EX. 5.4 (6th), 5.7 (7th)

Every year I get asked about this, because Atkins is being a bit "sneaky" in the way he asks the question.

In class, we learned that $V_m(s) \approx V_m(l)$ is a very good approximation for most cases,

i.e., $\left(\frac{\partial G}{\partial p}\right)_T = V$, $dG = V dp$ @ const T

$$\int dG = V \int dp = n V_m \int dp$$
$$\Delta G = n V_m \Delta p$$

However, in some cases where really enormous pressure changes are made (e.g., geological) the V_m might be pressure dependent.
One such possibility is

$$V = V(1\,\text{atm})(1 - \kappa_T p)$$

where κ_T is the isothermal compressibility

RECALL: $\kappa_T = \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

κ_T is tabulated in the book (tables at the back) so I am not sure why Atkins doesn't mention this in the question.

Nonetheless, it is a good exercise which demonstrates a slightly different calculation of ΔG.

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(6th) (7th)
EX. 5.4, 5.7, cont'd

calculate ΔG for 35 g of ethanol ($\rho = 0.789\ g\,cm^{-3}$) subject to an isothermal pressure increase from 1 atm to 3000 atm.

<u>I would include</u>: V varies according to

$$V = V(1\,atm)(1 - \kappa_T p)$$

where $\kappa_T = 76.8\times10^{-6}\ atm^{-1}$

<u>SOL'N</u>

$$dG = V\,dp$$

$$\Delta G = \int_{p_i}^{p_f} V(1 - \kappa_T p)\,dp$$

$$= \frac{m}{\rho}\left[\int_{p_i}^{p_f} dp - \int_{p_i}^{p_f} \kappa_T p\,dp\right]$$

$$= \frac{m}{\rho}\left[p - \kappa_T \cdot \frac{p^2}{2}\right]\Bigg|_{p_i}^{p_f}$$

NOTE IN 6TH ED. ATKINS INTEGRATION IS <u>INCORRECT</u>

$$\frac{m}{\rho} = \frac{35\,g}{0.789\times10^{6}\,g\,m^{-3}} = 4.436\times10^{-5}\,m^3$$

$\int x\,dx = \frac{x^2}{2}$ — ATKINS misses this

$$= (4.436\times10^{-5}\,m^3)[2999\,atm - (76.8\times10^{-6}\,atm^{-1})/2$$

$$\times\{(3000\,atm)^2 - (1\,atm)^2\}]$$

$$= (4.436\times10^{-5}\,m^3)[2999\,atm - 345.6\,atm]$$

$$= 0.1177\ atm\ m^3 \cdot 101325\ Pa\ atm^{-1}$$

$$= 1.193\times10^4\ J$$

$$= \boxed{+11.9\ kJ}$$

(if you get 10.4 kJ, you forgot to divide by 2, as mentioned above).