Stat. Mech. S'04 #13

Unlike the ideal gas case where E is only a function of T (i.e. $E = \frac{3}{2} NkT$), for a van der Waals gas E is also a function of V.

(Reif p. 173)

$$dE = C_V\, dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV$$

now $\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{(V - bN)}$

then

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{NkT}{(V-bN)} - \frac{NkT}{(V-bN)} + a\left(\frac{N}{V}\right)^2 = a\left(\frac{N}{V}\right)^2$$

hence

$$E(T, V) = \int C_V\, dT + aN^2 \int \frac{dV}{V^2}$$

we are told $C_V = \frac{3}{2} Nk$ (as for an ideal gas)

hence

$$E(T, V) = \frac{3}{2} Nk\, \Delta T + aN^2 \int \frac{dV}{V^2}$$

As this is a free adiabatic expansion

$$\Delta E = 0 \quad (\text{as } \overset{\text{adiabatic}}{Q = 0} \text{ and } \overset{\text{free expansion}}{p\,dV = 0})$$

$$0 = \frac{3}{2} \cancel{N} k \overset{T_F - T_i}{\Delta T} - aN^{\cancel{2}} \frac{1}{V'}\Bigg|_{\frac{V}{3}}^{V}$$

$$\frac{3}{2} k \Delta T = a N \left(\frac{1}{V} - \frac{1}{V/3} \right) = a N \left(\frac{1}{V} - \frac{3}{V} \right) = -\frac{2aN}{V}$$

hence

$$\Delta T = -\frac{4Na}{3kV} \Rightarrow \boxed{T_f = T_i - \frac{4}{3} \frac{N}{k} \frac{a}{V}}$$