Physics 2700H: Assignment V

Jeremy Favro (0805980)
Trent University, Peterborough, ON, Canada

April 4, 2025

Problem 1. Show that the Joule-Kelvin coefficient is zero for an ideal gas.

Solution 1.

$$
\begin{aligned}
\mu_{JK} &= \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]\\
&= \frac{1}{C_p}\left[\frac{nRT}{P} - V\right]\\
&= \frac{1}{C_p}\left[\frac{nRT}{P} - \frac{nRT}{P}\right]\\
&= 0
\end{aligned}
$$

Problem 2. At the critical point, $(\partial P/\partial V)_T = 0$ and $(\partial^2 P/\partial V^2)_T = 0$. Show that, for a van der Waals gas (see Section 3.5.4), the critical point is at

$$
P_c = \frac{a}{27b^2}; V_c = 3nb; T_c = \frac{8a}{27Rb}
$$

Solution 2.

$$
(\partial P/\partial V)_T = \frac{2n^2 a}{V^3} - \frac{nRT}{(V-nb)^2}
$$

and

$$
(\partial^2 P/\partial V^2)_T = \frac{2nRT}{(V-nb)^3} - \frac{6n^2 a}{V^4}.
$$

Setting the first derivative to zero and solving for T gives $T = \frac{2na(V-nb)^2}{RV^3}$. Doing the same for the second derivative gives $T = \frac{3na(V-nb)^3}{RV^4}$. Dividing these two gives

$$
\begin{aligned}
1 &= \frac{\frac{2na(V-nb)^2}{RV^3}}{\frac{3na(V-nb)^3}{RV^4}}\\
1 &= \frac{2V}{3(V-nb)}\\
\implies 3nb &= V
\end{aligned}
$$

which can be back substituted to get $T = \frac{2na(3nb-nb)^2}{R(3nb)^3} = \frac{8a}{27Rb}$ which can, in combination with the volume be back substituted into the original Van der Waals equation to get $P = \frac{nR\frac{8a}{27Rb}}{3nb-nb} - \frac{n^2 a}{(3nb)^2} = \frac{a}{27b^2}$.

Problem 3. Show that the chemical potential of an ideal gas at temperature T varies with pressure as

$$\mu = k_B T \ln\left(\frac{P}{P_0}\right) + \mu_0$$

where μ_0 is the value at reference point of pressure P_0 and temperature T. The gas consists of a single type of particle only. This expression is of great use in chemistry.

Solution 3. Using the hint from the text that $\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \implies dG = V dP$ so $\int_{G_i}^{G_f} dG = \int_{P_i}^{P_f} V dP = \int_{P_i}^{P_f} \frac{nRT}{P} dP \implies N k_B T \ln\left(\frac{P_i}{P_f}\right) + G_i = G_f$. From here we can differentiate with respect to N and using $\left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu$ we get $k_B T \ln\left(\frac{P_i}{P_f}\right) + \mu_i = \mu_f$ which is the same as the given expression if we treat the f variables as the current "position" which is valid and just switch i for 0.

Problem 4. The Sackur-Tetrode equation (similar to Equation 5.11) gives the entropy of an ideal gas as

$$S = N k_B \left[\ln\left(\frac{V}{N}\left[\frac{4\pi mU}{3Nh^2}\right]^{3/2}\right) + \frac{5}{2}\right]$$

(a) Show that the chemical potential can be written in terms of entropy as

$$\mu = -T \left.\frac{\partial S}{\partial N}\right|_{U,V}$$

(b) Use the result of part (a) along with the fact that $U = (3/2)N k_B T$ for a monatomic gas to find an expression for the chemical potential as a function of V, N, and T.

(c) Evaluate the result in (b) numerically for helium gas at $T = 298\,\text{K}$ and $P = 1\,\text{atm}$.

(d) Discuss the implications of the fact that your answer in (c) is negative.

Solution 4.

(a) The derivative is $k_B \ln\left(\frac{V}{N}\left[\frac{2\pi m k_B T}{Nh^2}\right]^{3/2}\right)$ in its most simplified form (I think?) Where to go from there though I have no idea and I'm out of time.

(b) Substituting the given expression for U we get $\mu = -k_B T \ln\left(\frac{V}{N}\left[\frac{2\pi m k_B T}{Nh^2}\right]^{3/2}\right)$.

(c) Using the ideal gas equation for one mole of helium ($m = 4\times10^{-3}\,\text{kg}$, $N = N_A \approx 6.02\times10^{23}$) we get $V \approx 2.44\times 10^{-2}\,\text{m}^3$ which when plugged into the equation for μ we get $\mu = -k_B 298\,\text{K}\ln\left(\frac{2.44\times10^{-2}\,\text{m}^3}{N_A}\left[\frac{2\pi 4\times10^{-3}\,\text{kg}\,k_B\,298\,\text{K}}{N_A h^2}\right]^{3/2}\right) \approx -0.834\,\text{eV}\,\text{kg}^{-1}$.

(d) The chemical potential being negative means that the internal energy of the gas will decrease if more helium is added and other state variables are held constant.