

Problem P21.45 Solution:

I will solve this problem two ways: the first way ("sol. 1") is correct and gives the same answer as the back of the book. The second solution ("sol. 2") is not correct - I will explain why. The book does not say this explicitly, but you should assume the temperature range is such that O_2 has five degrees of freedom (i.e., it can rotate but not vibrate). This is true for "reasonable" temperatures - those within a factor of two of room temperature or so.

Sol. 1: (correct): (this is similar to example 21-6 in the text; page 534).

Assume we have 1.0 mol of gas molecules overall. Then $f(1.0 \text{ mol})$ are Argon (Ar), and $(1-f)(1.0 \text{ mol})$ are Oxygen (O_2). The point of the problem is to solve for f .

$$U_{O_2} = n_{O_2} \left(\frac{5}{2} RT \right) = \frac{5}{2} (1-f) (1.0 \text{ mol}) RT$$

$$U_{Ar} = n_{Ar} \left(\frac{3}{2} RT \right) = \frac{3}{2} (f) (1.0 \text{ mol}) RT$$

$$U_{total} = U_{O_2} + U_{Ar} = \left[\frac{5}{2} (1-f) + \frac{3}{2} f \right] (1.0 \text{ mol}) RT$$

This is the effective molar heat capacity of the gas mixture

$$C_V^{(eff)} = \frac{1}{n} \frac{dU_{total}}{dT} = \left[\frac{5}{2} (1-f) + \frac{3}{2} f \right] R$$

($n = 1 \text{ mol}$)

$$\gamma^{(eff)} = \frac{C_P^{(eff)}}{C_V^{(eff)}} = \frac{C_V^{(eff)} + R}{C_V^{(eff)}} = \frac{\frac{5}{2} (1-f) + \frac{3}{2} f + 1}{\frac{5}{2} (1-f) + \frac{3}{2} f}$$

This is the effective adiabatic constant for the gas mixture

For the problem at hand, $P_i V_i^{\gamma^{(eff)}} = P_f V_f^{\gamma^{(eff)}}$... plugging in $\left(\frac{P_i}{P_f} \right) = 3$ and $\left(\frac{V_f}{V_i} \right) = 2$, we get $\gamma^{(eff)} = \frac{\ln 3}{\ln 2} \approx 1.585$. Setting this equal to eq. (*) above, we

can solve for f to obtain $f = 0.79 \Rightarrow$ 79% Argon

Sol. 2 (incorrect). $P_i = P_{i,O_2} + P_{i,Ar}$

Dalton's Law of Partial Pressures: $f P_i = P_{i,Ar}$ and $(1-f) P_i = P_{i,O_2}$

$PV^\gamma = \text{const.}$ for each gas separately: $P_{f,Ar} = P_{i,Ar} \left(\frac{1}{2}\right)^{5/3}$ and $P_{f,O_2} = P_{i,O_2} \left(\frac{1}{2}\right)^{7/5}$

$$\underbrace{P_{f,Ar} + P_{f,O_2}} = P_{i,Ar} \left(\frac{1}{2}\right)^{5/3} + P_{i,O_2} \left(\frac{1}{2}\right)^{7/5}$$
$$= P_f = \frac{1}{3} P_i$$

$$\frac{1}{3} P_i = f P_i \left(\frac{1}{2}\right)^{5/3} + (1-f) P_i \left(\frac{1}{2}\right)^{7/5} \Rightarrow f = \frac{\left(\frac{1}{2}\right)^{7/5} - \frac{1}{3}}{\left(\frac{1}{2}\right)^{7/5} - \left(\frac{1}{2}\right)^{5/3}} \approx 71.3\% \text{ Argon}$$

This is inconsistent with sol. 1, so what happened?

The mistake in this solution comes in assuming we can treat each gas separately as an adiabatic expansion. The two gases are initially at the same temperature.

Suppose we increase the volume by some amount dV ... what is dT_i for each gas i ?

Using $PV = nRT$ and $PV^\gamma = \text{const.}$ ^(const. or n), you can show $\frac{dT_i}{dV} = (\text{const.})_i (1 - \gamma_i) \frac{1}{V \gamma_i} < 0$.

Since $\gamma_{Ar} > \gamma_{O_2}$, the Argon drops in temperature faster than the O_2 does, but the important point is that, in general, $dT_{Ar} \neq dT_{O_2}$. In assuming we have a reversible process, we need to allow the Argon and Oxygen to come into equilibrium before we continue the adiabatic expansion. That is, even though the gas mixture doesn't exchange heat with its surroundings, the Oxygen and Argon do exchange heat with each other, and so we cannot consider them to separately be expanding adiabatically.
