

- this is a 2-hour test
- please answer all 5 questions in the spaces provided
- 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 reversible cell  $\text{Pt(s)}|\text{H}_2(\text{g}, 1 \text{ bar})|\text{HCl}(\text{aq}, 0.100 \text{ mol kg}^{-1})|\text{AgCl(s)}|\text{Ag(s)}$  at 25 °C. The cell reaction is  $\text{H}_2(\text{g}) + 2\text{AgCl(s)} = 2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) + 2\text{Ag(s)}$ .

Data:  $\Delta G_{\text{fm}}^\circ(\text{AgCl, s}) = -109.8 \text{ kJ mol}^{-1}$

$\Delta G_{\text{fm}}^\circ(\text{Cl}^-, \text{aq}) = -131.2 \text{ kJ mol}^{-1}$

- a) Calculate  $\Delta G^\circ$  and show the standard cell voltage is  $E^\circ = 0.222 \text{ V}$ .

$$\Delta G^\circ = 2\Delta G_{\text{fm}}^\circ(\text{H}^+, \text{aq}) + 2\Delta G_{\text{fm}}^\circ(\text{Cl}^-, \text{aq}) + 2\Delta G_{\text{fm}}^\circ(\text{Ag, s}) - \Delta G_{\text{fm}}^\circ(\text{H}_2, \text{g}) - 2\Delta G_{\text{fm}}^\circ(\text{AgCl, s})$$

$$\Delta G^\circ = 0 + 2(-131.2) + 0 - 0 - 2(-109.8) = \boxed{-42.8 \text{ kJ mol}^{-1}}$$

$$\Delta G^\circ = -nFE^\circ \quad E^\circ = \frac{\Delta G^\circ}{-nF} = \frac{-42800 \text{ J}}{(-2)(96485 \text{ C mol}^{-1})} = \boxed{0.222 \text{ V}}$$

- b) Write the Nernst equation for the cell. (Do not assume ideal solutions.)

$$E = E^\circ - \frac{RT}{nF} \ln \left( \frac{a_{\text{H}^+}^2 a_{\text{Cl}^-}^2}{a_{\text{H}_2} a_{\text{AgCl}}^2} \right) = E^\circ - \frac{RT}{2F} \ln \left( \frac{(\gamma_+ m)^2 (\gamma_- m)^2}{p_{\text{H}_2} (1)^2} \right)$$

$$E = E^\circ - \frac{RT}{2F} \ln \left( \frac{\gamma_+^2 \gamma_-^2 m^4}{p_{\text{H}_2}} \right) = \boxed{E^\circ - \frac{RT}{2F} \ln \left( \frac{\gamma_+^4 m^4}{p_{\text{H}_2}} \right)}$$

- c) Use the measured cell voltage  $E = 0.355 \text{ V}$  to calculate the mean ionic activity coefficient ( $\gamma_{\pm}$ ) of 0.100 mol kg<sup>-1</sup> aqueous HCl.

$$0.355 \text{ V} = 0.222 \text{ V} - \frac{8.314(298.15)}{2(96458)} \ln \left[ \frac{\gamma_{\pm}^4 (0.100)^4}{1} \right]$$

$$-10.354 = \ln [\gamma_{\pm}^4 (0.100)^4]$$

$$-10.354 = 4 \ln \gamma_{\pm} + 4 \ln (0.100)$$

$$\ln \gamma_{\pm} = -0.282 \quad \gamma_{\pm} = e^{-0.282} = \boxed{0.754}$$

- d) To demonstrate that electrochemical cells can be used to measure partial pressures of gases, calculate the cell voltage if the H<sub>2</sub> pressure is changed from  $p_{\text{H}_2} = 1 \text{ bar}$  to  $p_{\text{H}_2} = 10^{-6} \text{ bar}$ .

at  $p_{\text{H}_2} = 10^{-6} \text{ bar}$ :

$$E = E^\circ - \frac{RT}{2F} \ln \left( \frac{\gamma_{\pm}^4 m^4}{p_{\text{H}_2}} \right)$$

$$= 0.222 - \frac{(8.314)(298.15)}{2(96485)} \ln \left( \frac{0.754^4 (0.100)^4}{10^{-6}} \right)$$

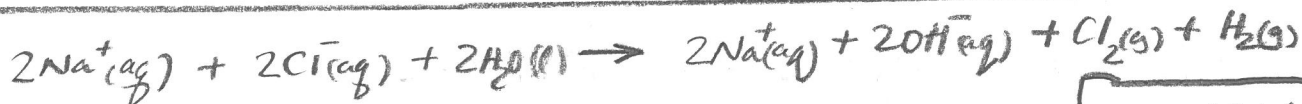
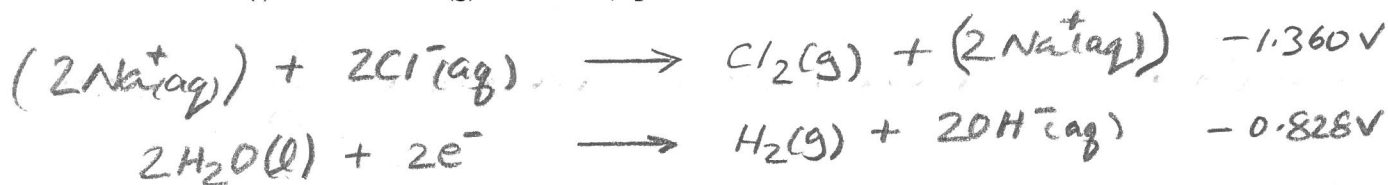
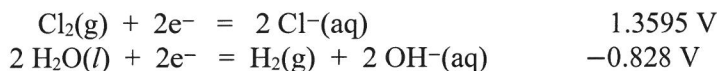
$$= 0.222 - 0.0446 = \boxed{0.177 \text{ V}}$$

2. This question refers to the chlor-alkali cell:  $\text{steel(s)}|\text{Cl}_2(\text{g})|\text{NaCl}(\text{aq})||\text{NaOH}(\text{aq})|\text{H}_2(\text{g})|\text{steel(s)}$ .

a) Why is this cell called a "diaphragm" cell? What is the purpose of the diaphragm?

the diaphragm, usually a mat of asbestos fibers, separated the NaCl solution from the product NaOH solution, while still allowing ionic conduction

b) Give the overall cell reaction and calculate  $E^\circ$  at  $25^\circ\text{C}$  using the standard reduction potentials:



$$\text{standard cell voltage} = -1.360 - 0.828 = \boxed{-2.188 \text{ V}}$$

c) The voltage applied to chlor-alkali cells ( $-4.5 \text{ V}$ ) is significantly larger than  $E^\circ$ , which means significantly larger electricity bills for operating chlor-alkali cells. Why is this necessary?

A larger applied cell voltage is used to produce  $\text{Cl}_2$ ,  $\text{NaOH}$  and  $\text{H}_2$  at a higher rate, suitable for commercial production ("time is money"! ). Also, the cell is irreversible.

d) Calculate the electrical work  $w_e$  required to produce  $1000 \text{ kg}$  of  $\text{Cl}_2$  ( $70.9 \text{ g mol}^{-1}$ ).

$$\begin{aligned} \text{electric work to} &= -nFE \\ \text{synthesize } 1.00 & \quad \swarrow \text{2 moles of electrons} \\ \text{mole (0.0709 kg) Cl}_2 & \quad \searrow \text{applied cell voltage} \\ &= -(2 \text{ mol})(96485 \text{ C mol}^{-1})(-4.5 \text{ V}) \\ &= 868,000 \text{ J mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{electric work to} &= \frac{868,000 \text{ J mol}^{-1}}{0.0709 \text{ kg mol}^{-1}} (1000 \text{ kg}) \\ \text{synthesize} & \\ \text{1000 kg Cl}_2 & \end{aligned}$$

(14,100 mol  $\text{Cl}_2$   
per tonne)

$$= 1.22 \times 10^{10} \text{ J}$$

3. a) In the front-page article *The Myth of the Green Hydrogen Revolution* published last week in the *Globe and Mail* (Canada's leading newspaper), author Eric Reguly writes:

"Today, hydrogen is made in pretty big quantities for ammonia-based fertilizers and other industrial products through a process called electrolysis, which splits water into hydrogen and oxygen."

This is incorrect! Give the main source of hydrogen used today and explain why it is not "green".

Almost all  $H_2$  produced commercially is from the reaction of natural gas (cheap!) with high temperature steam:  $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$   
 \* used "fossil" fuel \*  $CO_2$  emitted  $\therefore$  not "green"!

- b) A 17.3 gram Li ion battery for a cell phone is rated at 3.7 V and 1.1 ampere-hours. Calculate:

- i) the electric energy stored in the fully charged battery

$$(3.7 \text{ V})(1.1 \frac{\text{C}}{\text{s}}) 3600 \text{ s} = \boxed{14,600 \text{ J}}$$

- ii) the specific energy of the battery (electric energy per kg of battery mass)

$$\frac{14,600 \text{ J}}{17.3 \text{ g } (0.001 \text{ kg g}^{-1})} = 847,000 \frac{\text{J}}{\text{kg}} = \boxed{0.847 \text{ MJ kg}^{-1}}$$

- c) Use kinetic theory to calculate the specific energy of argon gas (kinetic energy per kg of Ar atoms,  $39.9 \text{ g mol}^{-1}$ ) at 300 K.

kinetic energy of 1.00 mole of Ar =  $\frac{1}{2} M \langle v^2 \rangle$  ← argon molar mass

$$= \frac{1}{2} M \frac{3RT}{M} = \frac{3}{2} RT$$

$$= \frac{3}{2} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) 300 \text{ K}$$

$$= 3740 \text{ J mol}^{-1}$$

$$\text{kinetic energy per kg of Ar} = \frac{3740 \text{ J mol}^{-1}}{0.0399 \text{ kg mol}^{-1}} = \boxed{93,800 \frac{\text{J}}{\text{kg}}}$$

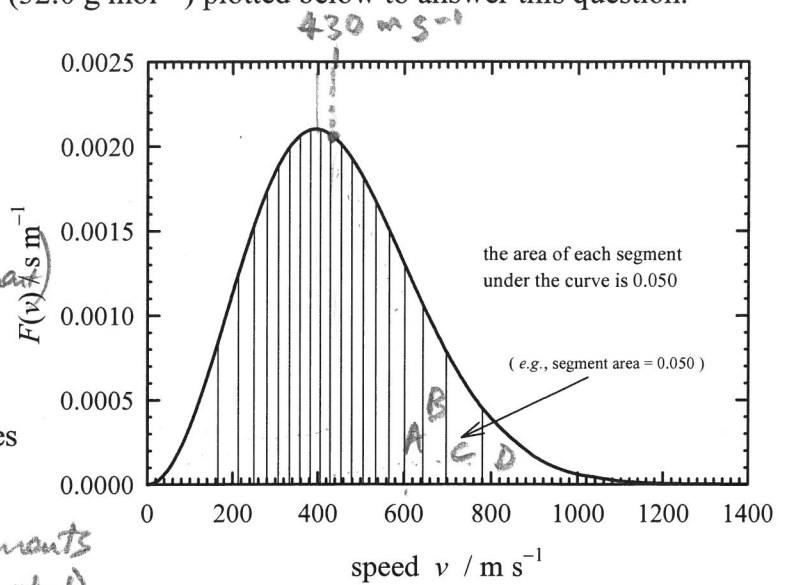
4. Use the speed distribution for O<sub>2</sub> molecules (32.0 g mol<sup>-1</sup>) plotted below to answer this question.

a) Show  $F(v)$  is normalized. Why is this important for probability calculations?

$$\int_0^{\infty} F(v) dv = \text{area under the curve}$$

$$= (20 \text{ segments})(0.050 \text{ per segment})$$

$$= 1$$



b) Give the probability of finding O<sub>2</sub> molecules with speeds greater than 600 m s<sup>-1</sup>.

$$\int_{600 \text{ m/s}}^{\infty} F(v) dv = \text{area of segments A+B+C+D}$$

$$= 4(0.050) = \boxed{0.20} \quad (20\% \text{ probability})$$

c) 50 % of molecules have speeds less than the **median speed**, and 50 % of molecules have speeds greater than the median speed. Give the median speed of the O<sub>2</sub> molecules.

$$\left. \begin{array}{l} 10 \text{ segments below } 430 \text{ m s}^{-1} \\ 10 \text{ segments above } 430 \text{ m s}^{-1} \end{array} \right\} \text{median speed} = \boxed{430 \text{ m s}^{-1}}$$

d) Give the most probable speed of the O<sub>2</sub> molecules.

$$\text{max } F(v) \text{ at } \boxed{400 \text{ m s}^{-1}} = v_{mp}$$

e) Calculate the temperature of the O<sub>2</sub> molecules.

$$v_{mp} = \sqrt{\frac{2RT}{M}} \quad T = \frac{M v_{mp}^2}{2R}$$

$$T = \frac{(0.0320 \text{ kg mol}^{-1})(400 \text{ m s}^{-1})^2}{2(8.314 \text{ J K}^{-1} \text{ mol}^{-1})}$$

$$\boxed{T = 308 \text{ K}}$$

5. a) A gas contains: 5 molecules moving at the speed  $200 \text{ m s}^{-1}$   
 30 molecules moving at the speed  $400 \text{ m s}^{-1}$   
 15 molecules moving at the speed  $600 \text{ m s}^{-1}$

Calculate: i) the average speed  $\langle v \rangle$

$$\langle v \rangle = \frac{5(200 \text{ m s}^{-1}) + 30(400 \text{ m s}^{-1}) + 15(600 \text{ m s}^{-1})}{5 + 30 + 15} = \boxed{440 \text{ m s}^{-1}}$$

ii) the most probable speed  $v_{\text{mp}}$

$$\boxed{400 \text{ m s}^{-1}}$$

iii) the root-mean-squared speed  $v_{\text{rms}} = \langle v^2 \rangle^{1/2}$

$$\begin{aligned} \sqrt{\langle v^2 \rangle} &= \sqrt{\frac{5(200 \text{ m s}^{-1})^2 + 30(400 \text{ m s}^{-1})^2 + 15(600 \text{ m s}^{-1})^2}{5 + 30 + 15}} \\ &= \sqrt{208,000 \text{ m}^2 \text{ s}^{-2}} = \boxed{456 \text{ m s}^{-1}} \end{aligned}$$

- b) A substance (molar mass  $200 \text{ g mol}^{-1}$ ) has a very low vapor pressure,  $p = 10^{-5} \text{ Pa}$  at  $300 \text{ K}$ .

i) Why is it almost impossible to directly measure this pressure with a pressure gauge?

- very small ( $\approx 0$ ) pressure (read as zero on most gauges)
- trace gas impurities (e.g. air, pump oil) would give large errors

ii) Calculate the mass of the substance that will effuse through a  $0.100 \text{ cm}$  diameter hole in a Knudsen cell in 48 hours at  $300 \text{ K}$ . Can the vapor pressure of the substance be reliably measured by the effusion technique? Comment briefly.

$$\text{wall collision rate} = Z_c = \frac{p}{\sqrt{2\pi m k T}} = \frac{p N_{\text{Av}}}{\sqrt{2\pi N_{\text{Av}}^2 m N_{\text{Av}} k T}}$$

$$Z_c = \frac{p N_{\text{Av}}}{\sqrt{2\pi M R T}} = \frac{10^{-5} (6.022 \times 10^{23})}{\sqrt{2\pi (0.200)(8.314) 300}} = 1.08 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1}$$

$$\text{leak rate through hole of radius } 0.05 \text{ cm} = Z_c A = Z_c [\pi r^2]$$

$$\begin{aligned} &= 1.08 \times 10^{17} \frac{\text{molecules}}{\text{m}^2 \text{ s}} [\pi (0.0005 \text{ m})^2] = 8.45 \times 10^{10} \frac{\text{molecules}}{\text{s}} \\ &= \frac{8.45 \times 10^{10} \text{ s}^{-1}}{N_{\text{Avogadro}}} = 1.40 \times 10^{-13} \frac{\text{mol}}{\text{s}} = 2.80 \times 10^{-11} \frac{\text{g}}{\text{s}} \end{aligned}$$

$$\text{In 48 h} = 172800 \text{ s}; \quad \text{mass loss} = (2.80 \times 10^{-11}) (172800) \\ (\text{Small, but barely measurable!}) = \boxed{4.8 \times 10^{-6} \text{ g}}$$