Problems and solutions Chapter 2

P.A. The density and the mean free path. (a) Show, from the ideal gas laws, that the pressure P of a dilute gas in thermal equilibrium is related to the number density n by $P = nm\left\langle v^2 \right\rangle / 3$ where m is the mass of the molecules and $\left\langle v^2 \right\rangle$ is the average squared velocity. (b) Under standard conditions (0^{o} C, 1 atm) the density of a pure gas is $1.429 \cdot 10^{-3}$ gcm^{-3}. Suggest the possible chemical identity of the gas and compute the root mean squared velocity at room temperature. (c) Assuming a collision cross section of 40 Å^2, (an interaction radius of 1.8 Å), compute the mean free path. (d) Discuss whether the computed mean free path is large or small by providing a suitable distance for comparison. With this result check if our assumption that the gas is dilute enough to be nearly ideal is reasonable. (e) Plot the mean free path against pressure. At what low pressure will a molecule be likely to survive one second before colliding with another molecule? (We gave you a mixed bag of units. That is how real life is).

S.A. (a). Temperature is a measure of the random kinetic energy of the molecules. At thermal equilibrium the gas has no net motion so that its center of mass is at rest and the entire kinetic energy is that of the random motion. Since there is no preferred direction

$$k_{\mathrm{B}}T = \frac{1}{2}nm\left\langle v_x^2 \right\rangle = \frac{1}{2}nm\left\langle v_y^2 \right\rangle = \frac{1}{2}nm\left\langle v_z^2 \right\rangle = \frac{1}{2}nm\frac{1}{3}\left\langle v^2 \right\rangle$$

or $\frac{3}{2}k_{\mathrm{B}}T = \frac{1}{2}nm\left\langle v^2 \right\rangle$ where k_{B} is Boltzmann's constant and $\left\langle v^2 \right\rangle$ is the variance of the velocity distribution, $\left\langle v_x^2 \right\rangle + \left\langle v_y^2 \right\rangle + \left\langle v_z^2 \right\rangle = \left\langle v^2 \right\rangle$.

(Option: In general, show that the entire kinetic energy of the gas is the kinetic energy of the directed motion of the center of mass plus the random kinetic energy of the molecules).

For an ideal gas $PV = Nk_{\mathrm{B}}T$ or

$$P = nk_{\mathrm{B}}T = \frac{1}{3}nm\left\langle v^2 \right\rangle$$

(b). To infer the identity of the gas compute the mass M of a mole of molecules. For one mole of an ideal gas $PV = RT$ where R is the gas constant and V is the volume per mole. n is the number density so the product $\rho = nm$ is the mass density, and using $1\mathrm{atm} = 1.013 \cdot 10^6 \left(\mathrm{erg}/\mathrm{cm}^3\right)$, erg=gr·cm^2/sec^2

$$M = \rho V = \rho\frac{RT}{P} = 1.429 \cdot 10^{-3}\frac{\mathrm{gr}}{\mathrm{cm}^3}\frac{8.831 \cdot 10^7 \left(\mathrm{erg}/\mathrm{K} \cdot \mathrm{mol}\right)273(\mathrm{K})}{1.013 \cdot 10^6 \left(\mathrm{erg}/\mathrm{cm}^3\right)} \cong 34\mathrm{gr} \cdot \mathrm{mol}^{-1}$$

The gas is probably molecular oxygen, O_2.

Next compute the density at the temperature of 300K and under atmospheric pressure. It follows from (a) that at a constant pressure the density scales inversely to the temperature.

$$\rho(300\mathrm{K}) = \frac{273}{300}\rho(300\mathrm{K}) \cong 1.3 \cdot 10^{-3}\frac{\mathrm{gr}}{\mathrm{cm}^3}$$

From the density at room temperature, the RMS velocity is

$$\sqrt{\left\langle v^2 \right\rangle} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3 \cdot 1.013 \cdot 10^6 \left(\mathrm{erg}/\mathrm{cm}^3\right)}{1.3 \cdot 10^{-3}\left(\mathrm{gr}/\mathrm{cm}^3\right)}} = 4.84 \cdot 10^4 \frac{\mathrm{cm}}{\mathrm{sec}}$$

(c). The mean free path is computed from $\lambda = 1/n\sigma$. n is the number density of the target gas, $n = P/k_{\mathrm{B}}T$ and $\sigma = 40\text{Å}^2 = 40 \cdot \left(10^{-8}\mathrm{cm}\right)^2 = 4 \cdot 10^{-15}\mathrm{cm}^2$

$$\lambda = \frac{k_\mathrm{B}T}{\sigma P} = \frac{\left(0.082(\mathrm{liter}\cdot\mathrm{atm/K})10^3\left(\mathrm{cm}^3/\mathrm{liter}\right)\big/6.022\cdot10^{23}(\mathrm{molecule/mol})\right)300\mathrm{K}}{4\cdot10^{-15}(\mathrm{cm}^2)\cdot1(\mathrm{atm})} \cong 1\cdot10^{-5}\,\mathrm{cm}$$

We compare $\lambda \cong 1\cdot10^{-5}\,\mathrm{cm} = 10^3\text{Å}$ to the range d of the force between the molecules. For a rough estimate of d use $\sigma = \pi d^2$ or $d = \sqrt{40\text{Å}^2/\pi} \cong 3.6\text{Å}$. Since d is twice the radius of the hard spheres, cf. Figure 2.3, the mean free path ($\cong 10^3\text{Å}$) is almost three orders of magnitude larger than the hard sphere radius ($\cong 1.8\text{Å}$). For most of the time the molecules of the gas are very much isolated.

(e). From the above $\lambda \cong \dfrac{1\cdot10^{-5}(\mathrm{cm}\cdot\mathrm{atm})}{P(\mathrm{atm})}$ and the time τ between collisions is $\lambda/\langle v\rangle$ where $\langle v\rangle$ is the mean speed, $\langle v\rangle = \sqrt{\dfrac{8k_\mathrm{B}T}{\pi m}}$. Therefore the mean time between collisions and the pressure are related by

$$\tau = \frac{k_\mathrm{B}T}{\langle v\rangle\sigma P} = \frac{\dfrac{82}{6.022\cdot10^{23}}\left(\dfrac{\mathrm{cm}^3\mathrm{atm}}{\mathrm{K}\cdot\mathrm{mol}}\right)\cdot300(\mathrm{K})}{4.5\cdot10^4\left(\dfrac{\mathrm{cm}}{\mathrm{sec}}\right)4\cdot10^{15}(\mathrm{cm}^2)P(\mathrm{atm})}$$

A time interval of one second is equivalent to a (very very low) pressure of roughly $2.3\cdot10^{-10}$ atm.

P.C. Derive equation (2.1) and hence compute the flux of O_2 molecules incident on the wall of a room under ordinary conditions. Is the flux of N_2 molecules the same and if not, how different is it? In chapter 12 we will conclude that this flux is rather high. Can you suggest what is the number against which we will compare the flux to decide when it is high?

S.C. To compute the flux of molecules striking the surface of the container, take z to be the direction perpendicular to the wall. At thermal equilibrium, half the molecules are moving from left to right and the other half from right to left along the z direction. If n is the number density of the gas, the number density of molecules moving towards the wall is $n/2$. The flux of molecules striking the wall is therefore $n\left\langle |v_z| \right\rangle / 2$. If v is the velocity of a molecule its z component is $v\cos\theta$ where θ is the angle of the velocity with respect to the z axis. Averaging over θ,

$$\langle \cos\theta \rangle = \frac{\int_0^1 \cos\theta \, d\cos\theta}{\int_0^1 d\cos\theta} = \frac{1}{2}$$

the flux of molecules striking the wall is $I = n\langle v \rangle / 4$. With 1 atm= 760 torr and with $k_{\mathrm{B}} \cong 1.035 \cdot 10^{-19} \mathrm{cm}^3 \cdot \mathrm{torr/K}$ and $R = 8.3145 \cdot 10^7 \ \mathrm{gr} \cdot \mathrm{cm}^2 / \mathrm{sec}^2\, \mathrm{K} \cdot \mathrm{mol}$.

$$I\left(\mathrm{molecules} / \mathrm{cm}^2 \cdot \mathrm{sec}\right) = \frac{1}{4} \frac{P(\mathrm{torr})}{k_B\left(\mathrm{cm}^3 \cdot \mathrm{torr/K}\right) \cdot T(\mathrm{K})} \sqrt{\frac{8 \cdot R\left(\mathrm{gr} \cdot \mathrm{cm}^2 / \mathrm{sec}^2\, \mathrm{K} \cdot \mathrm{mol}\right) \cdot T(\mathrm{K})}{\pi \cdot M(\mathrm{gr/mol})}}$$

$$\cong 3.5 \cdot 10^{22} \frac{P(\mathrm{torr})}{\sqrt{M(\mathrm{gr/mol}) \cdot T(\mathrm{K})}}$$

For molecular oxygen at 1 torr and room temperature there are about $3.5 \cdot 10^{20}$ molecules striking an area of $1\,\mathrm{cm}^2$ of the surface per second. The flux of N_2 is comparable.

The number of atoms at the surface of the solid is of the order of $10^{15}\ \mathrm{cm}^{-2}$ so that the flux is sufficient to saturate all the available surface sites in much less than 1 sec.

P.E. The rate constant for bimolecular collisions. In the text we defined the number, Z, of collisions per unit volume and unit time as Z= $n_A\omega = n_A n_B v\sigma$. n_A and n_B are the number densities of the two gases. By analogy to chemical kinetics, where the corresponding number of *reactive* collisions is written as $kn_A n_B$ and k is called the reaction rate constant, we can call $k = v\sigma$the collision rate constant. (a) If we define k as the loss of flux in the experiment of figure 2.1, equation (2.10), show that this recovers the result $k = v\sigma$. (b) The collision cross section is energy dependent. The collision rate constant for thermal partners is therefore given by $k = \langle v\sigma \rangle$ where the averaging is over a thermal distribution of the relative velocity v[*]. It is however customary to define an effective collision cross section by $k = \langle v\sigma \rangle \equiv \langle v \rangle \sigma_{eff}$. $\langle v \rangle = (8k_B T/\pi\mu)^{1/2}$. $k_B = R/N_A$ is Boltzmann's constant namely the gas constant per molecule and not per mole. Show that in practical units

$$k(\mathrm{cm^3 mol^{-1} s^{-1}}) \cong 8.76 \cdot 10^{11} \left(T/\mu(\mathrm{amu})\right)^{1/2} \sigma_{eff}(\text{Å}^2)$$

$$\omega(\mathrm{s^{-1}}) \cong P(\mathrm{atm})(298/T) 4.11 \cdot 10^{-8} k(\mathrm{cm^3 mol^{-1} s^{-1}})$$

(c) Go to a source of chemical kinetics rate data and conclude that our k above is significantly larger than a typical bimolecular reaction rate constant. Why? Some bimolecular reactions are known to be fast. Can their rate constants be larger than the collision rate constant ? (No, but why not?).

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[*] Prove that if A and B both have a thermal distribution of velocities at the same temperature T then their relative velocity also has a thermal distribution at the same temperature T. If necessary, go first to section 2.2.7. Next prove that if A and B both have a thermal distribution of velocities but at two different temperatures then their relative velocity also has a thermal distribution and determine the temperature T for the distribution of the relative velocity.

S.E. (a). The flux along the beam diminishes because of collisions with the target gas. The flux is the number of molecules crossing a unit are per unit time. Let $I(x)$ be the flux at the distance x along the beam, equation (2.1). Then $I(x) - I(x+\Delta x)$ is the number of collisions in the volume Δx per unit time. The number of collisions per unit volume and per unit time is $\left(I(x) - I(x+\Delta x)\right)/\Delta x$ in the limit where $\Delta x \to 0$. This is, cf. equation (2.3),

$$-\frac{dI}{dx} = \frac{I}{\lambda} = \frac{vn_\mathrm{A}}{1/\sigma n_\mathrm{B}} = n_\mathrm{A} n_\mathrm{B}\, v\sigma$$

(b). The ‘effective cross section’ is defined by the measured rate constant for collisions, k, by $k = \langle v\rangle \sigma_\mathrm{eff}$ where the mean speed is, as before, $\langle v\rangle = \sqrt{\frac{8k_\mathrm{B}T}{\pi m}}$. In practical units this is rewritten as $\langle v\rangle = \sqrt{\frac{8RT}{\pi\mu}}$ where R is the gas constant and μ is the reduced mass per mole. Then, using N_A for Avogadro’s number to convert from rate per molecule to rate per mole

$$k(\mathrm{cm^3 sec^{-1} mol^{-1}}) = N_\mathrm{A}\sqrt{\frac{8\cdot 8.314\cdot 10^7(\mathrm{erg\cdot K^{-1}mol^{-1}})\cdot T(\mathrm{K})}{\pi\,\mu(\mathrm{gr\cdot mol^{-1}})}}\cdot 10^{-16}\sigma_\mathrm{eff}(\text{Å}^2)$$

$$\cong 8.76\cdot 10^{11}\sqrt{\frac{T(\mathrm{K})}{\mu(\mathrm{gr\cdot mol^{-1}})}}\cdot \sigma_\mathrm{eff}(\text{Å}^2)$$

The number of collisions per unit time is, section 2.1.5, $\omega = nk$ where n is the number density of the gas that the molecule moves through. In mol/cm^3

$$n(\mathrm{mol\cdot cm^{-3}}) = \frac{P}{RT} = \frac{P(\mathrm{atm})}{82.05\ (\mathrm{cm^3\cdot atm/K\cdot mol})\cdot T(\mathrm{K})} = 4.1\cdot 10^{-5}P(\mathrm{atm})\frac{298}{T(\mathrm{K})}$$

$$\omega(\mathrm{sec^{-1}}) = n(\mathrm{mol\cdot cm^{-3}})k(\mathrm{cm^3 sec^{-1} mol^{-1}}) = 4.1\cdot 10^{-5}P(\mathrm{atm})\frac{298}{T(\mathrm{K})}k(\mathrm{cm^3 sec^{-1} mol^{-1}})$$

(c) Reaction rate constants for fast elementary chemical reactions are typically in the range of 10^{13} to 10^{14} $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}\mathrm{sec}^{-1}$. These are reactions (e.g., radical recombination, $\mathrm{CH_3} + \mathrm{CH_3} \to \mathrm{C_2H_6}$) that proceed without any activation energy. The corresponding effective reaction cross sections are from a few to tens of Å^2. These are comparable or even larger than the (total) cross sections for atom-atom collisions. But of course the comparison is physically not sensible. We define the total collision cross section by the rate of *all* collisions, where a collision occurs if the two partners exercised a force on one another. If a reaction took place then of course the two partners were under the influence of their mutual force. The total collision cross section has at least to be comparable to or, as is usually the case, much larger than the reaction cross section. The conclusion that will be reinforced in chapter 3: Fast bimolecular reactions are governed by long range forces. Hence they will have particularly large total collision cross sections.

P.G. The Morse functional form, $V(R) = \varepsilon\left[1 - \exp(-(R - R_m)/2\rho)\right]^2 - \varepsilon$, is also often used. This has the short range exponential form as in equation (2.13). (a) Show that the Morse potential satisfies the scaling law (2.22). (b) The Morse potential is more flexible because the range parameter ρ can be fitted independently of the position, R_m, of the minimum. In particular verify that this allows fitting the harmonic frequency, the anharmonicity and the rigid-rotor rotational constant as three independent parameters. In this fashion data from spectroscopy can be directly used to infer the potential, Herzberg (1950).

S.G. First verify that the equilibrium distance is R_m by checking that the first derivative of the potential (=the force) vanishes at R_m. Then introduce reduced (= dimensionless) variables by scaling distances by R_m and scaling energies by the well depth ε,

$$z \equiv \frac{R}{R_m} \quad , \quad \rho^* \equiv \frac{\rho}{R_m} \quad , \quad V^* \equiv \frac{V}{\varepsilon}$$

Thereby rewrite the Morse potential as

$$V(R) = \varepsilon\left\{\left[1 - \exp\left(-(R - R_m)/2\rho\right)\right]^2 - 1\right\} = \varepsilon\left\{\left[1 - \exp\left(-R_m\left(\frac{R}{R_m} - 1\right)\Big/2\rho\right)\right]^2 - 1\right\}$$

$$= \varepsilon\left\{\left[1 - \exp\left(-(z-1)/2\rho^*\right)\right]^2 - 1\right\} = \varepsilon V^*(z)$$

Unlike the case of the Lennard-Jones potential, here the shape of the reduced potential is not universal because it does depend on the value of the reduced range parameter ρ^*

(b). Very near the equilibrium position the Morse potential can be evaluated by a Taylor expansion of the exponent, $\exp(-(z-1)/2\rho^*) \xrightarrow{z \ll 1} 1 - (z-1)/2\rho^*$ which allows us to write $\left[1 - \exp\left(-(R - R_m)/2\rho^*\right)\right]^2 \to 4\left(-(R - R_m)/2\rho^*\right)^2$

$$V(R) \to -\varepsilon + \frac{1}{2}\left(\frac{2\varepsilon}{\rho^2}\right)(R - R_m)^2 \quad \text{harmonic limit}$$

$$\equiv -\varepsilon + \frac{1}{2}k_e(R - R_m)^2 \quad \text{harmonic potential}$$

The force constant k_e is defined in terms of the harmonic potential. The harmonic vibration frequency is determined by $2\varepsilon/\rho^2$. The rotation constant is determined by the equilibrium bond distance R_m which is an independent parameter. The (dimensionless) anharmonicity is determined by the ratio ρ^*.

P.I. Use the conservation of energy condition, equation (2.27), to show that for a collision of hard spheres the particles do not feel any force if the impact parameter is larger than the hard sphere diameter, $b > d$. Hence derive equation (2.35).

S.I. For any potential, the region that can be sampled by the relative motion as described by classical mechanics is the region where the kinetic energy of the relative motion is not negative. From Equation (2.27) this region is specified as

$$\frac{1}{2}\mu\left(\frac{dR}{dt}\right)^2 = E_T\left(1-\frac{b^2}{R^2}\right) - V(R) \geq 0$$

For the relative motion of two hard spheres the potential is infinitely repulsive for $R \leq d$ and vanishes for $R > d$. If $b > d$ the inequality requires that only the region $R > b$ can be sampled. Since $b > d$ and $R > b$ it follows that the two hard spheres do not approach to within the range d of their potential. Only for those initial conditions where $b \leq d$ do the two spheres feel the force between them. So collisions can only be said to take place for $b \leq d$ and the cross section is

$$\sigma = \int_0^{\substack{\text{the largest impact paramater}\\ \text{for which a force acted}}} 2\pi b \mathrm{d}b = \pi d^2$$

P.K. *Orbiting*. At low collision energies there will be more than one solution for the distance R_0 of closest approach as determined from equation (2.30). The easy way to see it is to solve (2.30) by graphical means, i.e., to plot $V_{\text{eff}}(R) = V(R) + E_T b^2 / R^2$ vs. R and see where $V_{\text{eff}}(R) = E_T$. The largest root is the turning point of the collision. The other two roots are the inner and outer turning points for a state that is bound in the inner hollow of the effective potential. Such a bound A-B molecule can dissociate by tunneling. As the collision energy is increased the turning point eventually coincides with the very top of the barrier in the effective potential. Above this energy there is only one turning point. For a Lennard-Jones (12,6) potential, determine this energy. The collision at this energy will just manage to crawl over the top of the barrier. It will do so very very slowly and the collision partners will have lots of time to rotate about one another. Hence 'orbiting'.

S.K. Orbiting occurs when the maximum of the effective potential

$$V_{\text{eff}}(R) = V(R) + \frac{E_T b^2}{R^2}$$

coincides with the turning point of the trajectory. The impact parameter at the top of the barrier is determined by the condition $\left(\partial V_{\text{eff}}(R)/\partial R\right) = 0$ to be

$$b^2 = \frac{R^3}{2E_T}\frac{dV(R)}{dR}$$

The impact parameter when the turning point is R is $b^2 = R^2\left(1 - V(R)/E_T\right)$. Equating the two values of b determines of the value of R at orbiting as the largest root of

$$\left(1 - \frac{V(R)}{E_T}\right) - \frac{R}{2E_T}\frac{dV(R)}{dR} = 0$$

The equation has a real root only for such low collision energies that satisfy

$$E_T \le \max\left(V(R) + \frac{R}{2}\frac{dV(R)}{dR}\right)$$