

CHEM 402—Physical Chemistry
Chapter 21 Homework solutions

SOLUTIONS TO PROBLEMS

Solutions to numerical problems

P21.2 For discrete rather than continuous variables the equation analogous to the equation for obtaining \bar{v} (Example 21.1) is $\langle v_x \rangle = \sum_i v_{i,x} (N_i/N) = (1/N) \sum_i N_i v_{i,x}$ with (N_i/N) the analogue of $f(v)$

$$N = 40 + 62 + 53 + 12 + 2 + 38 + 59 + 60 + 2 = 328$$

$$\begin{aligned} \text{(a)} \quad \langle v_x \rangle &= \frac{1}{328} [40 \times 80 + 62 \times 85 + \dots + 2 \times 100 + 38 \times (-80) \\ &\quad + 59 \times (-85) + \dots + 2 \times (-100)] \text{ km h}^{-1} \\ &= \boxed{2.8 \text{ km h}^{-1}} \text{ east} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \langle |v_x| \rangle &= \frac{1}{328} \{40 \times 80 + 62 \times 85 + \dots + 2 \times 100 + 38 \times 80 \\ &\quad + 59 \times 85 + \dots + 2 \times 100\} \text{ km h}^{-1} \\ &= \boxed{86 \text{ km h}^{-1}} \end{aligned}$$

$$\text{(c)} \quad \langle v_x^2 \rangle = \frac{1}{328} \{40 \times 80^2 + 62 \times 85^2 + \dots + 2 \times 100^2\} (\text{km h}^{-1})^2 = 7430 (\text{km h}^{-1})^2$$

$$\sqrt{\langle v_x^2 \rangle} = \boxed{86 \text{ km h}^{-1}} \quad \left[\text{that } \sqrt{\langle v_x^2 \rangle} = \langle |v_x| \rangle \text{ in this case is coincidental.} \right]$$

P21.4 $\kappa = \frac{1}{3} \lambda \bar{v} C_{V,m} [\text{A}]$ [21.23]

$$\bar{v} = \left(\frac{8kT}{\pi m} \right)^{1/2} \quad [21.7] \propto T^{1/2}$$

Hence, $\kappa \propto T^{1/2} C_{V,m}$, so $\frac{\kappa'}{\kappa} = \left(\frac{T'}{T} \right)^{1/2} \times \left(\frac{C'_{V,m}}{C_{V,m}} \right)$

At 300 K, $C_{V,m} \approx \frac{3}{2}R + R = \frac{5}{2}R$ At 10 K, $C_{V,m} \approx \frac{3}{2}R$ [rotation not excited]

Therefore, $\frac{\kappa'}{\kappa} = \left(\frac{300}{10} \right)^{1/2} \times \left(\frac{5}{3} \right) = \boxed{9.1}$

P21.6 Radioactive decay follows first-order kinetics (Chapter 22); hence the two contributions to the rate of change of the number of helium atoms are

$$\frac{dN}{dt} = k_r [\text{Bk}] \quad (\text{radioactive decay}) \quad \frac{dN}{dt} = -Z_W [\text{A}] \quad [\text{Problem 21.5}]$$

Therefore, the total rate of change is

$$\frac{dN}{dt} = k_r [\text{Bk}] - Z_W A \quad \text{with } Z_W = \frac{p}{(2\pi mkT)^{1/2}}$$

$$[\text{Bk}] = [\text{Bk}]_0 e^{-k_r t} \text{ and } p = \frac{nRT}{V} = \frac{nN_A kT}{V} = \frac{NkT}{V}$$

Therefore, the pressure of helium inside the container obeys

$$\frac{dp}{dt} = \frac{kT}{V} \frac{dN}{dt} = \frac{kk_r T}{V} [\text{Bk}]_0 e^{-k_r t} - \frac{(pAkT/V)}{(2\pi mkT)^{1/2}}$$

If we write $a = \frac{kk_r T [\text{Bk}]_0}{V}$, $b = \left(\frac{A}{V}\right) \times \left(\frac{kT}{2\pi m}\right)^{1/2}$, the rate equation becomes

$$\frac{dp}{dt} = ae^{-k_r t} - bp, \quad p = 0 \text{ at } t = 0$$

which is a first-order linear differential equation with the solution

$$p = \left(\frac{a}{k_r - b}\right) \times (e^{-bt} - e^{-k_r t})$$

Since $[\text{Bk}] = \frac{1}{2}[\text{Bk}]_0$ when $t = 4.4$ h, it follows from the radioactive decay law ($[\text{Bk}] = [\text{Bk}]_0 e^{-k_r t}$) that (Chapter 22)

$$k_r = \frac{\ln 2}{(4.4) \times (3600 \text{ s})} = 4.4 \times 10^{-5} \text{ s}^{-1}$$

We also know that $[\text{Bk}]_0 = \left(\frac{1.0 \times 10^{-3} \text{ g}}{244 \text{ g mol}^{-1}}\right) \times (6.022 \times 10^{23} \text{ mol}^{-1}) = 2.5 \times 10^{18}$

$$\begin{aligned} \text{Then, } a &= \frac{kk_r T [\text{Bk}]_0}{V} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (4.4 \times 10^{-5} \text{ s}^{-1}) \times (298 \text{ K}) \times (2.5 \times 10^{18})}{1.0 \times 10^{-6} \text{ m}^3} \\ &= 0.45 \text{ Pa s}^{-1} \end{aligned}$$

and $b = \left(\frac{\pi \times (2.0 \times 10^{-6} \text{ m})^2}{1.0 \times 10^{-6} \text{ m}^3}\right) \times \left(\frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{(2\pi) \times (4.0) \times (1.6605 \times 10^{-27} \text{ kg})}\right)^{1/2} = 3.9 \times 10^{-3} \text{ s}^{-1}$

$$\begin{aligned} \text{Hence, } p &= \left(\frac{0.45 \text{ Pa s}^{-1}}{[(4.4 \times 10^{-5}) - (3.9 \times 10^{-3})] \text{ s}^{-1}}\right) \times (e^{-3.9 \times 10^{-3}(t/s)} - e^{-4.4 \times 10^{-5}(t/s)}) \\ &= (120 \text{ Pa}) \times (e^{-4.4 \times 10^{-5}(t/s)} - e^{-3.9 \times 10^{-3}(t/s)}) \end{aligned}$$

$$\text{(a) } t = 1 \text{ h, } p = (120 \text{ Pa}) \times (e^{-0.16} - e^{-14}) = \boxed{100 \text{ Pa}}$$

$$\text{(b) } t = 10 \text{ h, } p = (120 \text{ Pa}) \times (e^{-1.6} - e^{140}) = \boxed{24 \text{ Pa}}$$

P21.8 $\kappa \propto \frac{1}{R}$ [21.27, and the discussion above 21.27]

Because both solutions are aqueous their conductivities include a contribution of 76 mS m^{-1} from the water. Therefore,

$$\frac{\kappa(\text{acid soln})}{\kappa(\text{KCl soln})} = \frac{\kappa(\text{acid}) + \kappa(\text{water})}{\kappa(\text{KCl}) + \kappa(\text{water})} = \frac{R(\text{KCl soln})}{R(\text{acid soln})} = \frac{33.21 \Omega}{300.0 \Omega}$$

P21.18 This is essentially one-dimensional diffusion and therefore eqn 21.72 applies.

$$c = \frac{n_0 e^{-x^2/4Dt}}{A(\pi Dt)^{1/2}} \quad [21.72]$$

and we know that $n_0 = \left(\frac{10 \text{ g}}{342 \text{ g mol}^{-1}} \right) = 0.0292 \text{ mol}$

$$A = \pi R^2 = 19.6 \text{ cm}^2, \quad D = 5.21 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \quad [\text{Table 21.8}]$$

$$\begin{aligned} A(\pi Dt)^{1/2} &= (19.6 \text{ cm}^2) \times [(\pi) \times (5.21 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}) \times (t)]^{1/2} \\ &= 7.93 \times 10^{-2} \text{ cm}^3 \times (t/\text{s})^{1/2} \end{aligned}$$

$$\frac{x^2}{4Dt} = \frac{25 \text{ cm}^2}{(4) \times (5.21 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}) \times t} = \frac{1.20 \times 10^6}{(t/\text{s})}$$

$$\begin{aligned} \text{Therefore, } c &= \left(\frac{0.0292 \text{ mol} \times 10^{22}}{(7.93 \times 10^{-2} \text{ cm}^3) \times (t/\text{s})^{1/2}} \right) \times e^{-1.20 \times 10^6 / (t/\text{s})} \\ &= (369 \text{ M}) \times \left(\frac{e^{-1.20 \times 10^6 / (t/\text{s})}}{(t/\text{s})^{1/2}} \right) \end{aligned}$$

(a) $t = 10 \text{ s}, \quad c = (369 \text{ M}) \times \left(\frac{e^{-1.2 \times 10^5}}{10^{1/2}} \right) \approx \boxed{0}$

(b) $t = 1 \text{ yr} = 3.16 \times 10^7 \text{ s}, \quad c = (369 \text{ M}) \times \left(\frac{e^{-0.038}}{(3.16 \times 10^7)^{1/2}} \right) = \boxed{0.063 \text{ M}}$

COMMENT. This problem illustrates the extreme slowness of diffusion through typical macroscopic distances; however, it is rapid enough through distances comparable to the dimensions of a cell. Compare to Problem 21.40.

P21.20 Kohlrausch's law states that the molar conductance of a strong electrolyte varies with the square root of concentration

$$\Lambda_m = \Lambda_m^\circ - \mathcal{K}c^{1/2}$$

Therefore a plot of Λ_m versus $c^{1/2}$ should be a straight line with y-intercept Λ_m° . The data and plot (Figure 21.1) are shown below

$c/(\text{m mol dm}^{-3})$	NaI		KI		
	$c^{1/2}$	$\Lambda_m/(\text{S cm}^2 \text{ mol}^{-1})$	$c/(\text{mmol dm}^{-3})$	$c^{1/2}$	$\Lambda_m/(\text{S cm}^2 \text{ mol}^{-1})$
32.02	5.659	50.26	17.68	4.205	42.45
20.28	4.503	51.99	10.88	3.298	45.91
12.06	3.473	54.01	7.19	2.68	47.53
8.64	2.94	55.75	2.67	1.63	51.81
2.85	1.69	57.99	1.28	1.13	54.09
1.24	1.11	58.44	0.83	0.91	55.78
0.83	0.91	58.67	0.19	0.44	57.42

Solutions to theoretical problems

- P21.23** The most probable speed of a gas molecule corresponds to the condition that the Maxwell distribution be a maximum (it has no minimum); hence we find it by setting the first derivative of the function to zero and solve for the value of v for which this condition holds.

$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} = \text{const} \times v^2 e^{-mv^2/2kT} \quad \left[\frac{M}{R} = \frac{m}{k} \right].$$

$$\frac{df(v)}{dv} = 0 \quad \text{when} \quad \left(2 - \frac{mv^2}{kT} \right) = 0.$$

$$\text{So, } v(\text{most probable}) = c^* = \left(\frac{2kT}{m} \right)^{1/2} = \left(\frac{2RT}{M} \right)^{1/2}.$$

The average kinetic energy corresponds to the average of $\frac{1}{2}mv^2$. The average is obtained by determining $\langle v^2 \rangle = \int_0^\infty v^2 f(v) dv = 4\pi (m/2\pi)^{3/2} \times (1/kT)^{3/2} \int_0^\infty v^4 e^{-mv^2/2kT} dv$.

The integral evaluates to $(3/8)\pi^{1/2}(m/2kT)^{-5/2}$. Then

$$\langle v^2 \rangle = 4\pi \left(\frac{m}{2\pi} \right)^{3/2} \times \left(\frac{1}{kT} \right)^{3/2} \times \left(\frac{3}{8}\pi^{1/2} \right) \times \left(\frac{2kT}{m} \right)^{5/2} = \frac{3kT}{m};$$

$$\text{thus } \langle \epsilon \rangle = \frac{1}{2}m \langle v^2 \rangle = \frac{3}{2}kT.$$

- P21.25** Write the mean velocity initially as a ; then in the emerging beam $\langle v_x \rangle = K \int_0^a v_x f(v_x) dv_x$ where K is a constant that ensures that the distribution in the emergent beam is also normalized. That is, $1 = K \int_0^a f(v_x) dv_x = K (m/2\pi kT)^{1/2} \int_0^a e^{-mv_x^2/2kT} dv_x$. This integral cannot be evaluated analytically but it can be related to the error function by defining

$$x^2 = \frac{mv_x^2}{2kT}$$

which gives $dv_x = (2kT/m)^{1/2} dx$. Then

$$\begin{aligned} 1 &= K \left(\frac{m}{2\pi kT} \right)^{1/2} \left(\frac{2kT}{m} \right)^{1/2} \int_0^b e^{-x^2} dx \quad [b = (m/2kT)^{1/2} \times a] \\ &= \frac{K}{\pi^{1/2}} \int_0^b e^{-x^2} dx = \frac{1}{2} K \text{erf}(b) \end{aligned}$$

where erf(z) is the error function [Table 9.2]: erf(z) = $(2/\pi^{1/2}) \int_0^z e^{-x^2} dx$.

$$\text{Therefore, } K = \frac{2}{\text{erf}(b)}.$$

The mean velocity of the emerging beam is

$$\begin{aligned} \langle v_x \rangle &= K \left(\frac{m}{2\pi kT} \right)^{1/2} \int_0^a v_x e^{-mv_x^2/2kT} dv_x = K \left(\frac{m}{2\pi kT} \right)^{1/2} \left(\frac{-kT}{m} \right) \int_0^a \frac{d}{dv_x} \left(e^{-mv_x^2/2kT} \right) dv_x \\ &= -K \left(\frac{kT}{2m\pi} \right)^{1/2} \left(e^{-ma^2/2kT} - 1 \right). \end{aligned}$$

where $v^2 = v_x^2 + v_y^2$. The probability $f(v)dv$ that the molecules have a two-dimensional speed, v , in the range $v, v + dv$ is sum of the probabilities that it is in any of the area elements $dv_x dv_y$ in the circular shell of radius v . The sum of the area elements is the area of the circular shell of radius v and thickness dv which is $\pi(v + dv)^2 - \pi v^2 = 2\pi v dv$. Therefore

$$f(v) = 2\pi \left(\frac{m}{2\pi kT} \right) v e^{-mv^2/2kT} \left[\frac{M}{R} = \frac{m}{k} \right]$$

The mean speed is determined as $\bar{c} = \int_0^\infty v f(v) dv = \int_0^\infty m/(kT) v^2 e^{-mv^2/2kT} dv$.

Using standard integrals this evaluates to $\bar{c} = (\pi kT/2m)^{1/2} = (\pi RT/2M)^{1/2}$.

COMMENT. The two-dimensional gas serves as a model of the motion of molecules of surfaces. See Chapter 24.

P21.26 Rewriting eqn 21.4 with $(M/R) = (m/k)$

$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT}$$

The proportion of molecules with speeds less than c is

$$P = \int_0^c f(v) dv = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^c v^2 e^{-mv^2/2kT} dv$$

Defining $a \equiv \frac{m}{2kT}$

$$P = 4\pi \left(\frac{a}{\pi} \right)^{3/2} \int_0^c v^2 e^{-av^2} dv = -4\pi \left(\frac{a}{\pi} \right)^{3/2} \frac{d}{da} \int_0^c e^{-av^2} dv$$

Defining $x^2 \equiv av^2$, $dv = a^{-1/2} dx$

$$\begin{aligned} P &= -4\pi \left(\frac{a}{\pi} \right)^{3/2} \frac{d}{da} \left\{ \frac{1}{a^{1/2}} \int_0^{ca^{1/2}} e^{-x^2} dx \right\} \\ &= -4\pi \left(\frac{a}{\pi} \right)^{3/2} \left\{ -\frac{1}{2} \left(\frac{1}{a} \right)^{3/2} \int_0^{ca^{1/2}} e^{-x^2} dx + \left(\frac{1}{a} \right)^{1/2} \frac{d}{da} \int_0^{ca^{1/2}} e^{-x^2} dx \right\} \end{aligned}$$

Then we use $\int_0^{ca^{1/2}} e^{-x^2} dx = (\pi^{1/2}/2) \operatorname{erf}(ca^{1/2})$

$$\frac{d}{da} \int_0^{ca^{1/2}} e^{-x^2} dx = \left(\frac{dca^{1/2}}{da} \right) \times (e^{-c^2 a}) = \frac{1}{2} \left(\frac{c}{a^{1/2}} \right) e^{-c^2 a}$$

where we have used $\frac{d}{dz} \int_0^z f(y) dy = f(z)$

Substituting and cancelling we obtain $P = \operatorname{erf}(ca^{1/2}) - (2ca^{1/2}/\pi^{1/2}) e^{-c^2 a}$

Now, $c = (3kT/m)^{1/2}$, so $ca^{1/2} = (3kT/m)^{1/2} \times (m/2kT)^{1/2} = (3/2)^{1/2}$, and

$$P = \operatorname{erf}\left(\sqrt{\frac{3}{2}}\right) - \left(\frac{6}{\pi}\right)^{1/2} e^{-3/2} = 0.92 - 0.31 = \boxed{0.61}$$

Therefore (b) $\boxed{61 \text{ percent}}$ of the molecules have a speed less than the root mean square speed and (a) $\boxed{39 \text{ percent}}$ have a speed greater than the root mean square speed. (c) For the proportions in terms of the mean speed \bar{c} , replace c by $\bar{c} = (8kT/\pi m)^{1/2} = (8/3\pi)^{1/2} c$, so $\bar{c}a^{1/2} = 2/\pi^{1/2}$.

Then $P = \operatorname{erf}(\bar{c}a^{1/2}) - (2\bar{c}a^{1/2}/\pi^{1/2}) \times (e^{-\bar{c}^2 a}) = \operatorname{erf}(2/\pi^{1/2}) - (4/\pi)e^{-4/\pi} = 0.889 - 0.356 = \boxed{0.533}$

That is, $\boxed{53 \text{ percent}}$ of the molecules have a speed less than the mean, and $\boxed{47 \text{ percent}}$ have a speed greater than the mean.

P21.28 An effusion oven has constant volume, fixed temperature, and effusion hole of area A . Gas escapes through the hole, which makes the effusion rate negative.

$$-\frac{dN}{dt} = Z_{\text{W}}A = \frac{pAN_{\text{A}}}{(2\pi MRT)^{1/2}} \quad [21.16]$$

For a perfect gas, $pV = nRT = NRT/N_{\text{A}}$ and, therefore, $N = N_{\text{A}}pV/RT$.

Differentiation gives $\frac{dN}{dt} = \frac{N_{\text{A}}V}{RT} \frac{dp}{dt}$. Substitution into the first equation yields:

$$\begin{aligned} \frac{N_{\text{A}}V}{RT} \frac{dp}{dt} &= -\frac{pAN_{\text{A}}}{(2\pi MRT)^{1/2}} \\ \frac{dp}{dt} &= -\left(\frac{RT}{2\pi M}\right)^{1/2} \frac{A}{V} p = -\frac{p}{\tau} \quad \text{where the time constant is } \tau = \left(\frac{2\pi M}{RT}\right)^{1/2} \frac{V}{A} \\ \frac{dp}{p} &= -\frac{dt}{\tau} \\ \int_{p_0}^p \frac{dp}{p} &= -\frac{1}{\tau} \int_0^t dt \\ \ln\left(\frac{p}{p_0}\right) &= -\frac{t}{\tau} \quad \text{or} \quad p = p_0 e^{-t/\tau} \end{aligned}$$

When $t = t_{1/2}$, $p = (1/2)p_0$. Substitution into the above equation gives

$$\ln\left(\frac{p_0}{2p_0}\right) = -\frac{t_{1/2}}{\tau} \quad \text{or} \quad t_{1/2} = \tau \ln(2) = \left(\frac{2\pi M}{RT}\right)^{1/2} \frac{V}{A} \ln(2)$$

The final equation indicates that the half-life for effusive loss is independent of p_0 . Furthermore, the half-life increases with both the V/A and $M^{1/2}$ factors. It decreases with the factor $T^{-1/2}$.