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

\[
p = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}
\]

for the pressure,

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

for the entropy, and

\[
U = \frac{3NkT}{2} - \frac{aN^2}{V}
\]

for the internal energy. Here \(N, a, b, k,\) and \(\Phi\) 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

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

from (1),

\[
ds = \frac{3Nk}{2T} \, dT + \frac{Nk}{V - Nb} \, dV
\]

from (2), and

\[
dU = \frac{3Nk}{2} \, dT + \frac{aN^2}{V^2} \, dV
\]

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

\[
dT = -\frac{2T}{3(V - Nb)} \, dV.
\]

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

\[
\left( \frac{\partial U}{\partial p} \right)_S = \frac{aN^2}{V^2} - \frac{NkT}{V - Nb} - \frac{aN(V - Nb) - kTV^2}{6aN(V - Nb)^2 - 5kTV^3}.
\]
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 $\gamma = 5 / 3$. 