Computing a Partial Derivative for a Van der Waals Gas—C.E. Mungan, Spring 2014

In an article in Phys. Rev. ST Phys. Educ. Res. **10**, 010101 (2014) we are given the following problem. Compute $(\partial U / \partial p)_S$ given the three relations

$$p = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2} \tag{1}$$

for the pressure,

$$S = Nk\left\{ \ln\left[\frac{(V - Nb)T^{3/2}}{N\Phi} \right] + \frac{5}{2} \right\} \tag{2}$$

for the entropy, and

$$U = \frac{3NkT}{2} - \frac{aN^2}{V} \tag{3}$$

for the internal energy. Here *N*, *a*, *b*, *k*, and Φ are all constants.

Each equation has two variables *T* and *V* on the right side. So take the differentials of each of these equations to get

$$dp = \frac{Nk}{V - Nb} dT + \left[\frac{2aN^2}{V^3} - \frac{NkT}{(V - Nb)^2} \right] dV \tag{4}$$

from (1),

$$dS = \frac{3Nk}{2T} dT + \frac{Nk}{V - Nb} dV \tag{5}$$

from (2), and

$$dU = \frac{3Nk}{2} dT + \frac{aN^2}{V^2} dV \tag{6}$$

from (3). Now, to hold *S* constant in the desired partial derivative, we want $dS = 0$. It then follows from (5) that

$$dT = -\frac{2T}{3(V - Nb)} dV\,. \tag{7}$$

We substitute this result into (4) and (6) and take their ratio to obtain the final solution

$$\left(\frac{\partial U}{\partial p} \right)_S = \frac{\dfrac{aN^2}{V^2} - \dfrac{NkT}{V - Nb}}{\dfrac{2aN^2}{V^3} - \dfrac{5NkT}{3(V - Nb)^2}} = 3V(V - Nb) \frac{aN(V - Nb) - kTV^2}{6aN(V - Nb)^2 - 5kTV^3}\,. \tag{8}$$

This is the same solution as presented in the article in Tables V and VI, but with considerably less algebra. For a monatomic ideal gas one has $a = 0$ and $b = 0$, so that (8) becomes $(\partial U / \partial p)_S = 3V / 5$, consistent with the fact that $U = pV / (\gamma - 1)$ where $V = (\text{constant} / p)^{1/\gamma}$ for an adiabatic process with $\gamma = 5 / 3$.