

Assigned problems for Lecture 3 are listed below. The questions occur in the following editions of “Physical Chemistry” by P.W. Atkins:

10th edition	9th edition	8th edition
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**Note:** The letter “P” in front of a number indicates that the question is in the “Problem” category as opposed to the “Exercise” category in Atkins’ books. Updates are highlighted in yellow.

## Set I

### Question 3.01

1B.1	20.1	21.1
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**1B.1(a)** Determine the ratios of (i) the mean speeds, (ii) the mean translational kinetic energies of H<sub>2</sub> molecules and Hg atoms at 20 °C.

**1B.1(b)** Determine the ratios of (i) the mean speeds, (ii) the mean kinetic energies of He atoms and Hg atoms at 25 °C.

### Question 3.02

1B.5	20.2	21.2
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**1B.5(a), 10th Ed.** Assume that air consists of N<sub>2</sub> molecules with a collision diameter of 395 pm. Calculate (i) the mean speed of the molecules, (ii) the mean free path, (iii) the collision frequency in air at 1.0 atm and 25 °C.

**20.2(a)/21.2(a), 9th, 8th Ed.** A 1.0 dm<sup>3</sup> glass bulb contains  $1.0 \times 10^{23}$  H<sub>2</sub> molecules. If the pressure exerted by the gas is 100 kPa, what are (a) the temperature of the gas, (b) the root mean square speeds of the molecules? (c) Would the temperature be different if they were O<sub>2</sub> molecules? (Briefly explain).

**1B.5(b)** The best laboratory vacuum pump can generate a vacuum of about 1 nTorr. At 25 °C and assuming that air consists of N<sub>2</sub> molecules with a collision diameter of 395 pm, calculate (i) the mean speed of the molecules, (ii) the mean free path, (iii) the collision frequency in the gas.

### Question 3.03

1B.3	20.3	21.7
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**1B.3(a)** Use the Maxwell–Boltzmann distribution of speeds to estimate the fraction of N<sub>2</sub> molecules at 400 K that have speeds in the range 200 to 210 m s<sup>-1</sup>.

**1B.3(b)** Use the Maxwell–Boltzmann distribution of speeds to estimate the fraction of CO<sub>2</sub> molecules at 400 K that have speeds in the range 400 to 405 m s<sup>-1</sup>.

### Question 3.04

Self-test 1B.2	Self-test 20.1	Self-Test 21.1
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**Self-test 1B.2** Evaluate the root-mean-square speed of the molecules by integration. Use mathematical software or use a standard integral in the Resource section.

See the link: <http://chem240.cs.uwindsor.ca/resources/Handouts---Problems-and-Exams/st1-6.pdf>

Graphic from 9th edition:

**Self-test 20.1** Evaluate the root mean square speed of the molecules by integration. You will need the integral

$$\int_0^{\infty} x^4 e^{-ax^2} dx = \frac{3}{8} \left( \frac{\pi}{a^5} \right)^{1/2} \quad [c = (3RT/M)^{1/2}, 515 \text{ m s}^{-1}]$$

### Question 3.05

P1B.3	P20.20	P21.23
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**PIB.3** Start from the Maxwell–Boltzmann distribution and derive an expression for the most probable speed of a gas of molecules at a temperature  $T$ . Go on to demonstrate the validity of the equipartition conclusion that the average translational kinetic energy of molecules free to move in three dimensions is  $\frac{3}{2}kT$ .

### Set II

### Question 3.06

1B.6	20.5	21.3
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**1B.6(a)** At what pressure does the mean free path of argon at 20 °C become comparable to the diameter of a 100 cm<sup>3</sup> (a container with 1 dm<sup>3</sup> volume in older editions) vessel that contains it? ( $\sigma = 0.36 \text{ nm}^2$ ).

**1B.6(b)** At what pressure does the mean free path of argon at 20 °C become comparable to 10 times the diameters of the atoms themselves?

**Note: The temperature is 20°C in the 8th and 9th editions, 25 °C in the 10th**

### Question 3.07

1B.7	20.6	21.4
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**1B.7(a)** At an altitude of 20 km the temperature is 217 K and the pressure 0.050 atm. What is the mean free path of N<sub>2</sub> molecules? ( $\sigma = 0.43 \text{ nm}^2$ ).

**1B.7(b)** At an altitude of 15 km the temperature is 217 K and the pressure 12.1 kPa. What is the mean free path of N<sub>2</sub> molecules? ( $\sigma = 0.43 \text{ nm}^2$ ).

**Question 3.08**

Missing	20.7	21.5
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**20.7(a), 9th Ed.** How many collisions does a single Ar atom make in 1.0 s when the temperature is 25°C and the pressure is (a) 10 atm, (b) 1.0 atm, (c) 1.0  $\mu\text{atm}$ ? (Note:  $\mu$  means micro, multiply by a factor of  $10^{-6}$ ).

**20.7(b), 9th Ed.** How many collisions per second does an  $\text{N}_2$  molecule make at an altitude of 15 km? ( $\sigma = 0.43 \text{ nm}^2$ )

**Question 3.09**

Missing	20.8	21.6
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**20.8(a), 9th Ed.** Calculate the mean free path of molecules in air using  $\sigma = 0.43 \text{ nm}^2$  at 25°C and (a) 10 atm, (b) 1.0 atm, (c) 1.0  $\mu\text{atm}$ .

**20.8(b), 9th Ed.** Calculate the mean free path of carbon dioxide molecules using  $\sigma = 0.52 \text{ nm}^2$  at 25°C and (a) 15 atm, (b) 1.0 bar, (c) 1.0 Torr.

**Clarifications:****Question 3.01**

1B.1	20.1	21.1
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**Ex. 21.1b 8th Ed., (24.10b 7th Ed.).** The final answer should be 0.096 not 0.092. **Not sure if this is corrected in 9th and 10th editions.**

**Question 3.06**

1B.6	20.5	21.3
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You are asked "at what pressure does the mean free path of Ar at 25 °C become comparable to the size of a 1 dm<sup>3</sup> vessel that contains it?" This would be much simpler if they pointed out that the container is cubic...as it stands now, you are to assume that the length of the container is 1 dm (10 cm) long. Note that the values for the collisional cross-sections are given in Tables in all editions. The manner in which this question is asked is adjusted in the 10th edition (finally!).

## Solutions to B-list “missing” problems

## Question 3.08

Missing	20.7	21.5
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**E21.4(b)** The mean free path is

$$\lambda = \frac{kT}{2^{1/2}\sigma p} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (217 \text{ K})}{2^{1/2} [0.43 \times (10^{-9} \text{ m})^2] \times (12.1 \times 10^3 \text{ Pa atm}^{-1})} = \boxed{4.1 \times 10^{-7} \text{ m}}$$

**E21.5(b)** Obtain data from Exercise 21.4(b)

The expression for  $z$  obtained in Exercise 21.5(a) is  $z = [16/(\pi mkT)]^{1/2} \sigma p$

Substituting  $\sigma = 0.43 \text{ nm}^2$ ,  $p = 12.1 \times 10^3 \text{ Pa}$ ,  $m = (28.02 \text{ u})$ , and  $T = 217 \text{ K}$  we obtain

$$z = \frac{4 \times (0.43 \times 10^{-18} \text{ m}^2) \times (12.1 \times 10^3 \text{ Pa})}{[\pi \times (28.02) \times (1.6605 \times 10^{-27} \text{ kg}) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (217 \text{ K})]^{1/2}} = \boxed{9.9 \times 10^8 \text{ s}^{-1}}$$

## Question 3.09

Missing	20.8	21.6
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**E21.6(b)** The mean free path is

$$\lambda = \frac{kT}{2^{1/2}\sigma p} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (25 + 273) \text{ K}}{2^{1/2} [0.52 \times (10^{-9} \text{ m})^2] p} = \frac{5.5\bar{0} \times 10^{-3} \text{ m Pa}}{p}$$

$$\text{(a)} \quad \lambda = \frac{5.5\bar{0} \times 10^{-3} \text{ m Pa}}{(15 \text{ atm}) \times (1.013 \times 10^5 \text{ Pa atm}^{-1})} = \boxed{3.7 \times 10^{-9} \text{ m}}$$

$$\text{(b)} \quad \lambda = \frac{5.5\bar{0} \times 10^{-3} \text{ m Pa}}{(1.0 \text{ bar}) \times (10^5 \text{ Pa bar}^{-1})} = \boxed{5.5 \times 10^{-8} \text{ m}}$$

$$\text{(c)} \quad \lambda = \frac{5.5\bar{0} \times 10^{-3} \text{ m Pa}}{(1.0 \text{ Torr}) \times (1.013 \times 10^5 \text{ Pa atm}^{-1} / 760 \text{ Torr atm}^{-1})} = \boxed{4.1 \times 10^{-5} \text{ m}}$$