Chemistry 232 **Test 2** (24 March 2017) **Name:** ____________

- 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!*

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1. The high-temperature battery no H_2O here! molten LiCl!

$$Pt(s)\,|\,Li(l)\,|\,LiF(l)\,|\,F_2(g, 1\text{ bar})\,|\,Pt(s) \qquad T = 900\text{ K}$$

is technically attractive because of its high voltage and low weight.

a) Write:

i) the anode reaction (oxidation) $2Li(\ell) \rightarrow 2Li^+(\ell) + 2e^-$

ii) the cathode reaction (reduction) $2e^- + F_2(g) \rightarrow 2F^-(\ell)$

iii) the overall cell reaction $2Li(\ell) + 2F_2(g) \rightarrow 2Li^+(\ell) + 2F^-(\ell)$

iv) the Nernst equation for the cell voltage E

pure liquids

$a_{LiCl(\ell)} = 1$

$a_{Li(\ell)} = 1$

$a_{F_2(g)} = P_{F_2}$

$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{LiF(\ell)}}{a_{Li(\ell)}\, a^2_{F_2(g)}}$$

$$E = E^\circ - \frac{RT}{2F} \ln \frac{1}{a_{F_2(g)}} \quad (= E^\circ \text{ if } P_{F_2} = 1\text{ bar})$$

$$\boxed{E = E^\circ}$$

b) Calculate the cell voltage at 900 K. *Data*: $\Delta G_{fm}^\circ(\text{LiF}, l, 900\text{ K}) = -336.14\text{ kJ mol}^{-1}$

$$\Delta G^\circ = 2\Delta G^\circ_{fm}(LiF, \ell) - 2\Delta G^\circ_{fm}(Li, \ell) - \Delta G^\circ_{fm}(F_2, g)$$

$$= -nFE^\circ = 2(-336.14\text{ kJ mol}^{-1}) - 0 - 0 = -672.28\text{ kJ/mol}$$

(reversible cell, no salt bridge, so $\Delta G^\circ = nFE^\circ = w_e$)

$$E^\circ = \frac{-\Delta G^\circ}{2F} = \frac{-2(-336140\text{ J mol}^{-1})}{2(96485\text{ C mol}^{-1})} = \boxed{3.484\text{ V}}$$

c) Describe how the operation of the battery could be modified to manufacture lithium and fluorine (useful chemicals not found in nature) from the salt lithium fluoride.

Apply a voltage $< -E^\circ$ to the cell

(left electrode > 3.484 V positive relative to the right electrode)

to run an electrolysis cell reduce $Li^+(\ell)$ to $Li(\ell)$

oxidize $2F^-(\ell)$ to $F_2(g)$

2. a) In the "hydrogen economy" proposed for the future, electricity will be generated by using fuel cells for the oxidization of hydrogen:

$$H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow H_2O(l)$$

i) Calculate the maximum electric work that can be obtained from oxidation of one mole of H_2 at 25 °C and 1 bar in a fuel cell. *Data*: $\Delta G_{fm}°(H_2O, l) = -285.83 \text{ kJ mol}^{-1}$

maximum electric work for a reversible cell with

$$\Delta G = w_e$$

$$\boxed{w_e = -285.83 \text{ kJ mol}^{-1}}$$

$+285.83 \text{ kJ mol}^{-1}$ electrical work done <u>on</u> surroundings

ii) Oxidizing hydrogen in a fuel cell can provide significantly more electrical work than burning hydrogen to generate electricity using a heat engine. Explain.

no Carnot limitation $\left(w \propto 1 - \frac{T_C}{T_H} \right)$

"all" of w_e is available

iii) Briefly describe how a fuel cell differs from a battery.

reactants continuously pumped into anode and cathode compartments (e.g. H_2 to anode, O_2 to cathode) and products continuosly pumped out

b) Suppose you are asked to measure trace amounts of aqueous I^- ions at concentrations far too low ($< 10^{-9}$ mol kg^{-1}) to be determined by titration methods. It looks hopeless.

But then you remember the wonders of electrochemistry and construct the cell:

$$\text{Ag(s)} \overset{Ⓛ}{|} \text{AgI(s)} \mid \text{NaI(aq, 0.010 mol kg}^{-1}) \,||\, \text{solution X} \overset{Ⓡ}{|} \text{AgI(s)} \mid \text{Ag(s)}$$

The cell voltage measured at 25 °C is $E = 0.447$ V. Calculate the molality of I^- ions in solution X.

$$Ⓛ \quad Ag(s) + I^-(0.010 \tfrac{mol}{kg}) \rightarrow AgI(s) + e^-$$

$$Ⓡ \quad e^- + AgI(s) \rightarrow Ag(s) + I^-(m_X?)$$

overall $\quad I^-(aq, 0.010 \tfrac{mol}{kg}) \rightarrow I^-(aq, m_X)$

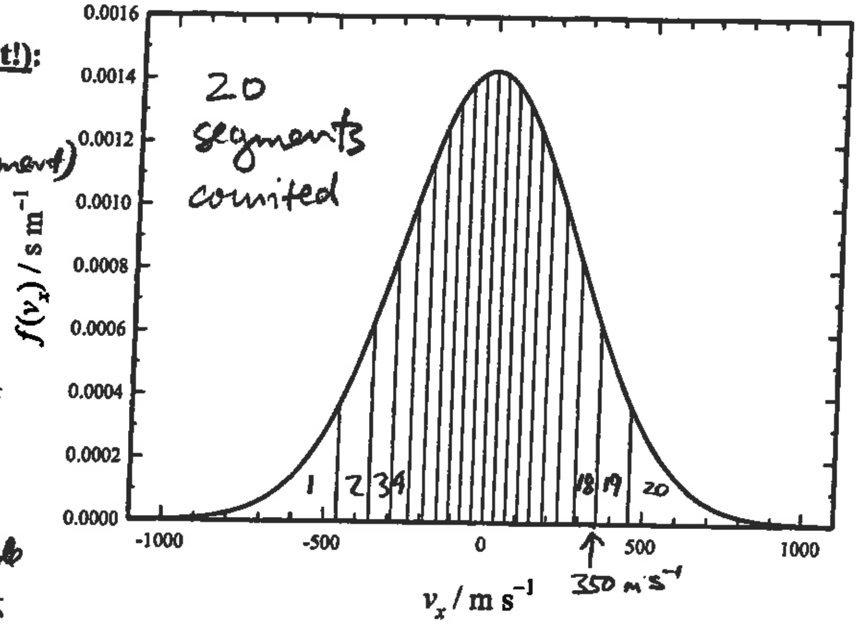
$$E = E° - \frac{RT}{F} \ln\left(\frac{m_X}{0.010 \text{ mol kg}^{-1}}\right) \qquad \frac{m_X}{0.010 \text{ mol kg}^{-1}} = e^{-EF/RT}$$

$$m_X = \left(0.010 \tfrac{mol}{kg}\right) e^{-0.447(96485)/(8.314)298.15}$$

$$= \left(0.010 \tfrac{mol}{kg}\right) e^{-17.4}$$

$$\boxed{m_X = 2.78 \times 10^{-10} \text{ mol kg}^{-1}}$$

3. a) The diagram below gives the velocity distribution $f(v_x)$ of argon atoms. The area of each segment under the curve is 0.050.



<u>Using the graph (not an equation sheet!)</u>:

i) show that $f(v_x)$ in normalized

(20 segment) X (0.050 per segment)

= 1 = area under the $f(v_x)$ curve

ii) give the most probable value of v_x

maximum $f(v_x)$ at $\boxed{v_x = 0}$ = most probable value of v_x

iii) estimate the fraction of atoms with $v_x < 0$ m s^{-1}

segments 1 + 2 + 3 + ... + 10

(10 segments) X (0.050) = 0.50 = $\boxed{\frac{1}{2}}$

iv) estimate the fraction of atoms with $v_x > 350$ m s^{-1}

$\approx$ (0.1)(segment 18) + segment 19 + segment 20

$\approx$ 0.005 + 0.050 + 0.050

= 0.105

b) The kinetic energy of an atom of mass m moving at speed v is $mv^2/2$. Which of the following expressions for the <u>average</u> kinetic energy of the atom is correct?

i) ~~$m\langle v\rangle^2/2$~~ **ii)** [✓ $m\langle v^2\rangle/2$]

<u>Justify your answer</u>.

$$\text{average kinetic energy} = \left\langle \frac{1}{2} m v^2 \right\rangle$$

$$= \frac{1}{2} m \langle v^2 \rangle$$

(m, $\frac{1}{2}$ constants)

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

$$\left(\langle v \rangle^2 = \frac{8RT}{\pi M} \neq \langle v^2 \rangle \right)$$

4. a) A tank is filled with helium ($M = 4.00$ g mole^{-1}) at 100.0 Pa and 350 K.

i) Calculate the number of helium atoms colliding with the wall of the tank per second per square centimeter wall area.

$$Z_c = \frac{P}{\sqrt{2\pi m k T}} = \frac{N_A P}{\sqrt{2\pi N_A m N_A k T}} = \frac{N_A P}{\sqrt{2\pi M R T}}$$

$$= \frac{6.0221\times10^{23}(100.0)}{\sqrt{2\pi(0.00400)(8.314)350}} = 7.04\times10^{24}\ m^{-2}\ s^{-1}$$

$$= (7.04\times10^{24}\ m^{-2}\ s^{-1})(10^{-2}\ m\ cm^{-1})^2 = 7.04\times10^{20}\ cm^{-2}\ s^{-1}$$

ii) Helium leaks out of the tank through a hole into a vacuum chamber at a rate 0.37 grams per hour. Calculate the diameter of the hole.

leak rate $$\frac{dN}{dt} = \frac{0.37\ g}{3600\ s}\ \frac{1}{4.00\ g\ mol^{-1}}\ (6.0221\times10^{23}\ mol^{-1})$$

$$\frac{dN}{dt} = 1.547\times10^{19}\ (\text{atoms})\ s^{-1} = Z_c A$$

hole area $$A = \frac{dN/dt}{Z_c} = \frac{1.547\times10^{19}\ s^{-1}}{7.04\times10^{24}\ m^{-2}\ s^{-1}} = 2.20\times10^{-6}\ m^2$$

$A = \pi(d/2)^2$ hole diameter $d = \sqrt{4A/\pi} = \boxed{0.00167\ m}$ (1.67 mm)

iii) Calculate the number of times per second a helium atom collides with another helium atom inside the tank. *Data*: He collision area = 0.21 × 10^{-18} m^2

$$Z_{11} = \frac{P_1}{kT}\sqrt{2}\,\sigma\sqrt{\frac{8kT}{\pi m_1}} = \frac{P_1}{kT}\sqrt{2}\,\sigma\sqrt{\frac{8RT}{\pi M_1}}$$

$$= \frac{100.0}{1.381\times10^{-23}(350)}\sqrt{2}\sqrt{\frac{8(8.314)350}{\pi(0.00400)}}$$

$$\boxed{Z_{11} = 8.36\times10^{6}\ \text{collisions}\ s^{-1}}$$

b) Why are rates of molecular collisions important for chemistry?

Necessary for chemical reactions (e.g. A + B → products)
(can be rate determining)
Also important for deciding diffusion and heat conduction rates

5. a) A molecule initially located at position $x = 0$ at time $t = 0$ is allowed to diffuse for time t

i) Why is it impossible to predict the position x of the diffusing molecule?

random steps left or right, can't be predicted (unknown trajectory)

ii) Solving Fick's equation shows that the probability distribution of the molecule is

$$P(x) = \sqrt{\frac{1}{4\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right)$$

By comparing the expression for $P(x)$ with the Gaussian distribution of random errors ε

$$f(\varepsilon) = \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right)$$

of variance σ^2, show that the variance in the position of the diffusing molecule is $2Dt$.

$$P(x) = \frac{1}{\sqrt{4\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right) = \frac{1}{\sqrt{2\pi(2Dt)}}\exp\left(-\frac{x^2}{2(2Dt)}\right)$$

$$= \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left(-\frac{x^2}{2\sigma^2}\right) = f(x)$$

iii) Suggest why the statistics of random errors and diffusion are closely related.

left or right diffusion steps are random

iv) The diffusion coefficient of copper atoms in solid copper is $1.3 \times 10^{-30}\ \mathrm{m^2\ s^{-1}}$ at 25 °C. Calculate the mean displacement and the root-mean-square displacement of a copper atom after diffusion for 4.5 billion years (approximate age of the earth) at 25 °C.

$\boxed{\langle x\rangle = 0}$ (left or right diffusion steps equally probable)

$\langle x^2\rangle = 2Dt$

$$t = (4.5\times10^{9}\,\mathrm{yr})\left(365\,\frac{\mathrm{d}}{\mathrm{yr}}\right)\left(24\,\frac{\mathrm{h}}{\mathrm{d}}\right)\left(3600\,\frac{\mathrm{s}}{\mathrm{h}}\right) = 1.42\times10^{17}\,\mathrm{s}$$

rms displacement $= \sqrt{\langle x^2\rangle} = \sqrt{2Dt} = \sqrt{2(1.3\times10^{-30}\,\mathrm{m^2\,s^{-1}})(1.42\times10^{17}\,\mathrm{s})}$

$= \sqrt{3.69\times10^{-13}\,\mathrm{m^2}} = \boxed{6.07\times10^{-7}\,\mathrm{m}}$ SLOW!

b) Hydrogen and helium are used in high-performance heat exchangers because their thermal conductivities are large relative to other gases. Give two reasons for the relatively large thermal conductivities of H_2 and He.

$\kappa \propto \frac{1}{\sqrt{m}}\,\frac{1}{\sigma}$ (from eq. sheet) small m, small σ

He, H_2 are light and small $\Rightarrow$ large $\frac{1}{\sqrt{m}}$ and large $\frac{1}{\sigma}$

$\Rightarrow$ large κ