Chemistry 232 **Test 2** (23 March 2018) **Name:**

- please answer all **5 questions** in the spaces provided
- this is a **2-hour test**
- 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. This question refers to the zinc-bromine battery:

$$Zn(s)\,|\,ZnBr_2(aq,\ 2.50\ mol\ kg^{-1})\,|\,Br_2(\mathbf{g},\ 1\ bar)\,|\,Pt(s)$$

a) Write: i) the anode reaction (oxidation)

$$\boxed{Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-}$$

ii) the cathode reaction (reduction)

$$\boxed{2e^- + Br_2(g) \longrightarrow 2Br^-(aq)}$$

two moles of electrons: $n = 2$

iii) the overall cell reaction

$$\boxed{Zn(s) + Br_2(g) \longrightarrow Zn^{2+}(aq) + 2Br^-(aq)}$$

or

$$\left(Zn\,s + Br_2(g) \rightarrow ZnBr_2(aq) \right)$$

b) Write the Nernst equation for the battery and calculate the battery voltage (E) at 25 °C.
Data: $E^o = 1.672$ V and $\gamma_\pm = 0.762$.

$a_{Zn(s)} = 1 \qquad a_{Br_2(g)} = 1$ (a pure solid and a pure gas at standard pressure)

$$a_{ZnBr_2(aq)} = a_{Zn^{2+}(aq)}\, a^2_{Br^-(aq)} \qquad (\text{use } m = m_{ZnBr_2(aq)})$$

$$= (\gamma_+ m_{Zn^{2+}})(\gamma_- m_{Br^-})^2 = (\gamma_+ m)(\gamma_- 2m)^2 = \gamma_\pm^3 4 m^3$$

Nernst equation:

$$E = E^o - \frac{RT}{nF}\ln Q = E^o - \frac{RT}{2F}\ln\left(\frac{a_{ZnBr_2(aq)}}{a_{Zn(s)}\, a_{Br_2(g)}}\right)$$

$$= E^o - \frac{RT}{2F}\ln\left(\frac{4\gamma_\pm^3 m^3}{(1)\ (1)}\right)$$

$$= 1.672 - \frac{8.314(298.15)}{2(96485)}\ln\left[4(0.762)^3 2.5^3\right] = 1.672 - 0.0426\ \text{V}$$

$$\boxed{E = 1.629\ \text{V}}$$

2. a) i) Production of lithium has more than tripled since 2000. What is driving this demand?

$\boxed{\text{lithium ion batteries}}$ for phones, computers, cameras, cars...

ii) Electrolysis of aqueous LiCl solutions is unsuitable for lithium production. Why?

$\boxed{\text{lithium reduces water}}$

$$Li(s) + H_2O(\ell) \rightarrow Li^+(aq) + OH^-(aq) + \tfrac{1}{2}H_2(g)$$

iii) Devise a cell to produce lithium by the electrolysis of molten LiCl. Give the cell **reaction.**

anode: $2Cl^-(\ell) \rightarrow Cl_2(g) + 2e^-$

cathode: $2e^- + Li^+(\ell) \rightarrow 2Li(\ell)$

$$\boxed{2LiCl(\ell) \rightarrow 2Li(\ell) + Cl_2(g)}$$

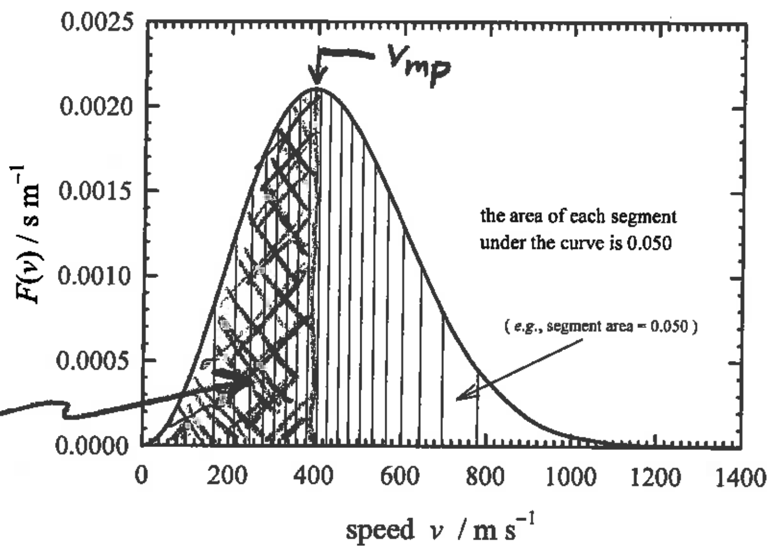
$$\begin{matrix}\text{steel(s)} \\ \text{or} \\ \text{Pt(s)}\end{matrix} \Big| \; Cl_2(g) \; \Big| \; LiCl(\ell) \; \Big| \; Li(\ell) \; \Big| \begin{matrix}\text{steel(s)} \\ \text{or} \\ \text{Pt(s)}\end{matrix}$$

b) The distribution of molecular speeds in a sample of O_2 is described by the function plotted below.

i) Give the most probable speed of the O_2 molecules.

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

$$\left(\int_0^{v_{mp}} F(v)\,dv = 0.425 \right)$$



ii) Estimate the percentage of O_2 molecules with speeds less than the most probable speed.

about $8\frac{1}{2}$ segments $\Longrightarrow$ $8.5(0.050)$ (= area $< v_{mp}$)

probability $= 8.5(0.050) = 0.425$ $\boxed{42.5\%}$

iii) Calculate the temperature of O_2 molecules. Use 32.00 g mol^{-1} for the molecular weight.

$$v_{mp} = \sqrt{\frac{2RT}{M}} \qquad v_{mp}^2 = \frac{2RT}{M}$$

$$T = \frac{M}{2R} v_{mp}^2 = \frac{0.03200 \text{ kg mol}^{-1}}{2(8.314 \text{ J K}^{-1}\text{mol}^{-1})}(400 \text{ m s}^{-1})^2 = \boxed{308 \text{ K}}$$

3. This question refers to the velocity distribution function $f(v_x) = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mv_x^2}{2kT}\right)$.

a) The Boltzmann distribution, a fundamental law of nature, states that the probability of finding molecules with energy E_i is proportional to $\exp(-E_i/kT)$. Explain why the velocity distribution function $f(v_x)$ illustrates Boltzmann's law.

$$f(v_x) \propto e^{-\left(\frac{1}{2}mv_x^2\right)/kT} = e^{-(\text{kinetic energy})/kT}$$

b) Why is it important that distribution functions such as $f(v_x)$ be normalized?

For probability calculations and for calculating quantities such as $\langle v_x \rangle$, $\langle v_x^2 \rangle$, $\langle v_x > 0 \rangle$, ...

c) Use $f(v_x)$ and the definite integral $\int_{-\infty}^{+\infty} u^2 e^{-au^2} du = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$ to prove $\langle v_x^2 \rangle = kT/m$.

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 f(v_x)\, dv_x = \int_{-\infty}^{\infty} v_x^2 \sqrt{\frac{m}{2\pi kT}}\, e^{-mv_x^2/2kT}\, dv_x$$

$$= \sqrt{\frac{m}{2\pi kT}} \int_{-\infty}^{\infty} v_x^2 e^{-av_x^2}\, dv_x \qquad \left(\text{use } a = m/2kT\right)$$

$$= \sqrt{\frac{m}{2\pi kT}}\, \frac{1}{2a}\sqrt{\frac{\pi}{a}} = \cancel{\sqrt{\frac{m}{2\pi kT}}}\, \frac{1}{\frac{2m}{2kT}} \cancel{\sqrt{\frac{\pi}{\frac{m}{2kT}}}}$$

$$= \frac{kT}{m} \quad \left(= \langle v_y^2 \rangle = \langle v_z^2 \rangle \right)$$

d) Use the result $\langle v_x^2 \rangle = kT/m$ to show that the average kinetic energy of a molecule is $3kT/2$.

average kinetic energy $= \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m \langle v_x^2 + v_y^2 + v_z^2 \rangle$

(velocities in 3 directions x, y, z)

$$= \frac{1}{2} m \left[\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle\right] = \frac{1}{2} m \left(\frac{3kT}{m}\right)$$

$$= \frac{3}{2} kT$$

4. a) The pressure of an ideal gas is doubled at constant temperature. What effect does this have on:

i) the number of collisions per second for one gas molecule

$\boxed{\text{doubled}}$ $\quad \left(z_{11} = \frac{p_1}{kT}\sqrt{2}\,\sigma\sqrt{\frac{8kT}{\pi m_1}} \right)$

ii) the total number of molecular collisions per second per cubic meter

$\boxed{\text{quadrupled}}$ (4x) $\quad \left(Z_{11} = \left(\frac{p_1}{kT}\right)^2 \frac{\sigma}{\sqrt{2}}\sqrt{\frac{8kT}{\pi m_1}} \right)$

iii) the mean free path

$\boxed{\text{halved}}$ $\quad \left(\lambda = \frac{1}{(N/V)\sqrt{2}\,\sigma} = \frac{1}{(p/kT)\sqrt{2}\,\sigma} \right)$

iv) the viscosity

$\boxed{\text{no effect}}$ $\quad \left(\eta = \frac{5\pi}{16}\sqrt{\frac{kT}{\pi m}}\,\frac{1}{\sigma}\,m \right)$

b) The thermal conductivities of fiberglass and foam insulation are 0.043 J m^{-1} K^{-1} s^{-1} and 0.112 J m^{-1} K^{-1} s^{-1}, respectively. Which provides better insulation: a 5-cm-thick layer of fiberglass or a 12-cm-thick layer of foam? Justify your answer.

$$\frac{\text{fiberglass heat flux}}{\text{foam heat flux}} = \frac{-\kappa_{f.g.}\frac{\Delta T}{\Delta x_{f.g.}}}{-\kappa_{foam}\frac{\Delta T}{\Delta x_{foam}}} = \frac{\kappa_{f.g}}{\kappa_{foam}}\frac{\Delta x_{foam}}{\Delta x_{f.g}}$$

$$= \frac{0.043}{0.112}\,\frac{12}{5} = 0.92$$

$\boxed{\text{fiberglass better (lower heat flux)}}$

c) A siphon tube (300 cm long, 0.80 cm inner diameter) is used to ~~steal~~ drain gasoline from a tank. The inlet and outlet pressures are 1.011 bar and 1.000 bar, respectively. How long will it take to drain 45 L of gasoline from the tank? Use 0.00078 Pa s for the gasoline viscosity.

Hint: $\frac{dV}{dt} = -\frac{\pi R_0^4}{8\eta}\frac{dp}{dx} = -\frac{\pi R_0^4}{8\eta}\frac{P_2 - P_1}{L}$

$R_0 = 0.0040$ m $\quad L = 3.00$ m $\quad P_2 - P_1 = -0.011$ bar $= -1100$ Pa

$$\frac{dV}{dt} = -\underbrace{\frac{\pi(0.0040)^4}{8(0.00078)}\frac{(-1100)}{3.00}}_{\text{all SI units}} = 0.0000472\ \frac{m^3}{s}$$

$$= \left(0.0000472\ \frac{m^3}{s}\right)\left(1000\ \frac{L}{m^3}\right) = 0.0472\ \frac{L}{s}$$

$$\text{time to drain 45L} = \frac{45\ L}{0.0472\ \frac{L}{s}} = \boxed{950\ s}\quad (16\ \text{minutes})$$

5. This question refers to a clay particle suspended in water. *Data*:

($r = 0.275 \times 10^{-6}$ m)

particle diameter = 0.55×10^{-6} m
particle density = 1750 kg m^{-3}
$g = 9.80$ m s^{-2}

water viscosity = 0.000890 Pa s
water density = 997 kg m^{-3}
$T = 290$ K

a) **i)** Calculate the sedimentation speed (terminal speed) of the particle.

Hint: $$v_{\text{terminal}} = -\frac{1}{6\pi\eta r}\left[\left(\frac{4}{3}\pi r^3\right)\left(\rho_{\text{particle}} - \rho_{\text{water}}\right)\right]g$$

(all SI units)

$$\text{terminal speed} = -\frac{1}{6\pi(0.000890)(0.275\times10^{-6})}\left[\frac{4\pi}{3}(0.275\times10^{-6})^3(1750-997)\right]9.80$$

$$= \boxed{-1.39\times10^{-7}\ \text{m s}^{-1}}$$

ii) Calculate the distance the particle sinks in one day. (1 day = 24(3600) s = 86,400 s)

$$\text{distance} = (\text{speed})(\text{time})$$
$$= (1.39\times10^{-7}\ \text{m s}^{-1})\ 86400\ \text{s} = \boxed{0.0120\ \text{m}}$$

(12 mm)

b) **i)** Calculate the diffusion coefficient of the particle.

Hint: $$D = \frac{kT}{6\pi r\eta}$$

$$= \frac{1.381\times10^{-23}(290)}{6\pi(0.275\times10^{-6})0.000890}$$

$$= \boxed{8.68\times10^{-13}\ \text{m}^2\ \text{s}^{-1}}$$

ii) Calculate the rms displacement of the particle ($\sqrt{<x^2>}$) after diffusion for one day.

$$\sqrt{<x^2>} = \sqrt{2Dt} = \sqrt{2(8.68\times10^{-13}\ \text{m s}^{-2})(86400\ \text{s})}$$

$$= \boxed{0.000387\ \text{m}}$$

(0.39 mm)