (same initial conditions), the ratio of works is

$$\frac{W_A}{W_B} = \frac{(\gamma_B - 1)(2^{\gamma_A - 1} - 1)}{(\gamma_A - 1)(2^{\gamma_B - 1} - 1)} \tag{9}$$

Plugging $\gamma_A = 5/3$ and $\gamma_B = 7/5$ yields

$$\frac{W_A}{W_B} = \frac{2/5(2^{2/3} - 1)}{2/3(2^{2/5} - 1)} \approx 1.1031.$$

Problem 2: Gas mixing and free expansion

Problem summary. Two equal volumes V each contain monatomic ideal gases at (P_1, T_1) and (P_2, T_2). Valve opened, gases mix; find final P_f, T_f. Also discuss case when second side is vacuum (free expansion).

Solution

Let initial moles be $n_1 = P_1 V/(RT_1)$ and $n_2 = P_2 V/(RT_2)$. Total internal energy (monatomic ideal gas) is $U = nC_V T$ with $C_V = 3R/2$ per mole (here C_V is NOT NECESSARY). Since the container is rigid and adiabatic and no external work or heat is exchanged, total internal energy is conserved (no reaction):

$$n_1 C_V T_1 + n_2 C_V T_2 = (n_1 + n_2) C_V T_f \quad \Rightarrow \quad T_f = \frac{n_1 T_1 + n_2 T_2}{n_1 + n_2}. \tag{10}$$

Substitute n_i or use $n_i T_i = P_i V/R$ to get

$$T_f = \frac{P_1 + P_2}{P_1/T_1 + P_2/T_2}. \tag{11}$$

Total moles $n = n_1 + n_2 = (V/R)(P_1/T_1 + P_2/T_2)$ and total volume $2V$, so final pressure is

$$P_f = \frac{nRT_f}{2V} = \frac{P_1 + P_2}{2}. \tag{12}$$

(Algebraic cancellation makes P_f independent of initial temperatures when volumes are equal.)

Free expansion (one side vacuum)

If one side is initially vacuum and the other side contains an ideal gas at (P_i, T_i) with volume V, removing the partition allows the gas to freely expand into a total volume of $2V$. Because the container is rigid and adiabatic, the gas does no work on the surroundings and exchanges no heat. For an ideal gas, the internal energy depends only on temperature, so the internal energy remains constant and therefore

$$T_f = T_i.$$

Since n is unchanged and the final volume doubles, the final pressure is

$$P_f = \frac{P_i}{2}.$$

Molecular average energy and speed. For an ideal gas, the average translational kinetic energy per molecule is

$$\langle E \rangle = \frac{3}{2} k_B T.$$

Because $T_f = T_i$, the average energy per molecule remains the same during free expansion. The root-mean-square speed,

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}},$$

also remains unchanged because it depends only on temperature. Thus, although the gas occupies twice the volume and its pressure drops by a factor of two, the *average molecular energy and average molecular speed do not change*.

P.S. Entropy change for the gas is $\Delta S = nR\ln(2)$ (irreversible free expansion).

Problem 3: Hydrostatic equilibrium and isothermal atmosphere

Problem summary. Derive $dP/dh = -\rho g$ and solve for $P(h)$ and $\rho(h)$ for an isothermal ideal gas.

Solution

Consider a slab of cross-sectional area A and thickness dh at height h. Force balance:

$$P(h)A - P(h + dh)A - \rho(h)A dh\, g = 0.$$

Divide by A and take $dh \to 0$ to obtain

$$\frac{dP}{dh} = -\rho(g).$$

Use ideal gas: $P = nk_B T = (\rho/m)k_B T$ where m is particle mass. Substitute:

$$\frac{dP}{dh} = -\frac{\mu g}{k_B T} P.$$

Integrate:

$$P(h) = P(0)\exp\left(-\frac{\mu g h}{k_B T}\right), \qquad (similarly,\ \rho(h) = \rho(0)\exp\left(-\frac{\mu g h}{k_B T}\right).)$$

Problem 4: Molecular vs atomic gases, high temperature behavior

Problem summary. Compare boxes containing equal numbers of O_2 molecules and He atoms at the same temperature; discuss pressure equality and behavior at very high T (e.g. 10^5 K).

Solution

Even though an O_2 molecule contains two atoms, the pressure of an ideal gas is determined by the momentum transferred to the wall by collisions of *particles* (i.e., molecular centers of mass), not by the number of atoms bound inside each particle. Consider one particle of mass m with velocity component v_x toward a rigid wall. In an elastic reflection, the particle reverses its normal velocity, so the momentum transferred to the wall in one collision is

$$\Delta p = mv_x - m(-v_x) = 2mv_x.$$

Thus the impulse delivered to the wall depends only on the center-of-mass motion.

The collision flux of particles per unit area is $nf(v_x)v_x$ for $v_x > 0$, so the total momentum transfer per unit time (the pressure) is

$$P = \int_0^\infty nf(v_x)v_x(2mv_x)\,dv_x = \tfrac{1}{3}nm\langle v^2\rangle.$$

Using equipartition for translational motion,

$$\tfrac{1}{2}m\langle v^2\rangle = \tfrac{3}{2}k_BT,$$

we obtain the ideal-gas law

$$P = nk_BT.$$

Therefore, if the two boxes contain the same number of *particles* (O_2 molecules vs. He atoms) at the same temperature and volume, they exhibit the same pressure. The fact that each O_2 molecule contains two atoms does not matter: only the translational motion of the molecular center of mass contributes to wall collisions, while internal rotational and vibrational degrees of freedom affect internal energy but not the momentum transfer that produces pressure (unless chemical reactions or dissociation change the number of particles).

At very high temperatures (e.g. $T = 10^5$ K) additional physics arises:

- O_2 will dissociate into O atoms if the thermal energy is comparable to or larger than the bond dissociation energy; the dissociation increases particle number (molecules $\to$ atoms), so pressure at fixed T, V will increase.

- Ionization may occur: atoms can lose electrons and form ions and free electrons, changing number densities and leading to plasma behavior. The degree of ionization depends sensitively on T and particle density and is computed by the Saha equation.

Appendix A: O_2 dissociation quantitative estimates at $T = 10^5\,\mathrm{K}$

Numerical constants

- Boltzmann constant $k_B = 8.617333 \times 10^{-5}$ eV/K.

- O_2 bond dissociation energy $D_0(O_2 \to 2O) \approx 5.08$ eV/molecule (approx. 490 kJ/mol). **(main)**

- First ionization energy of O atom ≈ 13.62 eV.

Thermal energies at $T = 10^5\,\mathrm{K}$

$$k_B T \approx 8.6173 \text{ eV}, \tag{13}$$

$$\tfrac{3}{2} k_B T \approx 12.926 \text{ eV} \approx 1247 \text{ kJ/mol}. \tag{14}$$

Comparison: $\tfrac{3}{2} k_B T$ is much larger than the O_2 dissociation energy, therefore thermal collisions can readily break O_2 bonds. The electron ionization energy is comparable to $\tfrac{3}{2} k_B T$, so partial ionization is expected; full ionization depends on number density.

Electron gas remark

At these temperatures free electrons behave as a classical (non-degenerate) gas for typical laboratory densities. They satisfy an ideal-gas-like relation $P_e = n_e k_B T_e$ and have Maxwellian velocity distributions if collisional frequencies are sufficient to thermalize them.