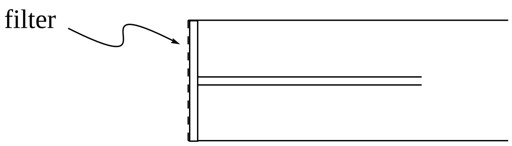
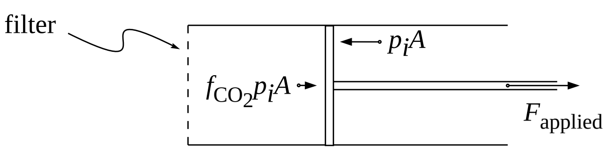
Carbon sequestration

Start with air at pressure p_i and CO_2 mole fraction f_{CO_2}. Calculate the minimum work required to extract N moles of CO_2 at pressure p_f isothermally at temperature T. At the end of the problem, set $p_f = p_i$.

Start with a cylinder of cross-sectional area A, with the piston plunged all the way in. The base of the cylinder is a filter that allows CO_2 to pass through, but no other gas (a "semi-permeable membrane"... see Enrico Fermi, *Thermodynamics*, page 101).



First stroke (purification). Pull piston out to volume $V_{\max} = \dfrac{NRT}{f_{CO_2} p_i}$.



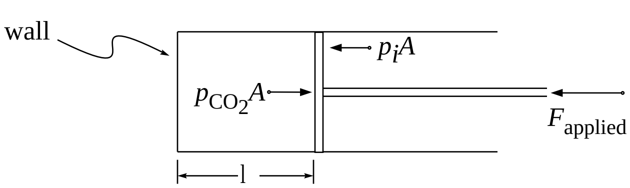
But

$$F_{\text{applied}} = p_i A - f_{CO_2} p_i A = p_i A(1 - f_{CO_2})$$

so

$$\begin{aligned}
\text{Work done} &= p_i A(1 - f_{CO_2})(\text{maximum length}) \\
&= p_i V_{\max}(1 - f_{CO_2}) \\
&= NRT\left(\frac{1 - f_{CO_2}}{f_{CO_2}}\right) \\
&= NRT\left(\frac{1}{f_{CO_2}} - 1\right) \qquad (1)
\end{aligned}$$

Second stroke (compression). Replace filter with regular wall, then push piston in to achieve pressure p_f. This happens at final volume V_f where $p_f V_f = NRT$



During the inward stroke,

$$p_{\mathrm{CO}_2} = \frac{NRT}{V}$$

so

$$F_{\text{applied}} = p_{\mathrm{CO}_2} A - p_i A = \left(\frac{NRT}{V} - p_i \right) A.$$

Thus

$$\begin{aligned}
\text{Work done} &= -\int_{\ell_{\max}}^{\ell_f} F_{\text{applied}}\, d\ell \\
&= -\int_{\ell_{\max}}^{\ell_f} \left(\frac{NRT}{V} - p_i \right) A\, d\ell \\
&= -NRT \int_{V_{\max}}^{V_f} \frac{dV}{V} + p_i (V_f - V_{\max}) \\
&= -NRT \ln \frac{V_f}{V_{\max}} + p_i (V_f - V_{\max}) \\
&= +NRT \ln \frac{V_{\max}}{V_f} - p_i (V_{\max} - V_f) \\
&= NRT \ln \frac{p_f}{f_{\mathrm{CO}_2} p_i} - p_i \left(\frac{NRT}{f_{\mathrm{CO}_2} p_i} - \frac{NRT}{p_f} \right) \\
&= NRT \left(\ln \frac{p_f}{f_{\mathrm{CO}_2} p_i} - \frac{1}{f_{\mathrm{CO}_2}} + \frac{p_i}{p_f} \right) \qquad (2)
\end{aligned}$$

Overall. Summing the works from both strokes,

$$\text{Total work} = NRT \left(\ln \frac{p_f}{f_{\mathrm{CO}_2} p_i} - 1 + \frac{p_i}{p_f} \right), \qquad (3)$$

or, if $p_f = p_i$,

$$\text{Total work} = NRT \left(\ln \frac{1}{f_{\mathrm{CO}_2}} \right) = -NRT \ln f_{\mathrm{CO}_2}. \qquad (4)$$

Debrief.

- Does this expression have the proper sign?

  We expect the work done to be positive – it requires work to purify a substance. Our equation $-NRT \ln f_{\mathrm{CO}_2}$ starts off with a negative sign, but the quantity f_{CO_2} is less than one, so $\ln f_{\mathrm{CO}_2}$ is negative, and the total work given by $-NRT \ln f_{\mathrm{CO}_2}$ is positive — as expected!

- Does this expression have the proper limit when $f_{\mathrm{CO}_2} = 1$?

  If you start off with pure CO_2, it shouldn't require any work to purify it, and sure enough it doesn't.

- Does this expression have the proper limit when $f_{\mathrm{CO}_2} = 0$?

  If there's no CO_2 present, you shouldn't be able to purify any CO_2 from the mixture. Sure enough, our expression claims it would require infinite work to carry out this feat.