PS 25: Problem 2.57

(a) The Van der Waals equation of state is given by

$$\left(P + \frac{N^2}{V^2}\right)(V - Nb) = NkT \quad (1)$$

Since the density $\rho = \frac{N}{V} \ll 1$, (1) can be approximated as

$$P(V - Nb) = NkT \quad (2)$$

Rearranging terms to isolate P,

$$P = \frac{NkT}{V - Nb} \quad (3)$$

The work done on the gas is

$$W = -\int_{V_1}^{V_2} P \, dV \quad (4)$$

Plugging in (3) into (4),

$$W_{VDW} = -\int_{V_1}^{V_2} \frac{NkT}{V - Nb} \, dV$$
$$= -NkT \int_{V_1}^{V_2} \frac{dV}{V - Nb} \quad (5)$$

Let $u \equiv V - Nb$, $du \equiv dV$.

$$W_{VDW} = -NkT \int_{V_1 - Nb}^{V_2 - Nb} \frac{du}{u}$$
$$= -NkT \ln(u) \Big|_{V_1 - Nb}^{V_2 - Nb}$$
$$= -NkT[\ln(V_2 - Nb) - \ln(V_1 - Nb)]$$

$$\boxed{W_{VDW} = NkT \ln\left[\frac{V_1 - Nb}{V_2 - Nb}\right]} \quad (6)$$

(b) Assuming the gas is ideal and subjected to the same conditions, recall the ideal gas law and isolate P once again:

$$PV = NkT \quad (7)$$
$$P = \frac{NkT}{V} \quad (8)$$

The work done on the gas is

$$W_{ideal} = -\int_{V_1}^{V_2} \frac{NkT}{V} \, dV$$
$$= -NkT \ln(V) \Big|_{V_1}^{V_2}$$
$$= -NkT[\ln(V_2) - \ln(V_1)]$$

$$\boxed{W_{ideal} = NkT \ln\left(\frac{V_1}{V_2}\right)} \quad (9)$$

Getting the difference of (6) and (9),

$$W_{VDW} - W_{ideal} = NkT \ln\left[\frac{V_1 - Nb}{V_2 - Nb}\right] - NkT \ln\left[\frac{V_1}{V_2}\right]$$

$$\boxed{W_{VDW} - W_{ideal} = NkT \ln\left[\frac{(V_1 - Nb)V_2}{(V_2 - Nb)V_1}\right]} \quad (10)$$

This implies that when $V_2 > V_1$ the ln term is less than zero and contributes a negative term: the work done by a non-ideal gas is less than the work done by an ideal gas. This may be due to the factor of Nb subtracted from the terms in the Van der Waals equation which accounts for the size of the particles.