

CHEM 330 – PHYSICAL CHEMISTRY I – Fall 2026

EXAM 1

Closed book, closed notes

No electronics allowed (discovery of use is an automatic 0)

Calculators may be used (do not use the calculator on your electronic devices)

Write your name clearly in the provided answer book

Time: 1 hour 30 minutes

Constants

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$g = 9.8 \text{ ms}^{-2}$$

Conversions

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$1 \text{ torr} = \text{Pa} = 133.3 \text{ Pa.}$$

Problem 1 (30 points)

A closed-tube mercury manometer attached to a temperature-controlled gas vessel reads a column height $h = 752 \text{ mm}$. The mercury is at 0°C , where its density is $\rho = 1.3596 \times 10^4 \text{ kg m}^{-3}$. The gas is held at $T = 298.15 \text{ K}$.

- Using the lecture relation $P = \rho gh$, compute the pressure in Pascal, and confirm from the definition of the Pascal that the dimensions work out ($\text{kg m}^{-1} \text{ s}^{-2}$). (6 points)
- Express this pressure in bar, in atmospheres, and in torr. Account for the discrepancy quantitatively; do not simply say that it is smaller or larger. (4 points)
- Assuming ideal behavior, compute the molar volume $\bar{V}$ in L mol^{-1} . (6 points)
- Compute the number density N/V and from it the mean nearest-neighbor separation, estimated as $\langle d \rangle \approx (V/N)^{1/3}$. Compare with a molecular diameter of order $0.35 \times 10^{-9} \text{ m}$ and state the physical criterion this comparison tests. (14 points)

Problem 2 (40 points)

Carbon dioxide is confined at $\bar{V} = 0.500 \text{ L mol}^{-1}$, and $T = 313.15 \text{ K}$. Use $a = 3.640 \text{ bar L}^2 \text{ mol}^{-2}$ and $b = 0.04267 \text{ L mol}^{-1}$.

- Compute the pressure predicted by the van der Waals equation, and evaluate the compressibility factor $Z = P\bar{V}/RT$. (12 points)
- Using the rearrangement given in the lecture, $Z = \bar{V}/(\bar{V} - b) - a/(RT\bar{V})$, separate $Z - 1$ into a repulsive (excluded-volume) contribution and an attractive contribution. Which dominates here? (10).
- Holding $\bar{V} = 0.500 \text{ L mol}^{-1}$ fixed, find the temperature at which $Z = 1$ exactly. Find its limiting value as $\bar{V} \rightarrow \infty$ (18 points)

EXAM 1 - SOLUTIONS

Problem 1

$$\begin{aligned} (a) \quad P &= \rho g h \\ &= (1.3596 \times 10^4) (9.8) (0.752) \\ &\quad \uparrow \quad \quad \quad \uparrow \quad \quad \quad \uparrow \\ &\quad \text{kg m}^{-3} \quad \text{ms}^{-2} \quad \text{m} \\ &= \underline{1.00197 \times 10^5 \text{ Pa}} \end{aligned}$$

$$\begin{aligned} (b) \quad 1.00197 \times 10^5 \text{ Pa} &= 0.99 \text{ atm} \\ &= 1.00197 \text{ bar} \\ &= 751.67 \text{ torr} \end{aligned}$$

It is slightly smaller than the expected 752 torr $\rightarrow$ it is a round-off error from the various elements we used in the conversion.

(c) The molar volume ($\bar{v}$)

$$\bar{V} = \frac{RT}{P} = \frac{(8.314)(298.15)}{1.00197 \times 10^5}$$

JK^{-1}
 $(\text{Nm} \rightarrow \text{kg m}^2 \text{s}^{-2})$
 Pa
 $(\text{kg m}^{-1} \text{s}^{-2})$

$$= 2.474 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$$

$$= \underline{24.74 \text{ L mol}^{-1}}$$

(d) Recall $PV = nRT$

$$= \underbrace{\lambda}_{\text{w}} N_A k_B T$$

$N \rightarrow$ number of molecules

$$\left(\frac{V}{N}\right) = \frac{k_B T}{P} = \frac{1.38 \times 10^{-23} \times 298.15}{1.00197 \times 10^5 \text{ Pa}}$$

$$= 4.106 \times 10^{-26} \text{ m}^3$$

$$\text{Thus, } \langle d \rangle = \left(\frac{V}{N} \right)^{1/3} =$$

$$3.45 \times 10^{-9} \text{ m}$$

$$\underline{3.45 \text{ nm}}$$

Given that the molecular diameter is 0.35 nm ,
the fraction of space occupied by the molecules is

$$\left(\frac{0.35}{3.45} \right)^3 = 8.5 \times 10^{-3}$$

So the molecules occupy a negligible volume and that they are very far away

from each other. Both these properties are required for an ideal gas.

Problem 2

(a) For a Van der Waals gas

$$\begin{aligned}
 P &= \frac{RT}{V-b} - \frac{a}{V^2} \\
 &= \frac{8.314 \text{ J K}^{-1} \times 313.15 \text{ K}}{(0.5 \times 10^{-3}) - (0.04267 \times 10^{-3})} - \frac{3.640 \times 10^5 \times 10^{-6}}{(0.5 \times 10^{-3})^2} \\
 &= \frac{2603.5291}{4.5733 \times 10^{-4}} - 145600 \\
 &= 5.6928 \times 10^6 - 1.4560 \times 10^6 \\
 &= 42.37 \times 10^5 \text{ Pa} = 42.37 \text{ bar}
 \end{aligned}$$

$$Z = \frac{P\bar{V}}{RT} = \frac{4.237 \times 10^6 \times 0.5 \times 10^{-3}}{8.314 \times 313.15}$$

$$= \underline{0.8137}$$

(b) From the rearranged form of the equation

$$Z = \frac{\bar{V}}{\bar{V} - b} - \frac{a}{RT\bar{V}}$$

$$= \frac{0.5 \times 10^{-3}}{0.5 \times 10^{-3} - 0.04267 \times 10^{-3}} - \frac{3.64 \times 10^{-1}}{8.314 \times 313.15 \times 0.5 \times 10^{-3}}$$

$$= \frac{0.5 \times 10^{-3}}{4.5733 \times 10^{-4}} - 0.2796$$

$$= 1.0933 - 0.2796$$

So, $z-1$, which measures deviation from ideality.

$$= \underbrace{0.0933}_{\text{repulsive}} - \underbrace{0.2796}_{\text{attractive}}$$

The contribution of the attractive term is about 3-times as large and is the major contributor to the deviation from ideality.

(c) Setting $z=1$

$$1 = \frac{\bar{V}}{\bar{V}-b} - \frac{a}{RT\bar{V}}$$

$$\frac{a}{RT\bar{V}} = \frac{\bar{V} - \bar{V} + b}{\bar{V} - b}$$

Inverting,

$$\frac{RT\bar{V}}{a} = \frac{\bar{V}-b}{b}$$

$$T = \frac{a(\bar{v} - b)}{bR}$$

$$= \frac{a}{bR} \left(1 - \frac{b}{\bar{v}}\right)$$

This is the Boyle temperature

$$T = \frac{3.640 \times 10^{-1}}{8.314 \times 0.04267 \times 10^{-3}} \left(1 - \frac{0.04267 \times 10^{-3}}{0.5 \times 10^{-3}}\right)$$

$$= 1026.0505 \times 0.91466$$

$$= \underline{938.48 \text{ K}}$$

As $\bar{v} \rightarrow \infty$

$$T \rightarrow \frac{a}{bR} \rightarrow 1026.5 \text{ K}$$

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