

- please answer all 5 questions in the spaces provided
- this is a 1-hour test (but you have 2 hours to write it)
- a calculator and the equation sheets provided may be used

- all questions are of equal value
- no books or notes are allowed
- no marks for unreadable answers

1. This question refers to the lead-acid cell:  $\text{Pb(s)}|\text{PbSO}_4\text{(s)}|\text{H}_2\text{SO}_4\text{(aq)}|\text{PbSO}_4\text{(s)}|\text{PbO}_2\text{(s)}|\text{Pb(s)}$

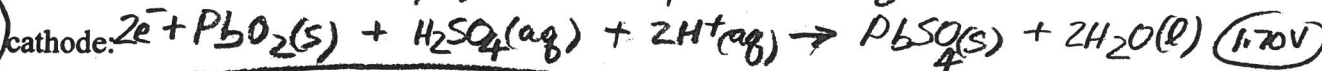
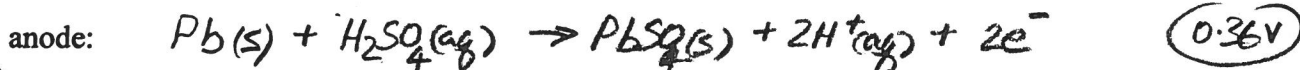
a) Almost 2 billion lead-acid cells are manufactured per year! What is their main application?

car and truck batteries for engine starting

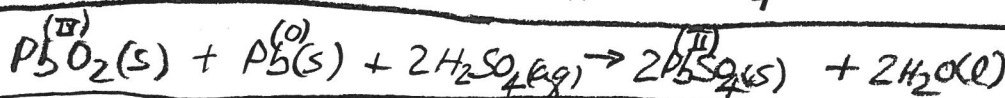
b) Are lead-acid cells reversible? Rechargeable? Explain briefly.

Yes - no irreversible mixing of electrolytes, therefore rechargeable, (Last ~ 5 years before replacement.)

c) Write the anode reaction, cathode reaction, and overall reaction for the lead-acid cell.



overall:



d) Use standard reduction potentials (next page) to calculate the standard cell potential ( $E^\circ$ ) at 25 °C.

$$E^\circ = 0.36\text{V} + 1.70\text{V} = 2.06\text{V}$$

e) Write the Nernst equation for the lead-acid cell.

(pure solids:  $a_{\text{Pb(s)}} = a_{\text{PbSO}_4\text{(s)}} = a_{\text{PbO}_2\text{(s)}} = 1$ )

$$E = E^\circ - \frac{RT}{2F} \ln\left(\frac{a_{\text{H}_2\text{O}}^2}{a_{\text{H}_2\text{SO}_4}}\right) \approx E^\circ - \frac{RT}{2F} \ln\left(\frac{1}{a_{\text{H}_2\text{SO}_4}^2}\right)$$

( $a_{\text{H}_2\text{O}} \approx 1$  because  $x_{\text{H}_2\text{O}} \approx 1$ )

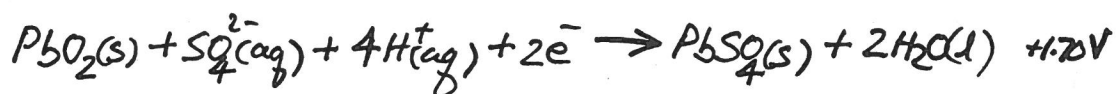
f) A lead-acid cell contains aqueous sulfuric acid at molality 6.00 mol kg<sup>-1</sup> at 25 °C. The mean ionic activity coefficient of H<sub>2</sub>SO<sub>4</sub> at this composition is  $\gamma_{\pm} = 0.16$ . Calculate the cell potential  $E$ .

$$\begin{aligned} a_{\text{H}_2\text{SO}_4} &= a_{\text{H}^+}^2 a_{\text{SO}_4^{2-}} = (\gamma_+ m_{\text{H}^+})^2 \gamma_{\text{SO}_4^{2-}} m_{\text{SO}_4^{2-}} = (\gamma_{\pm} 2m)^2 \gamma_{\pm} m \\ &= \gamma_+^2 \gamma_{\pm} 4m^2 = \gamma_{\pm}^3 4m^3 = (0.16)^3 4(6 \text{ mol kg}^{-1})^3 \\ &= 3.539 \end{aligned}$$

$$\begin{aligned} E &= E^\circ - \frac{RT}{2F} \ln\left(\frac{1}{a_{\text{H}_2\text{SO}_4}^2}\right) = 2.06 - \frac{8.314(298.15)}{2(96485)} \ln\left(\frac{1}{3.539^2}\right) \\ &= 2.06 - (-0.032) \\ &= 2.09\text{V} \end{aligned}$$

Reduction Reaction	$E^\circ/V$
$\text{Cu}^+ + e^- = \text{Cu}$	+0.52
$\text{Cu}^{2+} + 2e^- = \text{Cu}$	+0.34
$\text{Cu}^{2+} + e^- = \text{Cu}^+$	+0.16
$\text{Cu}(\text{NH}_3)_4^{2+} + 2e^- = \text{Cu} + 4\text{NH}_3$	0.00
$\text{F}_2 + 2e^- = 2\text{F}^-$	+2.87
$\text{Fe}^{2+} + 2e^- = \text{Fe}$	-0.44
$\text{Fe}^{3+} + 3e^- = \text{Fe}$	-0.04
$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$	+0.77
$\text{Fe}(\text{CN})_6^{3-} + e^- = \text{Fe}(\text{CN})_6^{4-}$	+0.36
$\text{Fe}(\text{CN})_6^{4-} + 2e^- = \text{Fe} + 6\text{CN}^-$	-1.16
$2\text{H}^+ + 2e^- = \text{H}_2$	0.00
$2\text{H}_2\text{O} + 2e^- = \text{H}_2 + 2\text{OH}^-$	-0.83
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- = 2\text{H}_2\text{O}$	+1.76
$\text{Hg}_2^{2+} + 2e^- = 2\text{Hg}$	+0.80
$\text{Hg}_2\text{Cl}_2 + 2e^- = 2\text{Hg} + 2\text{Cl}^-$	+0.27
$\text{Hg}^{2+} + 2e^- = \text{Hg}$	+0.86
$2\text{Hg}^{2+} + 2e^- = \text{Hg}_2^{2+}$	+0.91
$\text{I}_2 + 2e^- = 2\text{I}^-$	+0.54
$\text{K}^+ + e^- = \text{K}$	-2.93
$\text{Li}^+ + e^- = \text{Li}$	-3.04
$\text{Mg}^{2+} + 2e^- = \text{Mg}$	-2.36
$\text{Mn}^{2+} + 2e^- = \text{Mn}$	-1.18
$\text{Mn}^{3+} + e^- = \text{Mn}^{2+}$	+1.51
$\text{MnO}_2 + 4\text{H}^+ + 2e^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23
$\text{NO}_3^- + 2\text{H}^+ + e^- = \text{NO}_2 + \text{H}_2\text{O}$	+0.80
$\text{NO}_3^- + 4\text{H}^+ + 3e^- = \text{NO} + 2\text{H}_2\text{O}$	+0.96
$\text{Na}^+ + e^- = \text{Na}$	-2.71
$\text{Ni}^{2+} + 2e^- = \text{Ni}$	-0.26
$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^-$	+0.40
$\text{O}_2 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O}$	+1.23
$\text{O}_2 + 2\text{H}^+ + 2e^- = \text{H}_2\text{O}_2$	+0.70
$\text{Pb}^{2+} + 2e^- = \text{Pb}$	-0.13
$\text{PbO}_2 + 4\text{H}^+ + 2e^- = \text{Pb}^{2+} + 2\text{H}_2\text{O}$	+1.70 X
$\text{PbSO}_4 + 2e^- = \text{Pb} + \text{SO}_4^{2-}$	-0.36 ✓
$\text{Pt}^{2+} + 2e^- = \text{Pt}$	+1.19
$\text{Rb}^+ + e^- = \text{Rb}$	-2.93
$\text{Sn}^{2+} + 2e^- = \text{Sn}$	-0.14
$\text{Sn}^{4+} + 2e^- = \text{Sn}^{2+}$	+0.15
$\text{Zn}^{2+} + 2e^- = \text{Zn}$	-0.76

should be:



2. a) Give the numerical value of each of the following integrals. (Definite integrals not required here!)  
 average  $x$ -velocity  $f(v_x)$  is normalized

i)  $\int_{-\infty}^{\infty} v_x f(v_x) dv_x = \langle v_x \rangle = \boxed{0}$   
 equal number of molecules moving left and right

ii)  $\int_{-\infty}^{\infty} f(v_x) dv_x = \boxed{1} =$  probability of all possible  $x$ -velocities

iii)  $\int_0^{\infty} F(v) dv = \boxed{1}$   
 $F(v)$  is normalized

iv)  $\int_0^{\infty} f(v_x) dv_x = \boxed{\frac{1}{2}}$   
 one half of the molecules are moving "right" ( $v_x > 0$ )

b) Calculate the kinetic energy of one mole of helium at 500 K.  
 average translational kinetic energy per mole

monatomic, only translational kinetic energy

$$\begin{aligned} &= \frac{1}{2} M \langle v_x^2 \rangle + \frac{1}{2} M \langle v_y^2 \rangle + \frac{1}{2} M \langle v_z^2 \rangle \\ &= \frac{1}{2} M \langle v^2 \rangle = \frac{3}{2} RT = \frac{3}{2} (8.314 \frac{\text{J}}{\text{K mol}}) (500 \text{K}) \\ &= \boxed{6235 \text{ J mol}^{-1}} \end{aligned}$$

b) Use  $f(v_x) = \sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/2kT}$  and the definite integral  $\int_0^{\infty} x e^{-ax^2} dx = \frac{1}{2a}$

to prove the average velocity in the positive  $x$ -direction is  $\int_0^{\infty} v_x f(v_x) dv_x = \frac{\langle v \rangle}{4}$ .

$$\int_0^{\infty} v_x f(v_x) dv_x = \int_0^{\infty} v_x \sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/2kT} dv_x \quad a = \frac{m}{2kT}$$

$$= \sqrt{\frac{m}{2\pi kT}} \int_0^{\infty} v_x e^{-av_x^2} dv_x = \sqrt{\frac{m}{2\pi kT}} \frac{1}{2a}$$

$$= \sqrt{\frac{m}{2\pi kT}} \frac{1}{2} \frac{1}{\frac{m}{2kT}} = \sqrt{\frac{m}{2\pi kT}} \sqrt{\frac{kT^2}{m^2}}$$

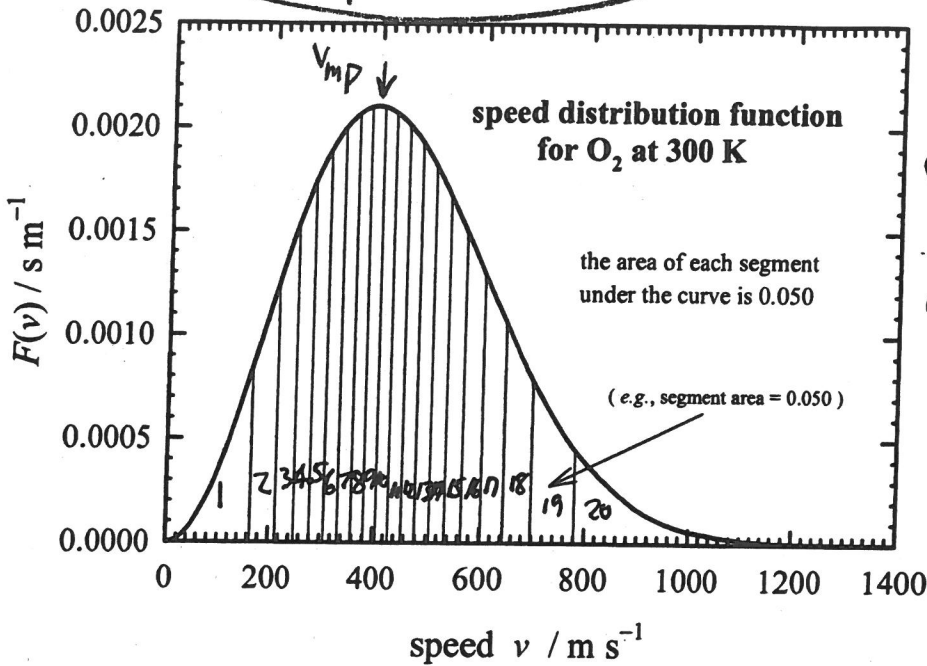
$$= \sqrt{\frac{kT}{2\pi m}} = \frac{1}{\sqrt{16}} \sqrt{\frac{16kT}{2\pi m}} = \frac{1}{4} \sqrt{\frac{8kT}{\pi m}} = \frac{1}{4} \langle v \rangle$$

c) Part b shows how the average velocity of molecules moving in one direction can be calculated. Why is this result important for calculating diffusion coefficients, thermal conductivities and molecular collision rates with walls?

Need to know the number of molecules moving toward (i.e.,  $v_x > 0$ ) a wall to calculate collision rates, toward a hole to calculate effusion rates, down a concentration gradient (diffusion) or down a temperature gradient (heat conduction)

3. a) Using the speed distribution function for O<sub>2</sub> plotted below:

$v_{mp} \approx 400 \text{ m s}^{-1}$



i) show  $F(v)$  is normalized

$(20 \text{ segments}) \times 0.050 = 1 = \int_0^{\infty} F(v) dv$

(area under  $F(v)$  curve)

ii) determine the fraction of O<sub>2</sub> molecules with speeds from 0 m s<sup>-1</sup> to 600 m s<sup>-1</sup>

$\int_0^{600} F(v) dv = 16 \text{ segments} \times 0.050 = 0.80$

iii) determine the most probable speed.

$\approx 400 \frac{\text{m}}{\text{s}}$  (from graph)

b) Explain in words why i)  $F(v) \rightarrow 0$  as  $v \rightarrow \infty$

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

$F(v) \propto e^{-\text{(Kinetic Energy)}/kT}$  as  $v \rightarrow \infty$ , kinetic energy  $\rightarrow \infty$  the probability drops to zero

ii)  $F(v) \rightarrow 0$  as  $v \rightarrow 0$

the number of velocity vectors that give speeds from  $v$  to  $v+dv$  is  $4\pi v^2 dv \rightarrow 0$  as  $v \rightarrow 0$

c) The diffusion coefficient of O<sub>2</sub> molecules in air is  $2.3 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  at 20 °C.

i) Calculate the root-mean-square displacement of O<sub>2</sub> molecules after diffusion for one hour in air at 20 °C.

$\sqrt{\langle x^2 \rangle} = \sqrt{2Dt} = \sqrt{2(2.3 \times 10^{-5} \text{ m}^2 \text{ s}^{-1})(3600 \text{ s})} = 0.407 \text{ m} \approx 4 \text{ cm}$

no suffocation

ii) Use the calculated rms displacement of O<sub>2</sub> molecules to suggest why it is a good idea to have forced-air ventilation in classrooms full of students.

Not enough O<sub>2</sub> provided by diffusion (too slow) - need fresh air pumped in (convection, not diffusion). (Also, CO<sub>2</sub> would not diffuse away sufficiently rapidly (worse).)

4. a) A gas effusion cell contains a mixture of neon isotopes at 300 K:

hole area  
 $A = \pi r^2 = \pi (0.00015 \text{ m})^2$   
 $= 7.07 \times 10^{-8} \text{ m}^2$

$^{20}\text{Ne}$  ( $20.0 \text{ g mol}^{-1}$ ) at 0.900 bar and  $^{22}\text{Ne}$  ( $22.0 \text{ g mol}^{-1}$ ) at 0.100 bar

The neon atoms leak through a small hole (diameter 0.30 mm) into a vacuum chamber.

i) Calculate the number of  $^{20}\text{Ne}$  atoms leaking out of the cell per second.

$$Z_c = \frac{1}{A} \frac{dN}{dt} = \frac{P}{\sqrt{2\pi M R T}} = \frac{P N_A}{\sqrt{2\pi M R T}} = \frac{P N_A}{\sqrt{2\pi M_{20} R T}}$$

$$= \frac{0.900 \times 10^5 (6.022 \times 10^{23})}{\sqrt{2\pi (0.0200) 8.314 (300)}} = 3.06 \times 10^{27} \text{ } ^{20}\text{Ne atoms m}^{-2} \text{ s}^{-1}$$

$$\frac{d^{20}\text{N}}{dt} = Z_c A = (3.06 \times 10^{27} \text{ m}^{-2} \text{ s}^{-1}) (7.07 \times 10^{-8} \text{ m}^2) = \boxed{2.16 \times 10^{20} \text{ s}^{-1}}$$

ii) Calculate the number of  $^{22}\text{Ne}$  atoms that leaking out of the cell per second.

$$\frac{d^{22}\text{N}}{dt} = Z_c A = \frac{P N_A A}{\sqrt{2\pi M_{22} R T}} = \frac{0.100 \times 10^5 (6.022 \times 10^{23}) (7.07 \times 10^{-8})}{\sqrt{2\pi (0.02200) 8.314 (300)}}$$

$$= \boxed{2.29 \times 10^{19} \text{ s}^{-1}} \quad \left( = \frac{^{22}\text{P}}{^{20}\text{P}} \sqrt{\frac{M_{20}}{M_{22}}} \frac{d^{20}\text{N}}{dt} \right)$$

iii) Show that the mole fraction of  $^{20}\text{Ne}$  in the gas leaking out of the cell is larger than the  $^{20}\text{Ne}$  mole fraction in the gas inside the cell, illustrating isotope enrichment by effusion.

$^{20}\text{N}$  mole fraction in effusion cell

$$= \frac{^{20}\text{P}}{^{20}\text{P} + ^{22}\text{P}} = \frac{0.900}{0.900 + 0.100} = 0.900$$

mole fraction of  $^{20}\text{Ne}$  in leaked gas

$$\frac{d^{20}\text{N}/dt}{d^{20}\text{N}/dt + d^{22}\text{N}/dt} = \frac{2.16}{2.16 + 0.229} = 0.904$$

b) The collisional cross-section area of  $^{20}\text{Ne}$  atoms is  $0.209 \text{ nm}^2$ . Calculate the diffusion coefficient of  $^{20}\text{Ne}$  at 300 K and 1.00 bar.

$$D = \frac{3\pi}{8} \sqrt{\frac{kT}{\pi m}} \frac{1}{c\sigma} = \frac{3\pi}{8} \sqrt{\frac{RT}{\pi M}} \frac{1}{\frac{N}{V}\sigma} = \frac{3\pi}{8} \sqrt{\frac{RT}{\pi M}} \frac{kT}{P\sigma}$$

$$= \frac{3\pi}{8} \sqrt{\frac{8.314(300)}{\pi (0.0200)}} \frac{(1.381 \times 10^{-23}) 300}{1.00 \times 10^5 (0.209 \times 10^{-18})} = 4.65 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$$

c)  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  have identical collision cross-section areas ( $\sigma$ ). Why? Would you expect  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$ , both at 300 K and 1.00 bar, to have identical diffusion coefficients? Explain. (NO)

Same  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  "electron clouds"

Same electronic structure ( $1s^2 2s^2 2p^6$ ) unaffected by 2 extra or two less neutrons (no electric charge) in the nuclei

But  $^{20}\text{D} \neq ^{22}\text{D}$   $D \propto \frac{1}{\sqrt{M}}$  so  $^{20}\text{D}/^{22}\text{D} = \sqrt{22.0/20.0} = 1.05$

5. a) Give the SI units of the heat flux density  $J_x$ , temperature gradient  $\partial T/\partial x$ , and thermal conductivity  $\kappa$  in Fourier's law of heat conduction:  $J_x = -\kappa \partial T/\partial x$ .

heat flow per unit area  
per unit time

$$J_x \quad \boxed{\text{J m}^{-2} \text{s}^{-1}}$$

$$\partial T/\partial x \sim \Delta T/\Delta x \sim \boxed{\text{K m}^{-1}}$$

$$\kappa \frac{\text{units of } J_x}{\text{units of } \partial T/\partial x} \sim \frac{\text{J m}^{-2} \text{s}^{-1}}{\text{K m}^{-1}} \sim \boxed{\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}}$$

- b) Two parallel metal plates separated by 0.00500 m are held at 20 °C and 30 °C. The area of each plate is 0.250 m<sup>2</sup>. When the space between the plates is filled with argon at 1.00 bar, the heat flow rate between the plates is 8.15 J s<sup>-1</sup>. Calculate the thermal conductivity of argon.

↑ x

$\boxed{30^\circ\text{C}}$   
 $\boxed{20^\circ\text{C}}$

$-8.15 \text{ J s}^{-1} = J_x A = -\kappa \frac{\partial T}{\partial x} A = -\kappa \frac{\Delta T}{\Delta x} A$   
(down)

$$\kappa = \frac{8.15 \text{ J s}^{-1}}{A} \frac{\Delta x}{\Delta T} = \frac{8.15 \text{ J s}^{-1}}{0.25 \text{ m}^2} \frac{0.00500 \text{ m}}{10 \text{ K}}$$

$$\boxed{\kappa = 0.0163 \text{ J m}^{-1} \text{s}^{-1} \text{K}^{-1}}$$

- c) Thermos™ flasks keep food and beverages hot or cold for hours. The space between the double walls of the flasks is evacuated. Why?

If the walls are separated by a vacuum, then no gas is available to conduct heat — a perfect insulator!

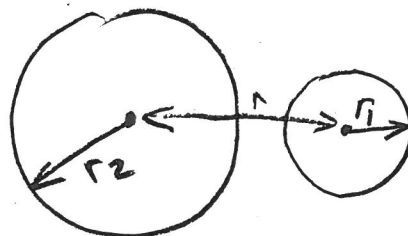


- d) Calculate the mean free path of argon atoms ( $\sigma = 0.416 \text{ nm}^2$ ) at 25 °C and 1.00 bar.

$$\lambda = \frac{kT}{p\sqrt{2}\sigma} = \frac{(1.381 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}{(1.00 \times 10^5 \text{ Pa}) \sqrt{2} (0.416 \times 10^{-18} \text{ m}^2)}$$

$$= 7.00 \times 10^{-8} \text{ m}$$

$$\boxed{\lambda = 70.0 \text{ nm}}$$



- e) Our treatment of mean free paths, molecular collision rates, diffusion and heat conduction in gases is based on the "hard-sphere" model. Briefly describe this model. What assumptions are made when this model is used?

- ① potential energy of 2 interacting molecules = 0 if  $r \geq r_1 + r_2$   
a distance  $r$  apart =  $\infty$  if  $r < r_1 + r_2$
- ② all collisions are elastic, meaning translational energy is conserved  
(no rotations or vibrations to absorb or release energy) ( $r_1 + r_2 = \text{collision diameter}$ )