

Rogers

Chem 206 Winter 2007 section 01

GENERAL CHEMISTRY II  
MIDTERM EXAMINATION

**INSTRUCTIONS: PLEASE READ THIS PAGE WHILE WAITING TO START YOUR EXAM.**

This test paper includes 8 pages; the last page includes potentially useful data and formulae, and a periodic table. Check that your paper is complete before starting. You can remove the periodic table if you wish. Answer all questions inside the space provided. Calculators are permitted; cell phones and electronic dictionaries are not allowed. You have 75 min to complete the test. *I suggest you scan the whole test quickly before starting & do the 'easy' stuff first.*

**GOOD LUCK!** *Suggestion: spend 1 min / mark  $\Rightarrow$  25 min left to finish uncertain problems & check.*

LAST NAME: marking scheme FIRST NAME: \_\_\_\_\_

STUDENT NUMBER: \_\_\_\_\_

Mark breakdown:

| <u>%</u> |         | <u>Averages</u> |  |
|----------|---------|-----------------|--|
| 61.7     | Page 2. | 6.2 / 10        | T/F (all topics)                         |
| 76.0     | Page 3. | 7.6 / 10        | $\Delta G^\circ$ + product-favourability |
| 66.3     | Page 4. | 6.6 / 10        | f.p. depression & ionic solutes          |
| ⊗ 54.8   | Page 5. | 6.0 / 11        | heat of phase $\Delta$ , $t$ , transfer  |
| ⊗ 39.6   | Page 6. | 3.6 / 10        | mechanisms + rates                       |

TOTAL:  $\frac{29.9}{50}$  (with  $\frac{49}{50}$  points possible)

PERCENT: 60.5% WELL DONE!

EARNED toward  
FINAL GRADE: / 20

# 1. ( / 10 marks) TRUE OR FALSE? Circle T or F to describe each of these statements. You do not need to explain anything.

- (a) T / F For a first order process, the time required for the reactant concentration to decrease by a factor of two depends on the reaction's rate constant but not on the initial reactant concentration.  
*not true for 0 or 2nd order processes*  
 1st order  $\Rightarrow$   $t_{1/2} = \frac{\ln 2}{k}$  as long as T is unchanged, knowing k is enough to find  $t_{1/2}$ !
- (b) T / F If a reaction is performed in a bomb calorimeter, the measured heat flow is not necessarily equal to the enthalpy change for the reaction, because the system is permitted to lose extra energy by performing work.  
 bomb:  $\Delta V = 0$   
 $\Delta H = q_p$  but P may change in sealed vessel (not  $q_w$ )  $\therefore$  extra energy CANNOT be lost by expansion  
*WRONG. TRUE*
- (c) T / F The concentration of dissolved  $O_2$  will be lower in a solution in contact with 1.0 atm of a gas mixture containing 20 mol %  $O_2(g)$  than in a solution in contact with 0.20 atm of pure  $O_2(g)$ .  
 $C_{O_2} = k P_{O_2}$  (Henry's law)  $\leftarrow$  partial pressure  
 pure:  $P_{O_2} = 0.20 \text{ atm}$   
 mixture:  $P_{O_2} = (1.0 \text{ atm} \times 0.20) = 0.20 \text{ atm}$   $\leftarrow$  SAME
- (d) T / F London dispersion forces are weak attractive forces that arise between molecules because of mutual polarization of electron clouds, which gives rise to transient dipoles.
- (e) T / F If one knows the enthalpy change for a process and the corresponding entropy change for the surroundings, one can calculate the direction in which the process will be spontaneous.

for spontaneity decisions, need  $\Delta G_{sys}^{\circ} = \Delta H_{sys}^{\circ} - T \Delta S_{sys}^{\circ}$   $\leftarrow$  not  $\Delta S_{surr}^{\circ}$ !  
 Remember,  $\Delta H_{sys}^{\circ}$  would let us determine  $\Delta S_{surr}^{\circ}$ , but still need to know  $\Delta S_{sys}^{\circ}$  to find  $\Delta S_{univ}^{\circ}$   
 $\Delta S_{sys}^{\circ} + \Delta S_{surr}^{\circ} = \Delta S_{univ}^{\circ}$   $\leftarrow$  linked to  $\Delta H_{sys}^{\circ}$

| Class Results (# correct / 60 students) |         |   |
|---|---------|---|
| * (a)                                   | 32 / 60 | = 53%   |
| (b)                                     | 46      | = 77%   |
| (c)                                     | 43      | = 72%   |
| (d)                                     | 51      | = 85%   |
| ** (e)                                  | 16      | = 27% $\leftarrow$ Problem. Please make sure you understand this one! |

10



# 2. ( / 10 marks) Consider the combustion of ethanol:  $\text{CH}_3\text{CH}_2\text{OH}(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{g})$

can treat as exact (6.56).

a) (7 marks) Is the reaction product-favoured at  $25^\circ\text{C}$ ? Explain and show all calculations.

Will be product-favoured if spontaneous in forward direction, as determined by  $\Delta G^\circ < 0$ .

$$\textcircled{1} \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

| Thermodynamic data at 298 K                  |                                |                          |
|--|--------------------------------|--------------------------|
| Substance                                    | $\Delta H_f^\circ$<br>(kJ/mol) | $S_f^\circ$<br>(J/mol·K) |
| $\text{CH}_3\text{CH}_2\text{OH}(\text{g})$  | -235.3                         | 282.7                    |
| $\text{O}_2(\text{g})$ element $\rightarrow$ | 0                              | 205.1                    |
| $\text{CO}_2(\text{g})$                      | -393.5                         | 213.7                    |
| $\text{H}_2\text{O}(\text{g})$               | -241.8                         | 188.8                    |

Find  $\Delta H^\circ$ : using Hess's law  $\sum n\Delta H_f^\circ \text{ products} - \sum n\Delta H_f^\circ \text{ reactants}$

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= [2\text{mol}(-393.5 \frac{\text{kJ}}{\text{mol}}) + 3\text{mol}(-241.8 \frac{\text{kJ}}{\text{mol}})] - [(1\text{mol})(-235.3 \frac{\text{kJ}}{\text{mol}}) + (3\text{mol})(0 \frac{\text{kJ}}{\text{mol}})] \\ &= -1512.4 \text{ kJ} - (-235.3 \text{ kJ}) \\ &= -1277.1 \text{ kJ} \leftarrow \text{heat released to surroundings (favourable)} \end{aligned}$$

Find  $\Delta S^\circ$ :

$$\begin{aligned} \Delta S^\circ_{\text{rxn}} &= [2\text{mol}(213.7 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + 3\text{mol}(188.8 \frac{\text{J}}{\text{mol}\cdot\text{K}})] - [1\text{mol}(282.7 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + 3\text{mol}(205.1 \frac{\text{J}}{\text{mol}\cdot\text{K}})] \\ &= 993.8 \text{ J/K} - (898.0 \text{ J/K}) \\ &= 95.8 \text{ J/K} \\ &= 0.0958 \text{ kJ/K} \leftarrow \text{system becomes more disordered (favourable)} \end{aligned}$$

Sub into equation  $\textcircled{1}$  to solve for  $\Delta G^\circ$  & determine spontaneity direction:

$$\begin{aligned} \Delta G^\circ &= -1277.1 \text{ kJ} - (298\text{K})(0.0958 \text{ kJ/K}) \quad \text{Units must match!} \\ &= -1277.1 \text{ kJ} - (28.55 \text{ kJ}) \end{aligned}$$

$\therefore \Delta G^\circ = -1305.6 \text{ kJ}$  for rxn as written, per 1 mole of ethanol.

Because  $\Delta G^\circ < 0$ , rxn is spontaneous forward  $\Rightarrow$  product-favoured.

NOTE: Both enthalpically + entropically favourable so will be product-favoured at ALL temperatures.

b) (3 marks) Would this reaction be more favourable or less favourable at  $-15^\circ\text{C}$ ? Explain in words; calculations will not be graded.

The reaction is entropically favourable ( $\Delta S^\circ_{\text{sys}} > 0$ ) because of the net formation of gas (3+1 moles converted to 2+3 moles(g)).

Thus, as temperature increases, the entropic favourability would be enhanced and the reaction would become even more product favoured. At lower temperatures, the reaction will be LESS FAVOURABLE.

Alternatively: since  $\Delta S^\circ > 0$ , the  $-T\Delta S^\circ$  term becomes a ~~larger~~ smaller negative term as temperature decreases, which makes  $\Delta G^\circ$  less negative, so product yield would decrease.



# 3. ( / 10 marks) Think about mixing water and salt, as you might do to prepare an extra-cold ice bath for making home-made ice cream.

a) (8 marks) What mass of NaCl must be dissolved in 575 mL of water to create a mixture that melts at  $-12.5^\circ\text{C}$ ? Use a van't Hoff factor of 1.87 for NaCl; properties of water are given on the formula page.

Solution with  $m_p = -12.5^\circ\text{C}$   $\therefore$   $12.5^\circ\text{C}$  lower than pure solvent ( $\text{H}_2\text{O}$ )

i.e.  $\Delta T_f = K_{f \text{H}_2\text{O}} m_{\text{solute}}$  where  $m_{\text{solute}}$  includes ALL dissociated ions.

2  
+  
1

solvent conc.  
molality =  $\frac{\text{mol solute}}{\text{kg solvent}}$   $\checkmark$  defn

$$m_{\text{solute}} = \frac{\Delta T_f}{K_{f \text{H}_2\text{O}}} = \frac{12.5^\circ\text{C}}{1.86^\circ\text{C} \cdot \text{kg} \cdot \text{mol}^{-1}} = 6.720 \frac{\text{mol solute}}{\text{kg H}_2\text{O}}$$

2

correct for i

$$m_{\text{NaCl}} = \frac{\text{total molality of solute particles} \times \text{\# ions per NaCl dissolved (i)}}{1.87} = \frac{(6.720 \text{ mol})}{\text{kg H}_2\text{O}} = 3.594 \frac{\text{mol NaCl}}{\text{kg H}_2\text{O}}$$

(-2 if no attempt; -1.5 if incorrect).

8 How do we prepare such a solution?

1.5

$$\frac{3.594 \text{ mol NaCl}}{1 \text{ kg H}_2\text{O}} = \frac{x}{0.575 \text{ kg H}_2\text{O}}$$

$$x = 2.066 \text{ mol NaCl}$$

because  $d_{\text{H}_2\text{O}} = 1.00 \text{ g/mL}$

$$m = 1.00 \text{ g} \times 575 \text{ mL}$$

$$= 575 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}}$$

$$= 0.575 \text{ kg}$$

1.5

$$m_{\text{NaCl}} \text{ needed} = \#n \times \text{MM}_{\text{NaCl}}$$

$$= (2.066 \text{ mol}) \times (58.45 \text{ g/mol})$$

$$= 120.8 \text{ g}$$

$$\therefore m = 121 \text{ g}$$

$\Rightarrow$  Dissolve 121g of NaCl in 575 ml of water...

b) (2 marks) Would this solution have a higher or a lower vapour pressure than pure water? Explain very briefly (one sentence).

2

The solution would have a lower vapour pressure than pure water, because the solute particles lower the proportion of molecules in the liquid that are volatile.

$$P_{\text{soln}} = X_{\text{solvent}} P_{\text{solvent}}^\circ$$

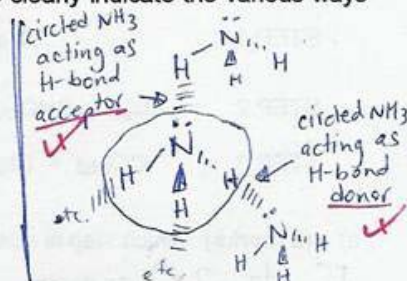
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# 4. ( / 11 marks) Ammonia ( $\text{NH}_3$ ) is used as a refrigerant.

- a) (3 marks) Name and briefly explain the nature of the strongest intermolecular force that exists between molecules in pure ammonia. Provide structural drawings to clearly indicate the various ways the molecules can interact in this fashion.

3 Hydrogen-bonding:  $\checkmark$   
 - part electrostatic AND covalent in nature  
 like dipole-dipole interaction, due to  $\delta^+$  &  $\delta^-$  attraction of highly  $\delta^+$  H and  $\delta^-$  N (because of large difference in N vs H electronegativity)  
 due to orbital overlap of N lone pair & H's nearly empty 1s



- b) (2 marks) At its boiling point ( $-33^\circ\text{C}$ ), the enthalpy of vaporization of ammonia is  $23.3 \text{ kJ/mol}$ . How much heat, " $q_{\text{NH}_3}$ ", is required to vaporize  $355 \text{ g}$  of ammonia at  $-33^\circ\text{C}$ ?

2

$$q_{\text{NH}_3} = \Delta H_{\text{vap}} \times \#n_{\text{NH}_3}$$

$$= (23.3 \frac{\text{kJ}}{\text{mol}}) (20.85 \text{ mol})$$

where  $\#n_{\text{NH}_3} = \frac{355 \text{ g}}{17.0304 \text{ g}\cdot\text{mol}^{-1}} = 20.85 \text{ mol}$

$\therefore q_{\text{NH}_3} = +485.7 \text{ kJ}$   $\leftarrow$  must be absorbed, since energy required to break H-bonds between molecules

- c) (6 marks) A standard refrigerator contains about  $515 \text{ g}$  of air ( $C_s = 1.0035 \text{ J/g}\cdot^\circ\text{C}$ ). Imagine your refrigerator was left open; it is now closed, filled with  $22^\circ\text{C}$  air and the walls/shelves are at  $7^\circ\text{C}$ . If the process from part (b) occurs within the cooling system, what is the minimum temperature the inside of the refrigerator (air + walls/shelves) could reach? Assume the refrigerator is perfectly insulated and the walls/shelves have a heat capacity of  $235 \text{ kJ}^\circ\text{C}$ . [If you could not do part (b), use  $275 \text{ kJ}$  for  $q_{\text{NH}_3}$ .]

ignoring  $\Delta T$  of  $\text{NH}_3$ ... because no information provided about  $C_s \text{ NH}_3$ .

\*Heat absorbed from air + walls/shelves by ammonia-evaporation process:

6

$$-q_{\text{NH}_3} = q_{\text{air}} + q_{\text{fridge}} \quad \text{assuming no other heat losses}$$

$$-485700 \text{ J} = (C_{s \text{ air}} m_{\text{air}} \Delta T_{\text{air}}) + (C_{\text{fridge}} \Delta T_{\text{fridge}})$$

note  $T_i \text{ air} = 22^\circ\text{C}$   
 $T_i \text{ fridge} = 7^\circ\text{C}$   
 $T_f \text{ both} = \text{same}$

$$-485700 \text{ J} = (1.0035 \frac{\text{J}}{\text{g}\cdot^\circ\text{C}}) (515 \text{ g}) (T_f - 22^\circ\text{C}) + (235000 \frac{\text{J}}{^\circ\text{C}}) (T_f - 7^\circ\text{C})$$

$$-485700 = 516.80 T_f - 11369.7 + 235000 T_f - 1645000$$

$$1170669.7 = 235516.8 T_f$$

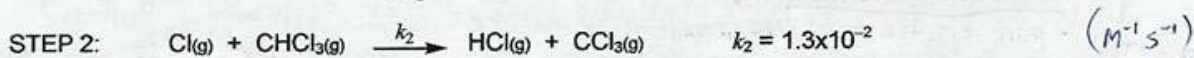
$$T_f = 4.97^\circ\text{C}$$

$$\rightarrow T_f \approx 5^\circ\text{C} \quad \text{solve for } T_f$$

11  
 If we ignore the fact that the ammonia itself would warm up well above its boiling point of  $-33^\circ\text{C}$  (as the problem requires), the fridge could cool to  $5^\circ\text{C}$ .



# 5. (9 marks) The following three-step mechanism has been proposed for the reaction of chlorine with chloroform. The numerical value (i.e., without units) of the rate constant for each step is provided.



a) (2 marks) Which step is rate limiting? Briefly explain your choice.

2 [ step 2 ✓ because the value of the rate constant  $k_2$  is smallest, which means this reaction is inherently the slowest one in the mechanism (eg. largest  $E_a$ , or greatest steric demand, etc). ]

b) (4 marks) Based on this proposed mechanism, what do you predict the reaction's overall rate law to be, and why?

The observed rate law will be based on the RLS's rate law. ✓  
 Thus:  $\text{rate}(\text{expected}) = k_2 [\text{Cl}][\text{CHCl}_3]$  ✓ since step 2 is bimolecular. (≠ value of  $k_{\text{obs}}$  not needed)

intermediate ✓ formed in step 1  
 BUT consumed also in reverse step 1

If step 1 comes to equilibrium:  $\text{rate}_1 = \text{rate}_{-1}$

$k_1 [\text{Cl}_2] = k_{-1} [\text{Cl}]^2$   
 solve for  $[\text{Cl}]$ :  $[\text{Cl}] = \sqrt{\frac{k_1}{k_{-1}} [\text{Cl}_2]}$  } sub this into rate<sub>2</sub> equation

So:  $\text{rate}(\text{expected}) = k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{Cl}_2]^{1/2} [\text{CHCl}_3]$

✓  $\Rightarrow \text{rate} = k_{\text{obs}} [\text{Cl}_2]^{1/2} [\text{CHCl}_3]$  where  $k_{\text{obs}} = 1.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  (not needed...)

c) (3 marks) Using the data in the table, determine the observed rate law for the reaction. Is the proposed mechanism consistent with experiment? Why or why not?

| Kinetics data (fabricated for exam purposes) for $\text{Cl}_2 + \text{CHCl}_3 \rightarrow \text{HCl} + \text{CCl}_4$ |                       |                         |                    | $k$ ( $\text{M}^{-2} \text{s}^{-1}$ ) |
|--|-----------------------|-------------------------|--------------------|---------------------------------------|
| Expt.  | $[\text{Cl}_2]_0$ (M) | $[\text{CHCl}_3]_0$ (M) | Initial rate (M/s) |                                       |
| 1  | 0.136                 | 0.212                   | 0.0248             | 6.32                                  |
| 2  | 0.272                 | 0.212                   | 0.0991             | 6.32                                  |
| 3  | 0.544                 | 0.424                   | 0.793              | 6.32                                  |
| 4  | 0.544                 | 0.848                   | 1.59               | 6.34                                  |

Expt. 1 vs. 2:  $[\text{Cl}_2]_0 \times 2 \Rightarrow \text{rate} \times 4 = 2^2$  second order in  $\text{Cl}_2$   
 Expt. 3 vs. 4:  $[\text{CHCl}_3]_0 \times 2 \Rightarrow \text{rate} \times 2 = 2^1$  first order in  $\text{CHCl}_3$

Thus: observed rate law is:  $\text{rate}_{\text{obs}} = k_{\text{obs}} [\text{Cl}_2]^2 [\text{CHCl}_3]$  ✓  $k$  value 6.33 not needed but worth an extra 0.5

9 ✓ Because the expected rate law is NOT second order in  $\text{Cl}_2$ , the proposed mechanism is NOT consistent with experiment. It must in some way be flawed.