Exercises 5.9(b): Calculate the change in molar Gibbs Energy of a perfect gas when its pressure is increased isothermal from 92.0 to 252.0 kPa at 50 ºC.

\[ dG = VdP - SdT \] Since isothermal
\[ dG = VdP \] Since Ideal
\[ dG = nRT/P \, dV \]
\[ \Delta G = nRT\ln(P_f/P_i) = 1 \text{ mol} \cdot 8.314 \text{ J/mol-K} \cdot 323 \text{K} \cdot \ln(252 \text{kPa}/92 \text{kPa}) = 2.71 \text{ kJ/mol} \]

Exercises 5.12(b): Estimate the change in the Gibbs energy of 1.0 L of water when the pressure acting on it is increased from 100 kPa to 300 kPa.

Since volume change for liquids is assumed to be small
\[ \Delta G = V\Delta P = 1 \text{ L} \cdot 200 \text{ kPa} = 200 \text{ L-kPa} = 200 \text{ J or 3.6 J/mol}. \]
Compare to previous answer to see how insensitive the free energy of solids and liquids are to pressure

Exercises 5.15(a): Evaluate \((\partial S/\partial V)_T\) for a van der Waals gas. For an isothermal expansion will \(\Delta S\) be greater for a perfect gas or a van der Waals gas? Explain your reasoning.

\[ p = \frac{RT}{(V-b)} - \frac{a}{V^2} \]
\[ (\partial S/\partial V)_T = (\partial p/\partial T)_V = (\partial (RT/(V-b)) - \frac{a}{V^2})/\partial T)_V = \frac{R}{(V-b)} \]
\[ S = S(V,T) \]
\[ dS = (\partial S/\partial V)_T dV + (\partial S/\partial T)_V dT = 0.0 \] isothermal
\[ dS = (\partial S/\partial V)_T dV \]
\[ dS = R/(V-b)dV \]
\[ \Delta S = R\ln((V_f-b)/(V_i-b)) \] for van der Waals gas
\[ \Delta S = R\ln(V_f/V_i) \] for ideal gas
\[ \Delta S \] is larger for the van der Waals gas as the argument for the \(\ln\) function has a smaller denominator.
Problem 5.10: Derive the thermodynamic equation of state:
\[
\left( \frac{\partial H}{\partial p} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_p
\]
Derive an expression for \( \left( \frac{\partial H}{\partial p} \right)_T \) for a) a perfect gas and b) a van der Waals gas. In the latter case estimate its value for 1.0 mol of Ar at 298 K and 10 atm. By how much does the enthalpy of argon change when the pressure is increased isothermally to 11 atm?

\[dH = TdS + Vdp\]
Divide by dp at constant T
\[\left( \frac{\partial H}{\partial p} \right)_T = T\left( \frac{\partial S}{\partial p} \right)_T + V\]
Use Maxwell Relation: \( \left( \frac{\partial S}{\partial p} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_p \)
\[\left( \frac{\partial H}{\partial p} \right)_T = V - T\left( \frac{\partial V}{\partial T} \right)_p\]

For an ideal gas \( V= nRT/P; \left( \frac{\partial V}{\partial T} \right)_p = nR/P \)
\[\left( \frac{\partial H}{\partial p} \right)_T = V - nRT/P = nRT/P - nRT/P = 0\]
For a van der Waals gas \( p = RT/(V-b) - a/V^2; T = ((V-b)/R)(p + a/V^2) \)
\[\left( \frac{\partial V}{\partial T} \right)_p = \left( \frac{1}{R} \right)(p + a/V^2) + ((V-b)/R)(-2a/V^3) = \left( \frac{1}{R} \right)(P - 2a/V^2 + 2ab/V^3)\]
\[\left( \frac{\partial V}{\partial T} \right)_p = \left( \frac{1}{RT} \right)(P - 2a/V^2 + 2ab/V^3)\]
\[\left( \frac{\partial V}{\partial T} \right)_p = \left( \frac{1}{RT} \right)(P - 2a/V^2 + 2ab/V^3)\]
From table 1.5 \( a = 1.337 \text{ atm-L}^2\text{-mol}^{-2}, b = 3.20 \times 10^{-2} \text{ L/mol} \)

I used excel to find that the volume is 2.425 L/mole for \( P = 10 \text{ atm and } 298 K \)
\[\left( \frac{\partial H}{\partial p} \right)_T = V - RT\left( P - 2a/V^2 + 2ab/V^3 \right)\]
\[= 2.425 \text{ L} - 298K \times 0.08205 \text{ L-atm/mol-K} \times \left( 10 \text{ atm} - 2 \times 1.337 \text{ atm-L}^2\text{-mol}^{-2} / (2.425 \text{ L/mol})^2 \right)
+ 2 \times 1.337 \text{ atm-L}^2\text{-mol}^{-2} \times 3.20 \times 10^{-2} \text{ L/mol} / (2.425 \text{ L/mol})^3\]
\[\left( \frac{\partial H}{\partial p} \right)_T = -0.15 \text{ L} = -15.05 \text{ J/atm}\]
d\(H = \left( \frac{\partial H}{\partial p} \right)_T \Delta P = -15.05 \text{ J/atm} \times 1 \text{ atm} = -15 \text{ J}\]
Problem 5.11: Prove the following relation:

\[ \left( \frac{\partial H}{\partial V} \right)_{T} = -V^{2} \left( \frac{\partial p}{\partial T} \right)_{V} \left( \frac{\partial (T/V)}{\partial V} \right)_{p} \]

Product Rule

\[ -V^{2}(\partial (T/V)/\partial V)_{p} = T - V(\partial T/\partial V)_{p} \]

\[ dH = TdS + Vdp \]

Divide by dV at constant T

\[ (\partial H/\partial V)_{T} = T(\partial S/\partial V)_{T} + V(\partial p/\partial V)_{T} \]

Use Maxwell Relation: \( (\partial S/\partial V)_{T} = (\partial p/\partial T)_{V} \)

\[ (\partial H/\partial V)_{T} = T(\partial p/\partial T)_{V} + V(\partial p/\partial V)_{T} \]

Euler’s Rule: \( (\partial T/\partial V)_{p}(\partial p/\partial T)_{V} = -1 \)

\[ (\partial p/\partial V)_{T} = -(\partial T/\partial V)_{p}(\partial p/\partial T)_{V} \]

Problem 5.14: The Joule coefficient \( \mu_{j} \), is defined as \( \mu_{j} = (\partial T/\partial V)_{U} \).

Show that \( \mu_{j}C_{V} = p - (\alpha/\kappa)T \)

\[ \alpha = (1/V)(\partial V/\partial T)_{p} \]

\[ \kappa = -(1/V)(\partial V/\partial p)_{T} \]

\[ C_{V} = (\partial U/\partial T)V \]

\[ \mu_{j}C_{V} = (\partial T/\partial V)_{U}(\partial U/\partial T)V \]

By definition

\[ \mu_{j}C_{V} = -(\partial U/\partial V)_{T} \]

Euler’s Rule & Reciprocal

\[ \mu_{j}C_{V} = p - T(\partial S/\partial V)_{T} \]

\[ dU = TdS - pdV \]

\( (\partial U/\partial V)_{T} = T(\partial S/\partial V)_{T} - p \)

Maxwell Relation

\[ \mu_{j}C_{V} = p - T(\partial p/\partial T)_{V} \]

Euler’s Rule \( (\partial p/\partial T)_{V}(\partial V/\partial T)_{p} = -1 \)

\[ (\partial p/\partial V)_{T} = -(\partial p/\partial V)_{T}(\partial V/\partial T)_{p} = -1 \]

\[ \mu_{j}C_{V} = p - T(\partial p/\partial T)_{V} \]

Since \( \alpha/\kappa = (1/V)(\partial V/\partial T)_{p}/-(1/V)(\partial V/\partial p)_{T} = -(\partial V/\partial T)_{p}(\partial p/\partial V)_{T} \)

Problem 5.33: The volume of a newly synthesized polymer was found to depend exponentially on the pressure as \( V = V_{0}e^{-(p/p^{*})} \), where \( p \) is the excess pressure and \( p^{*} \) is a constant. Deduce an expression for the Gibbs energy of the polymer as a function of excess pressure. What is the natural direction of change of the compressed material when the pressure is relaxed?

\[ dG = Vdp - SdT \]

Assume isothermal

\[ dG = Vdp \]

\[ dG = V_{0}e^{-(p/p^{*})}dp \]

Substitution for \( V \)

\[ dG = V_{0}e^{-(p/p^{*})}dp \]

Integrate \( \Phi_{0}e^{-(p/p^{*})}dp = -p^{*}e^{-(p/p^{*})} \)

\[ G = -V_{0}p^{*}e^{-(p/p^{*})} = -p^{*}V \]

\[ dG/dp = V = V_{0}e^{-(p/p^{*})} \]

When pressure is released sample should expand as \( V \) gets bigger \( G \) will get more negative, lower energy.