1 January 2002, Thermodynamics, Problem 1

Enthalpy is conserved during the Joule-Thomson process. A brief proof is as follows:

$$U_f - U_i = \Delta U = \int (-P_1 dV_1 - P_2 dV_2) = -P_1 \int_V^0 dV_1 - P_2 \int_0^{V_f} dV_2 = P_1 V - P_2 V_f$$
$$U_f + P_2 V_f = U_i + P_1 V$$
$$H_f = H_i$$

Now we must calculate the enthalpy. With a fixed number of particles:

$$dF = -PdV - SdT$$
$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{RT}{V-b} - \frac{a}{V^2}$$
$$F = -RTln(V-b) - \frac{a}{V} + f(T)$$

where f is an arbitrary function. The entropy can be obtained:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = Rln(V-b) - f'(T)$$
$$H = U + PV = F + TS + PV = -\frac{2a}{V} + f(T) - f'(T)T + \frac{RTV}{V-b}$$

This quantity is conserved throughout the process. We still haven't figured out what f is, and in fact I don't know how to, without making assumptions such as the heat capacity being known and constant. But let's say we can determine $\left(\frac{\partial S}{\partial T}\right)_V$ for some temperature range around the temperature T_1 that we are interested in. Then:

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_V = -Tf''(T)$$
$$f(T) = -C_V T lnT + cT + D$$

where c and D are two undetermined constants. Then we get:

$$H = -\frac{2a}{V} + D + C_V T + \frac{RTV}{V-b}$$

With this we can write down three equations in three unknowns (T_1, T_2, V_f):

$$-\frac{2a}{V} + C_V T_1 + \frac{RT_1 V}{V-b} = -\frac{2a}{V_f} + C_V T_2 + \frac{RT_2 V_f}{V_f - b}$$
$$\left(P_1 + \frac{a}{V^2}\right)(V-b) = RT_1$$
$$\left(P_2 + \frac{a}{V_f^2}\right)(V_f - b) = RT_2$$

After this it's all just messy algebra. Plug in for T_1 and T_2 into the first equation and solve for V_f. This equation is probably going to be very involved so you'll have to make assumptions of small changes and/or small parameters a and b. After you get that, plug it into the equation for T_2 and subtract the expression for T_1. That is the final answer. See the Russians' solution.