

Gravitational Potential Energy

A reviewer of our Long-Column Pressure Vessel simulations wrote, “As discussed by Ramberg (1971), isenthalpic cooling in a gravitational field is subject to an additional potential term:

$$dH = C_p dT + (1 - \alpha T) V dP - V \rho g dh = 0 \quad “$$

If we consider an adiabatic steady-state process, we can express the enthalpy of fluid leaving the system as

$$h_{out} = h_{in} + \frac{V_{out}^2 - V_{in}^2}{2} + g(z_{out} - z_{in})$$

Assuming very slow flow in porous media, we can safely neglect the kinetic energy contributions to enthalpy change, and consider only the fluid enthalpy itself and the gravitational potential terms.

In order to justify ignoring gravitational potential, $h_{in} - h_{out} \gg g(z_{in} - z_{out})$.

For the LUCI system, the gravity term for the LUCI system is approximately $10 \times 500 = 5,000 \text{ m}^2/\text{s}^2$.

For our conditions, CO₂ enthalpy at the bottom (85 bars, 36 C) is about 625,699 J/kg and at the top (35 bars, 24 C) is 769,147 J/kg. These enthalpy changes are thus on the order of $6.2\text{e}5 - 7.6\text{e}5 = 1.5\text{e}5 \text{ J/kg}$,

Our system has about 30 times more enthalpy change due to pressure change than due to gravitational potential change.

For more discussion of gravitational potential energy, see Stauffer et al. (2003), Waldbaum (Aug. 1971), and Ramberg (Dec. 1971).

Scale Analysis

We can look at this another way by doing a scale analysis of Equation 1 as presented by the Reviewer. Assuming that the average CO₂ density at the bottom of the column at 85 bars and 35 C is approximately 500 kg m⁻³ (specific volume (V) is 2 x 10⁻³ m³ kg⁻¹), we can make the following scale analysis of the terms in Eq. 1:

Assuming Cp (CO₂ at 85 bar, 35 C) ~ 0.01 J kg⁻¹ K⁻¹, and dT ~ 14 C, the first term in Eq. 1 is of order 0.14 J kg⁻¹.

For the second term in Eq. 1, the coefficient of thermal expansivity is approximately 0.0375 K⁻¹ at 85 bars ($-1/\rho * dp/dT = 1/500 \text{ kg m}^{-3} * -300 \text{ kg m}^{-3}/16 \text{ K} = 0.0375 \text{ K}^{-1}$), therefore the second term, assuming T is in K, is $(1 + 0.0375 \text{ K}^{-1} * 308 \text{ K}) * VdP \sim 10 * VdP$. Assuming dP is the hydrostatic pressure difference, this term becomes of order $10 * 2 * 10^{-3} \text{ m}^3 \text{ kg}^{-1} * 1000 \text{ kg m}^{-3} * 9.8 \text{ m s}^{-2} * 500 \text{ m} \sim 1e5 \text{ J kg}^{-1}$, assuming properties near the bottom of the system.

If we consider now the scale of this second term near the top of the column, say at 35 bars and 24 C, the density of CO₂ is about 73 kg m⁻³, and the thermal expansivity is approximately $-1/\rho * dp/dT = 1/73 \text{ kg m}^{-3} * -7 \text{ kg m}^{-3}/16 \text{ K} = 0.006 \text{ K}^{-1}$, so the second term becomes $(1 + 0.006 \text{ K}^{-1} * 297 \text{ K}) * VdP \sim 3 * VdP$. Again assuming dP is the hydrostatic pressure difference, this term is of order $3 * 1.37 * 10^{-2} \text{ m}^3 \text{ kg}^{-1} * 1000 \text{ kg m}^{-3} * 9.8 \text{ m s}^{-2} * 500 \text{ m} \sim 2e5 \text{ J kg}^{-1}$ near the top of the system.

The last term in Eq. 1, the gravitational potential term in question, $V \rho g d h$, is of order V times $500 \text{ kg m}^{-3} * 9.81 \text{ m s}^{-2} * 500 \text{ m} \sim V * 2e6 \text{ kg m}^{-1} \text{ s}^{-2}$ which is $2 * 10^{-3} \text{ m}^3 \text{ kg}^{-1} * 2e6 \text{ kg m}^{-1} \text{ s}^{-2} \sim 5e3 \text{ J kg}^{-1}$. This term is 20 or 40 times smaller than the VdP term, depending on whether we consider conditions near the bottom or top of the column, respectively.

As this scale analysis shows, the second term, the VdP term, dominates the enthalpy equation by more than an order of magnitude showing the gravitational potential term can be safely neglected from the enthalpy equation. In order for gravitational potential to be important, the vertical change in height would have to be 5 km or so, all else being equal.

Thus by two different scale analyses, we can show the gravitational potential term is about 20-40 times smaller than the Vdp term. We have added some sentences to address the importance of this gravitational potential term, along with the three references. (p. 9, lines 1-6).

Thermophysical properties used in the scale analysis above for pure CO₂ were obtained from the NIST Chemistry Webbook.