

CEM 924 (Spring 2001) - Problem Set #1 (KEY)

- (1) (a) (10 points) For pure N₂ gas at 300 K, what is the number density (molecules cm⁻³) of molecules at (i) standard atmospheric pressure (ii) 10⁻¹⁰ mbar (UHV and the pressure about 1000 km above the Earth's surface). Assume N₂ behaves as an ideal gas. You only need the equations given in the lecture notes.

For an ideal gas,

$$pV = nRT$$

$$n = \frac{pV}{RT}$$

$$= \frac{101325 \text{ Pa} \cdot 1 \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 300 \text{ K}} = 2.44 \times 10^{25} \text{ m}^{-3}$$

$$= 2.44 \times 10^{19} \text{ cm}^{-3}$$

At 10⁻¹⁰ mbar, the number density will be

$$n = 2.44 \times 10^{19} \text{ cm}^{-3} \times \frac{10^{-10} \text{ mbar}}{1013 \text{ mbar}} = 2.41 \times 10^6 \text{ cm}^{-3}$$

This is still a large number of molecules!

- (b) (10 points) Calculate the mean velocity of a N₂ molecule at (i) atmospheric pressure (ii) 10⁻¹⁰ mbar

At atmospheric pressure:

$$p = \frac{1}{3} n m \langle v^2 \rangle$$

$$\langle v^2 \rangle = \frac{101325 \text{ N m}^{-2}}{\frac{1}{3} \cdot 2.44 \times 10^{25} \text{ m}^{-3} \cdot \frac{0.028 \text{ kg mol}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}}}$$

$$= 267 \text{ N m kg}^{-1}$$

$$= 267 \text{ kg m s}^{-2} \text{ m kg}^{-1}$$

$$= 26.7 \times 10^4 \text{ m}^2 \text{ s}^{-2}$$

$$\langle v \rangle = 517 \text{ m s}^{-1}$$

At 10⁻¹⁰ mbar:

$$p = \frac{1}{3} n m \langle v^2 \rangle$$

$$\langle v^2 \rangle = \frac{101325 \text{ N m}^{-2} \frac{10^{-10} \text{ mbar}}{1013 \text{ mbar}}}{\frac{1}{3} 2.41 \times 10^{12} \text{ m}^{-3} \frac{0.028 \text{ kg mol}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}}}$$

$$\langle v \rangle = 517 \text{ m s}^{-1}$$

Of course, molecular velocity should not depend on pressure!

(c) (10 points) Calculate the gas phase collision frequency, z , for a N_2 molecule ($\sigma = 0.43 \text{ nm}^2$) at 10^{-10} mbar (the number of collisions a single molecule makes in 1 second).

$$z = \sqrt{2} \langle v \rangle \frac{N}{V}$$

$$= \sqrt{2} 0.43 \times 10^{-18} \text{ m}^2 493 \text{ m s}^{-1} 2.65 \times 10^{12} \text{ m}^{-3}$$

$$= 7.94 \times 10^{-4} \text{ s}^{-1}$$

(d) (15 points) Now, ignoring gas-gas collisions, if 10^{-10} mbar of N_2 is contained in a cubic chamber of internal dimensions $20 \times 20 \times 20 \text{ cm}$, what is the average collision rate of a *single* N_2 molecule with the inside walls of the chamber?

The areal impingement rate, Z_A , is

$$Z_A = \frac{p}{(2 m k T)^{1/2}}$$

$$= \frac{101325 \text{ N m}^{-2} \frac{10^{-10} \text{ mbar}}{1013 \text{ mbar}}}{2 \cdot 4.65 \times 10^{-26} \text{ kg} \cdot 1.38 \times 10^{-23} \text{ J K}^{-1} \cdot 300 \text{ K}}^{0.5}$$

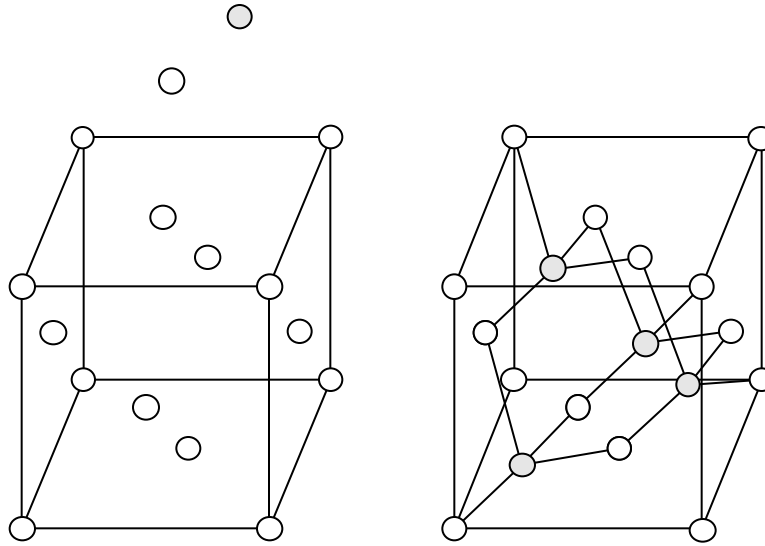
$$= 2.87 \times 10^{14} \text{ s}^{-1} \text{ m}^{-2}$$

The inside surface area of the six-sided cubic chamber is $6 \times (0.2 \times 0.2) \text{ m}^2$ or 0.24 m^2 . Therefore the total number of collisions with the wall is $2.87 \times 10^{14} \text{ s}^{-1} \cdot \text{m}^{-2} \times 0.24 \text{ m}^2$ or $6.89 \times 10^{13} \text{ s}^{-1}$.

The internal volume of the chamber is $(0.2 \times 0.2 \times 0.2) \text{ m}^3$ or $8 \times 10^{-3} \text{ m}^3$. At this pressure, there will be $(n \cdot V) \text{ N}_2$ molecules in the chamber. This is $2.44 \times 10^{12} \text{ m}^{-3} \times 8 \times 10^{-3} \text{ m}^3 = 1.95 \times 10^{10}$.

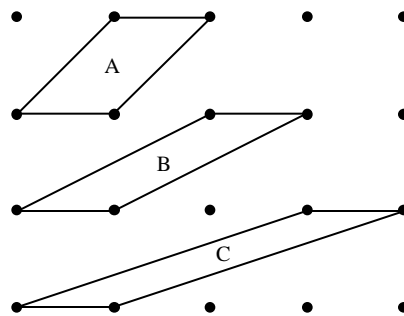
To achieve an impingement rate of $6.89 \times 10^{13} \text{ s}^{-1}$, each molecule must collide with the wall, on average, about 3533 times per second (some seven orders of magnitude higher than the gas-gas collisions rate).

- (2) (15 points) Briefly describe the operating principles of (a) a thermocouple gauge (b) a Pirani gauge (c) an ionization gauge (Bayard-Alpert design).
- (a) A thermocouple gauge consists of a wire filament heated by a constant current to which a thermocouple is attached. The thermocouple measures the temperature of the filament. At high pressures, gas molecule collisions with the filament cool it slightly through energy transfer and the filament temperature decreases. The variation in filament temperature with gas pressure is the basis of the measurement. At pressures near atmosphere, convection currents in the gauge tube perturb this relationship. At low pressures (below about 10^{-4} torr) there are insufficient molecular collisions for the temperature of the filament to be significantly altered with changing pressure.
- (b) A Pirani gauge operates by an indirect measurement of a heated filament resistance. It consists of two heated filaments, one is sealed in a tube at low pressures while the other is exposed to the test chamber. These two filaments form one "arm" of a Wheatstone bridge circuit. The other arm consists of two resistors in series. Gas collisions with the measurement filament change its temperature in a manner similar to the thermocouple gauge. A decrease in pressure results in an increase in filament temperature and an increased resistance in that arm of the circuit. The current flowing in the two arms of the Wheatstone bridge is compared by means of a sensitive voltmeter or ammeter and the system can be calibrated for pressure (non-linear).
- (c) An ionization gauge contains a heated filament that produces electrons by thermionic emission. The electrons are accelerated by a $\sim +150 \text{ V}$ potential on a cylindrical grid (or spiral wire). Some electrons are captured by the grid (this current constitutes the emission current and is controlled by a feedback circuit). A small fraction of the electrons pass through the walls of the grid and enter the cylinder where they create positive ions. These ions are collected by a collector wire in the center of the grid that is biased slightly negative with respect to the grid. The current measured at the collector is amplified and is converted into a pressure reading.
- (3) (10 points) A particular element crystallizes into a FCC crystal structure with a two atom basis located at $0\ 0\ 0$ and $0.25\ 0.25\ 0.25$. Draw this crystal structure. What can you say about the bond lengths and coordination geometry in this structure? Which element could this be?

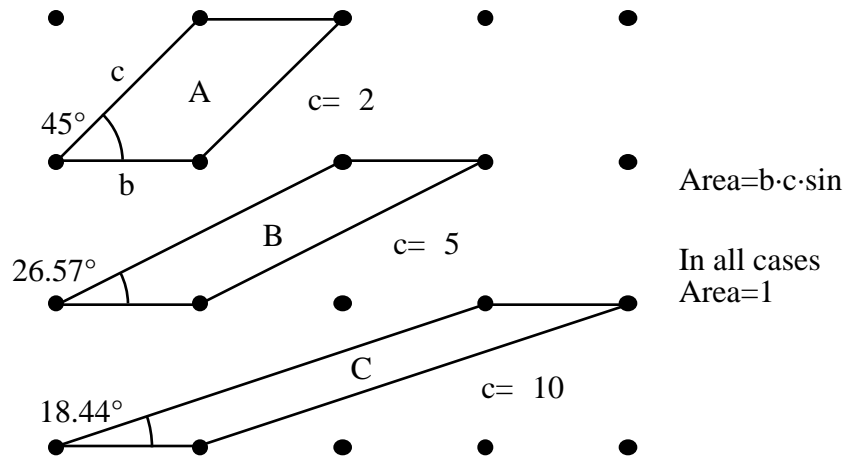


This is a diamond crystal structure (C, Si, Ge or α -Sn). The bond lengths are all the same and each atom is tetrahedrally coordinated.

- (4) (5 points) For the square 2-D plane lattice below, calculate the areas of the three surface nets shown assuming a lattice point spacing of 1.



Now use the Wigner-Seitz method to create a fourth unit cell. Calculate its area. What do you notice about these values?



The values are all equal. Similar arguments can be applied to 3-D lattices. In either case, the volume of any primitive cell is always constant.

Total 75 points