Problem Set 3
Statistical Mechanics
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Problem 5: Isochoric heat capacity C_V of Argon

Derive an expression describing the volume dependence of C_V for a gas assuming the pressure approximation $PV/(nRT) = 1 + B_2(T)n/V$, where $B_2(T)$ is the 2nd virial approximation. Calculate the approximate change of the molar isocoric heat capacity of Argon during an isothermal expansion starting at 10 bar and ending at 1bar at 323 K. Use the following values for B_2: -15.49 cm^3 mol^{-1} at 298 K, -11.06 cm^3 mol^{-1} at 323 K, -7.14 cm^3 mol^{-1} at 348 K. Hint: Neglect terms containing products of B_2.

(6 points)

Problem 6: State functions F and G

Show that the free energy, $F = F(T, V)$, and the free enthalpy, $G = G(T, P)$ are state functions.

(6 points)

Problem 7: Thermodynamic relations

Show:

(i) $\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$

(ii) $\left(\frac{\partial G}{\partial V}\right)_T = V\left(\frac{\partial P}{\partial V}\right)_T$

(iii) $\left(\frac{\partial H}{\partial G}\right)_T = \frac{1}{V}\left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right]$

(iv) $\left(\frac{\partial P}{\partial T}\right)_G = \frac{S}{V}$

(4 points)

Problem 8: Inversion temperature of Argon

In class we had discussed the Joule-Thomson coefficient μ_{JT}. We concluded that $\mu_{JT} < 0$ implies heating and $\mu_{JT} > 0$ means cooling of the gas. $\mu_{JT} = 0$

defines the inversion temperature T_{inv}. Determine T_{inv} for Argon using the approximate pressure $P \approx P_{ideal}(1 + B_2(T)n/V)$ and the following values for the 2nd virial coefficient $B_2(T)$ of Argon: (T/K, B_2/cm^3 mol^{-1}), (300, -15.5), (400, -1.0), (500, 7.0), (600, 12.0), (700, 15.0), (800, 17.7), (900, 20.0), (1000, 22.0).

(6 points)