

Spring 2018

**Chemistry 2000 Midterm #2A**

\_\_\_\_/54 marks

- 1) Please read over the test carefully before beginning. You should have 7 pages of questions, a blank “overflow” page and a double-sided data sheet with periodic table.
- 2) **DO NOT WRITE ON THE QR CODE!!!** Work on pages without a QR code will not be graded.
- 3) If your work is not legible, it will be given a mark of zero. Show your work for all calculations.
- 4) Marks will be deducted for incorrect information added to an otherwise correct answer.
- 5) You may use a calculator but only for calculation. No text-capable calculators are allowed.
- 6) You have 90 minutes to complete this test.

**Confidentiality Agreement:**

I agree not to discuss (or in any other way divulge) the contents of this exam until after 5:00 pm Mountain Time on Friday, March 23<sup>rd</sup>, 2018. I understand that breaking this agreement would constitute academic misconduct. The minimum punishment would be a mark of 0/54 on this exam and removal of the “overwrite midterm mark with final exam mark” option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: \_\_\_\_\_

Date: \_\_\_\_\_

Course: CHEM 2000 (General Chemistry II)

Semester: Spring 2018

The University of Lethbridge

**Question Breakdown**

Q1	Q2	Q3	Q4	Q5	Q6				Total
/ 7	/ 9	/ 10	/ 7	/ 7	/ 14				/ 54

1. Methanol melts at  $-97.9\text{ }^{\circ}\text{C}$  with an enthalpy of fusion of  $3117\text{ J/mol}$ . **[7 marks]**

(a) Calculate the total entropy change for  $1.45\text{ mol}$  of methanol **freezing** at its melting point.

[5 marks]

For melting of methanol:



Therefore, for freezing of methanol:



**Step 1: Convert temperature into Kelvin**

$$T = -97.9\text{ }^{\circ}\text{C} = 175.25\text{ K} = 175.3\text{ K}$$

1 decimal place so 4 sig. fig.

**Step 2: Calculate entropy change for freezing of 1 mol methanol**

$$\Delta S = \frac{q_{rev}}{T} \text{ and, at constant pressure, } q_{rev} = \Delta H \text{ therefore } \Delta_r S = \frac{\Delta_r H}{T}$$

$$\Delta_r S = \frac{-3117 \frac{\text{J}}{\text{mol}}}{175.3\text{ K}} = -17.79 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

4 sig. fig.

**Step 3: Calculate entropy change for freezing of 1.45 mol methanol**

$$\Delta_r S = \left(-17.79 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) (1.45\text{ mol}) = -25.8 \frac{\text{J}}{\text{K}}$$

3 sig. fig.

(b) The entropy change calculated in part (a) is negative. (*You did get a negative entropy change, did you not?*) Because of this, some people might conclude that you can never freeze methanol – that it would go against the second law of thermodynamics. Why are they wrong? [2 marks]  
*No credit will be given for answers that amount to “because they are”. Explain why this is a misinterpretation of the second law of thermodynamics and what the correct interpretation is.*

The entropy calculated in part (a) is the entropy change for the system.

The second law of thermodynamics states that the entropy of the universe must increase with every reaction.

It is possible to increase the entropy of the universe despite decreasing the entropy of the system – as long as the entropy of the surroundings is increased by a large enough amount.

2. In catalytic reforming, low-octane hydrocarbons are converted to higher-octane hydrocarbons suitable for use as fuels. One reaction that occurs during catalytic reforming is the conversion of heptane ( $C_7H_{16}$ ) to toluene ( $C_6H_5CH_3$ ) and hydrogen. During the reforming process, all reactants and products are in the gas phase.

Is this reaction thermodynamically allowed at 25 °C if the pressures of the reactants and products are as follows: [9 marks]

- Heptane: 5.3 bar
- Toluene: 1.2 bar
- $H_2$ : 3.0 bar

Don't forget to start with a balanced reaction!

*There are two equally valid approaches to this question. Both require calculation of the standard free energy change for the reaction and the reaction quotient for the actual reaction conditions.*

*Approach A is to calculate the free energy change for the reaction under these conditions using  $\Delta_r G = \Delta_r G^\circ + RT \ln Q$ . If  $\Delta_r G < 0$ , the reaction is thermodynamically allowed.*

*Approach B is to calculate the equilibrium constant for the reaction from the standard free energy change. If  $Q < K$ , the reaction is thermodynamically allowed.*

**Step 1: Write a balanced chemical equation for the reaction**



**Step 2: Convert temperature to Kelvin (if necessary)**

$$T = 25 \text{ }^\circ\text{C} = 298.15 \text{ K}$$

**Step 3: Calculate the standard free energy change for the reaction**

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = [\Delta_f G^\circ(C_6H_5CH_{3(g)}) + 4 \Delta_f G^\circ(H_{2(g)})] - \Delta_f G^\circ(C_7H_{16(g)})$$

$$\Delta_r G^\circ = \left[ \left( 122.3 \frac{\text{kJ}}{\text{mol}} \right) + 4 \left( 0 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left( 8.26 \frac{\text{kJ}}{\text{mol}} \right)$$

$$\Delta_r G^\circ = 114.04 \frac{\text{kJ}}{\text{mol}} = 114.0 \frac{\text{kJ}}{\text{mol}}$$

1 decimal place so 4 sig. fig.

**Step 4: Determine activities for all reactants and products**

$$a_{C_7H_{16(g)}} = \frac{5.3 \text{ bar}}{1 \text{ bar}} = 5.3$$

$$a_{C_6H_5CH_{3(g)}} = \frac{1.2 \text{ bar}}{1 \text{ bar}} = 1.2$$

$$a_{H_{2(g)}} = \frac{3.0 \text{ bar}}{1 \text{ bar}} = 3.0$$

**Step 5: Calculate reaction quotient**

$$Q = \frac{(a_{C_6H_5CH_{3(g)}})(a_{H_{2(g)}})^4}{(a_{C_7H_{16(g)}})} = \frac{(1.2)(3.0)^4}{(5.3)} = 18$$

2 sig. fig.

**Step 6A: Calculate free energy change for reaction under nonstandard conditions**

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

$$\Delta_r G = \left(114.0 \frac{\text{kJ}}{\text{mol}}\right) + \left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) (298.15 \text{ K}) \ln(18)$$

$$\Delta_r G = \left(114.0 \frac{\text{kJ}}{\text{mol}}\right) + \left(7.21 \frac{\text{kJ}}{\text{mol}}\right)$$

$$\Delta_r G = 121.3 \frac{\text{kJ}}{\text{mol}}$$

*The free energy change for the reaction under these conditions is positive therefore the reaction is not thermodynamically allowed under these conditions.*

**Step 6B: Calculate equilibrium constant from standard free energy change**

$$\Delta_r G^\circ = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^\circ}{RT}$$

$$\ln K = -\frac{\left(114.0 \frac{\text{kJ}}{\text{mol}}\right)}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) (298.15 \text{ K})} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\ln K = -46.00$$

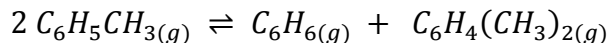
$$K = e^{-46.00}$$

$$K = 1.0 \times 10^{-20}$$

***compare to Q = 18***

*Q > K therefore the reaction is not thermodynamically allowed under these conditions.*

3. In the gas phase, toluene ( $C_6H_5CH_3$ ) can react with itself to make benzene ( $C_6H_6$ ) and xylenes ( $C_6H_4(CH_3)_2$ ). [10 marks]



At 25 °C, the equilibrium constant for this reaction is 0.16.

- (a) Calculate the standard free energy of formation for xylenes. [4 marks]

**Step 1: Calculate standard free energy change for reaction from equilibrium constant**

$$\Delta_r G^\circ = -RT \ln K$$

$$\Delta_r G^\circ = - \left( 8.314 \frac{J}{mol \cdot K} \right) \left( \frac{1 kJ}{1000 J} \right) (298.15 K) \ln(0.16)$$

$$\Delta_r G^\circ = 4.5 \frac{kJ}{mol}$$

**Step 2: Calculate standard free energy of formation for xylenes**

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = [\Delta_f G^\circ(C_6H_6(g)) + \Delta_f G^\circ(C_6H_4(CH_3)_2(g))] - 2 \Delta_f G^\circ(C_6H_5CH_3(g))$$

$$\Delta_f G^\circ(C_6H_4(CH_3)_2(g)) = \Delta_r G^\circ - \Delta_f G^\circ(C_6H_6(g)) + 2 \Delta_f G^\circ(C_6H_5CH_3(g))$$

$$\Delta_f G^\circ(C_6H_4(CH_3)_2(g)) = \left( 4.5 \frac{kJ}{mol} \right) - \left( 129.8 \frac{kJ}{mol} \right) + 2 \left( 122.3 \frac{kJ}{mol} \right)$$

$$\Delta_f G^\circ(C_6H_4(CH_3)_2(g)) = 119.3 \frac{kJ}{mol}$$

- (b) Calculate the equilibrium constant for this reaction at 1175 °C. [6 marks]

**Step 1: Match equilibrium constants to the corresponding temperature**

$$T_1 = 25 \text{ }^\circ\text{C} = 298.15 \text{ K}$$

$$T_2 = 1175 \text{ }^\circ\text{C} = 1448 \text{ K}$$

$$K_1 = 0.16$$

$$K_2 = ???$$

**Step 2: Calculate the standard enthalpy change for the reaction**

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta_r H^\circ = [\Delta_f H^\circ(C_6H_6(g)) + \Delta_f H^\circ(C_6H_4(CH_3)_2(g))] - 2 \Delta_f H^\circ(C_6H_5CH_3(g))$$

$$\Delta_r H^\circ = \left[ \left( 82.9 \frac{kJ}{mol} \right) + \left( 17.5 \frac{kJ}{mol} \right) \right] - 2 \left( 50.1 \frac{kJ}{mol} \right)$$

$$\Delta_r H^\circ = 0.2 \frac{kJ}{mol}$$

**Step 3: Crunch the numbers**

$$\ln \left( \frac{K_2}{K_1} \right) = \frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \left( \frac{K_2}{0.16} \right) = \left( \frac{\left( 0.2 \frac{kJ}{mol} \right) \left( \frac{1000 J}{1 kJ} \right)}{8.314 \frac{J}{mol \cdot K}} \right) \left( \frac{1}{298.15 \text{ K}} - \frac{1}{1448 \text{ K}} \right)$$

$$\ln \left( \frac{K_2}{0.16} \right) = 0.06$$

$$\frac{K_2}{0.16} = e^{0.06}$$

$$\frac{K_2}{0.16} = 1.07$$

$$K_2 = (0.16)(1.07) = 0.17$$

4. The following data were obtained for ammonia.

[7 marks]

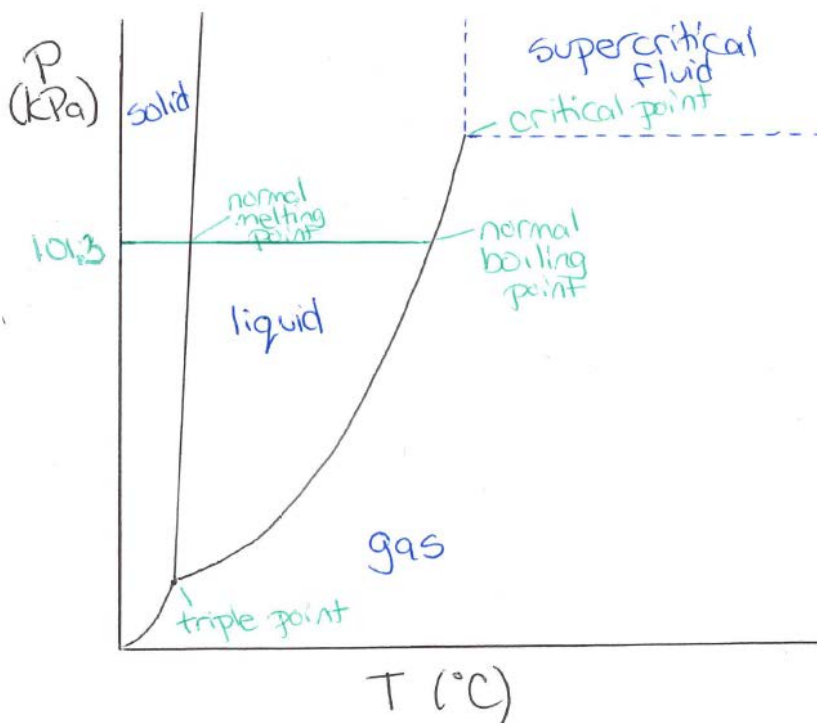
	temperature (°C)	pressure (kPa)
triple point	-77.75	6.060
critical point	132.41	11,357
normal boiling point	-33.33	101.3
normal melting point	-77.65	101.3

(a) Sketch a phase diagram for ammonia. On your diagram, you must label:

[5 marks]

- both axes
- regions corresponding to the four states of matter discussed in class

Your sketch does not need to be to-scale; however, it must be neat and all points used to make it must be clearly labeled. Relative values must be preserved. In other words, it must be clear which pressures/temperatures are larger/smaller/approximately the same.

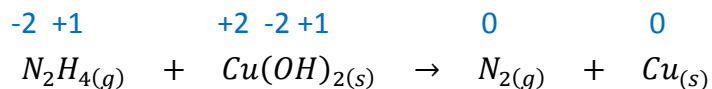


(b) Which is denser, liquid or solid ammonia? Explain how you determined this based on the data in this question. [2 marks]

Solid ammonia is denser.

The normal melting point is a (very slightly) higher temperature than the triple point. This means that the solid/liquid equilibrium line has a positive slope (melting point increases as pressure increases). As such, applying a pressure (which increases a substance's density) at a constant temperature can convert liquid to solid but cannot convert solid to liquid.

5. Consider the following unbalanced redox reaction performed in aqueous base: **[7 marks]**



(a) Assign oxidation numbers to all atoms in this reaction. Write them above each atom in the equation. **[3 marks]**

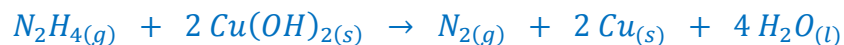
(b) Write a balanced equation for the oxidation half-reaction. **[1 mark]**



(c) Write a balanced equation for the reduction half-reaction. **[1 mark]**



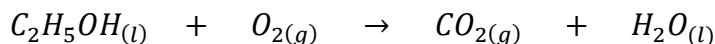
(d) Write a balanced equation for the overall reaction. **[1 mark]**



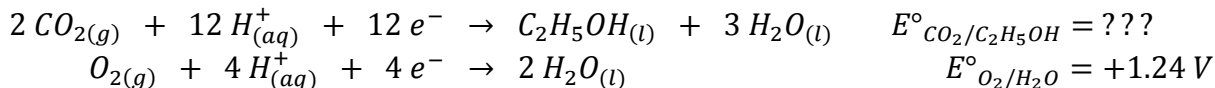
(e) What is the stoichiometric coefficient for the electrons ( $\nu_e$ )?  
(Some introductory texts refer to this as  $n$ .) **[1 mark]**

$$\nu_e = 4$$

6. Consider the following unbalanced redox reaction performed in aqueous acid: [14 marks]

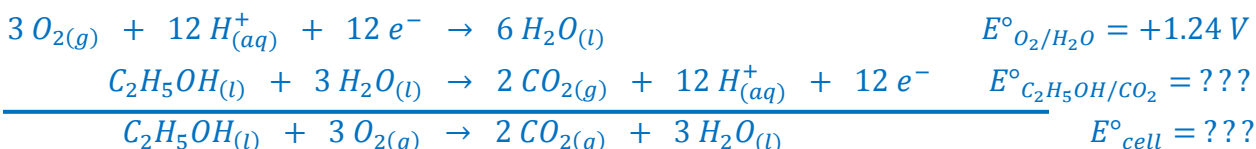


Equations for the two relevant reduction half-reactions are shown below:



- (a) Calculate  $E^\circ$  for this reaction. [6 marks]

**Step 1: Write a balanced chemical equation for the reaction (or phase change)**



**Step 2: Determine stoichiometric coefficient for electrons ( $\nu_e$ )**

$$\nu_e = 12$$

**Step 3: Calculate the standard free energy change for the reaction**

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = [2 \Delta_f G^\circ(CO_{2(g)}) + 3 \Delta_f G^\circ(H_2O_{(l)})] - [\Delta_f G^\circ(C_2H_5OH_{(l)}) + 3 \Delta_f G^\circ(O_{2(g)})]$$

$$\Delta_r G^\circ = \left[ 2 \left( -394.4 \frac{kJ}{mol} \right) + 3 \left( -237.19 \frac{kJ}{mol} \right) \right] - \left[ \left( -174.8 \frac{kJ}{mol} \right) + 3 \left( 0 \frac{kJ}{mol} \right) \right]$$

$$\Delta_r G^\circ = -1325.57 \frac{kJ}{mol} = -1325.6 \frac{kJ}{mol}$$

1 decimal place so 5 sig. fig.

**Step 4: Calculate standard potential from standard free energy change**

$$\Delta_r G^\circ = -\nu_e F E^\circ_{cell}$$

$$E^\circ_{cell} = -\frac{\Delta_r G^\circ}{\nu_e F}$$

$$E^\circ_{cell} = -\frac{\left( -1325.6 \frac{kJ}{mol} \right)}{(12) \left( 96485 \frac{C}{mol} \right)} \times \frac{1000 J}{1 kJ}$$

$$E^\circ_{cell} = +1.1449 \frac{J}{C} = +1.1449 V$$

5 sig. fig.

- (b) Calculate the standard reduction potential for the oxidation half-reaction. [2 marks]

$$E^\circ_{cell} = E^\circ_{O_2/H_2O} + E^\circ_{C_2H_5OH/CO_2}$$

$$E^\circ_{C_2H_5OH/CO_2} = E^\circ_{cell} - E^\circ_{O_2/H_2O}$$

$$E^\circ_{C_2H_5OH/CO_2} = (+1.1449 V) - (+1.24 V)$$

$$E^\circ_{C_2H_5OH/CO_2} = -0.10 V$$

2 decimal places so 2 sig. fig.

BUT the question is asking about  $E^\circ_{CO_2/C_2H_5OH}$  !

When reversing the direction of a half-reaction, switch the sign for the potential.

Therefore,

$$E^\circ_{CO_2/C_2H_5OH} = +0.10 V$$



6. *continued...*

(c) Calculate the cell potential for the combustion reaction operating with typical atmospheric pressures of oxygen and carbon dioxide at 25 °C: [6 marks]

- Oxygen: 0.19 bar
- Carbon dioxide:  $4.1 \times 10^{-4}$  bar

**Step 1: Convert temperature to Kelvin (if necessary)**

$$T = 25\text{ °C} = 298.15\text{ K}$$

**Step 2: Determine activities for all reactants and products**

$$a_{\text{C}_2\text{H}_5\text{OH}(\text{l})} = 1$$

$$a_{\text{O}_2(\text{g})} = \frac{0.19\text{ bar}}{1\text{ bar}} = 0.19$$

$$a_{\text{CO}_2(\text{g})} = \frac{4.1 \times 10^{-4}\text{ bar}}{1\text{ bar}} = 4.1 \times 10^{-4}$$

$$a_{\text{H}_2\text{O}(\text{l})} = 1$$

**Step 3: Calculate reaction quotient**

$$Q = \frac{(a_{\text{CO}_2(\text{g})})^2 (a_{\text{H}_2\text{O}(\text{l})})^3}{(a_{\text{C}_2\text{H}_5\text{OH}(\text{l})}) (a_{\text{O}_2(\text{g})})^3} = \frac{(4.1 \times 10^{-4})^2 (1)^3}{(1)(0.19)^3} = 2.5 \times 10^{-5}$$

**Step 4: Calculate standard potential from nonstandard potential using Nernst equation**

$E^\circ$  and  $\nu_e$  are known from part (a)

$$E = E^\circ - \frac{RT}{\nu_e F} \ln Q$$

$$E = (1.1449\text{ V}) - \frac{(8.314\text{ J mol}^{-1}\text{ K})(298.15\text{ K})}{(12)(96\,485\text{ C mol}^{-1})} \ln(2.5 \times 10^{-5}) \times \frac{1\text{ V}}{1\text{ J/C}}$$

$$E = 1.1449\text{ V} - (-0.02273\text{ V})$$

$$E = 1.1676\text{ V}$$