Exam 1, Chemistry 481, 27 Sep 2019

SHOW ALL WORK/EXPLAIN YOUR ANSWERS FOR FULL CREDIT

- 1. The compressibility factor $Z = P\bar{V}/RT$ is a measure of the deviation of a gas from ideality.
 - a. Determine an expression for the compressibility factor for a van der Waals gas, which is governed by the equation of state

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \tag{1}$$

where a and b are constants. (5 pts) We did this in class on 23 Sep. Take the van der Waals equation, multiply by \bar{V} and divide by RT to get

$$Z = \bar{V}/(\bar{V} - b) - a/(RT\bar{V})$$

b. A possible equation of state predicts that the compressibility is given by

$$Z = \frac{1}{1 - B/\bar{V}} - \frac{A}{T(\bar{V} + B)}$$
(2)

where A and B are constants. Express Z in terms of A, B, T, and ρ , where the molar density ρ (the molar density) is $\rho = 1/\bar{V}$. (5 pts) We have $\bar{V} = 1/\rho$, so (either form of the equation is correct)

$$Z = \frac{1}{1 - B\rho} - \frac{A}{T(1/\rho + B)} = \frac{1}{1 - B\rho} - \frac{A\rho}{T(1 + B\rho)}$$
(3)

2. Consider a gas which obeys the van der Waals equation of state [Eq. (1)]. At the critical point, the first and second derivatives $dP/d\bar{V}$ and $d^2P/d\bar{V}^2$ vanish. This occurs at only one value of the temperature (T_c) and the volume \bar{V}_c . For a gas which obeys the van der Waals equation of state [Eq. (1)] determine an expression for V_c in terms of (possibly), T_c , R, a or b. (15 pts) This problem was on Homework 3. From Eq. (1) we see that

$$\frac{dP}{dV} = -\frac{RT}{(\bar{V}-b)^2} - \frac{2a}{\bar{V}^3} = 0$$
(4)

and

$$\frac{d^2P}{dV^2} = \frac{2RT}{(\bar{V}-b)^3} + \frac{6a}{\bar{V}^4} = 0$$
(5)

The right hand side (setting the derivatives equal to zero) corresponds to chosing the critical point Multiply Eq. (4) by $3\bar{V}_c$ and add it to Eq. (5) to get

$$RT_c\left(-\frac{3}{\bar{V}_c(\bar{V}_c-b)^2} + \frac{2}{(\bar{V}_c-b)^3}\right) = 0$$

Divide by RT_c and multiply by $(V_c - b)^2$ to get

$$-\frac{3}{\bar{V}_c} + \frac{2}{\bar{V}_c - b} = 0$$

We can solve this to get

$$V_c = 3b$$

3. The Maxwell speed distribution is

$$f(s,T) = C(T)s^2 \exp(-\alpha s^2)$$

where s is the speed and m the mass of the particle, $\alpha = m/2k_BT$ and $C(T) = [2(m/k_BT)^3/\pi]^{1/2}$. For a fixed value of T, determine the value of s where f(s,T) attains its maximum? Give your answer in terms of m, k_B , and T. (15 pts) Possibly useful integrals

$$\int_0^\infty x e^{-ax^2} dx = \frac{1}{2a}, \quad \int_0^\infty x^2 e^{-ax^2} dx = \frac{\sqrt{\pi}}{4a^{3/2}}, \quad \int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2} dx$$

I have given this question on previous exams, for example fall 2017. For any function, at the maximum, the derivative vanishes. Here, the derivative of f(s) with respect to s, the independent variable is

$$\frac{df(s)}{ds} = C(T)\exp(-\alpha s^2) \left[2s - s^2 \times 2s\alpha\right] = C(T)\exp(-\alpha s^2) \left[2s - 2\alpha s^3\right]$$

Setting this equal to zero gives $2s = 2\alpha s^3$ or $s^2 = 1/\alpha$. Taking the square root of each side gives

$$s_{mp} = \sqrt{1/\alpha} = \sqrt{2k_BT/M}$$

You don't need the integrals!

- 4. For water $\bar{V}_c = 9.0 \times 10^{-2} \text{ dm}^3 \cdot \text{mol}^{-1}$. What is the ratio of the critical molar volume \bar{V}_c to the molar volume of liquid water at 1 atm and 298 K? (10 pts) We have done calculations like this in class. We know that the density of liquid water is 1 g/cm³. This number is pretty much independent of the pressure and temperature. Since the molar mass of water is 18 g/cm³, the molar volume of water is $\bar{V} = 18 \text{ cm}^3$ or $1.8 \times 10^{-2} \text{ dm}^3$. Thus the critical volume is 9/1.8 =5 times larger than the volume of the liquid.
- 5. Consider a harmonic oscillator. The energy levels are given by $E_n = (n + 1/2)\hbar\omega$ where $\omega = \sqrt{k/m}$ with k being the spring constant of the oscillator and m, the effective mass of the oscillator. The quantum number n ranges from 0 to ∞ . The partition function of the oscillator is $q = x^{1/2}/(1-x)$ where $x = \exp(-\hbar\omega\beta) = \exp(-\hbar\omega/k_BT)$. Answer the following questions. We had a very similar problem on homework 3, which was due just last monday.
 - a. At temperature T, give an expression in terms of x for the normalized probability that the oscillators will be in the energy level with quantum number n. (15 pts) Since all levels are nondegenerate

$$f_n = \exp(-E_n\beta)/q = \exp[-(n+1/2)\hbar\omega\beta] \times \frac{1-x}{x^{1/2}} = x^{1/2}x^n \frac{1-x}{x^{1/2}} = x^n(1-x)$$

- b. Determine $dx/d\beta$ in terms of \hbar , ω and x. (5 pts) $x = \exp(-\hbar\omega\beta)$, so $dx/d\beta = -\hbar\omega \exp(-\hbar\omega\beta) = -\hbar\omega x$
- c. Then determine an expression for the average energy of the harmonic oscillator in terms of \hbar , ω and x. Give your answer as a single fraction. Check your answer by comparing the low temperature limit with the answer you obtained in part (a) above. (20 pts) We know that $\langle E \rangle = -\frac{d \ln q}{d\beta} = -\frac{d \ln q}{dx} \times \frac{dx}{d\beta}$. To determine $d \ln q/dx$ first take the log of q and then differentiate. (this is worth 10 pts) Since $\ln q = \frac{1}{2} \ln x \ln(1-x)$, we have

$$\frac{d\ln q}{dx} = \frac{1}{2x} + \frac{1}{1-x} = \frac{1-x+2x}{2x(1-x)} = \frac{1+x}{2x(1-x)}$$

Then multiply by the result of part (b) to get (10 pts) $\langle E \rangle = \frac{1}{2}\hbar\omega(1+x)/(1-x)$. At low T, $x \to 0$, so $\lim_{T\to 0} \langle E \rangle = \frac{1}{2}\hbar\omega$, which checks with part (a)

6. Consider a two-level system with energies $+\varepsilon$ and $-\varepsilon$, where ε is a positive number. The upper level is doubly degenerate. Determine an expression for the partition function in terms of $x = \exp(-\varepsilon\beta)$. Give your answer as a single fraction. (10 pts) In general

$$q = \sum_{i} g_i \exp(-E_i/beta)$$

. Here, this is

$$g_1 \exp(-E_1\beta) + g_2 \exp(-E_2\beta) = 1 \times \exp(+\varepsilon\beta) + 2 \times \exp(-\varepsilon\beta) = 1/x + 2x = \frac{1+2x^2}{x}$$