

Rogers

Chem 206 Winter 2007 section 52

GENERAL CHEMISTRY II  
MIDTERM EXAMINATION

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

This test paper includes 7 pages; the last pages include 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: \_\_\_\_\_

Rogers

FIRST NAME: \_\_\_\_\_

marking scheme

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

Mark breakdown:

<u>%</u>		<u>Averages</u>	
55.9%	Page 2.	6.7 / 12	T/F all topics
46.4%	Page 3.	5.1 / 11	Henry's law, osmosis descriptions
65.4%	Page 4.	6.5 / 10	Kinetics: order, mechanism + time-evolution [].
76.6%	Page 5.	7.7 / 10	free energy + spontaneity

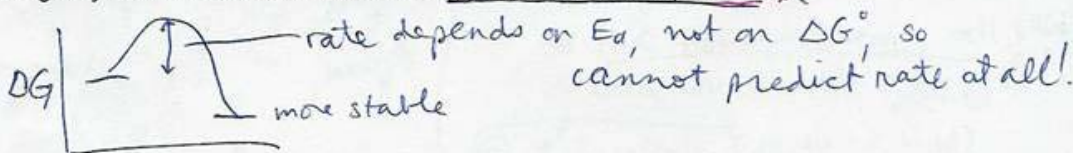
TOTAL: 26 / 42 (with 43 points possible)

PERCENT: 61.8 % well done!

EARNED toward  
FINAL GRADE: / 20

# 1. (12 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 the purpose of melting the ice on your front steps at home, calcium chloride ( $\text{CaCl}_2$ ) would be a better choice of salt than sodium chloride ( $\text{NaCl}$ ).  
 $\Delta T_f = i m K_f$   
 $i=2$  (for NaCl),  $i=3$  (for  $\text{CaCl}_2$ )  
 larger # ions released  $\Rightarrow$  greater depression of mp of  $\text{H}_2\text{O}$   
 $\therefore$  greater melting effect on ice
- (b) 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.  
 $\Delta H_{\text{system}}$   $\rightarrow$  tells about  $\Delta S_{\text{surr}}$ ,  $\therefore$  knowing  $\Delta S_{\text{surr}}$  not helpful  
 need  $\Delta S_{\text{system}}$  also. before can conclude regarding spontaneity
- (c) T/F The rate-limiting (or rate-determining) step in a reaction's mechanism is the elementary step with the largest rate constant.  
 $\rightarrow$  slowest step  $\Rightarrow$  largest  $E_a$   
 $\therefore$  smallest  $k$ .
- (d) 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 not permitted to lose energy by performing work.  
 yes.  $\Delta V = 0$  in bomb.  
 pressure may build up since cannot do work of expansion  
 $\Delta H_{\text{rxn}} = q_p$  constant P  
 not  $q_v$ . unless  $\Delta P = 0 \dots$
- (e) T/F If a solution contains equal moles of two volatile components, the vapour above this solution will contain equal moles of the two components.  
 If have same volatility, yes, but not if  $P_A^\circ \neq P_B^\circ$   
 $\therefore$  not always true (usually NOT)  
 $P_{\text{vap Soln}} = \chi_A P_A^\circ + \chi_B P_B^\circ$   
 $\chi_A = 0.5$ ,  $\chi_B = 0.5$   
 not same? (usually NOT)
- (f) T/F If a reaction's products are more thermodynamically stable than its reactants, then a sample containing only these reactants will react at a very high rate to form products.  
 $\times$



Class results: (correct / total students 34)  $\times 100\%$

- (a) 64.7%  
 (b) 67.6%  
 \*(c) 20.6%  $\leftarrow$  please review this!  
 (d) 58.8%  
 \*(e) 47.1%  
 (f) 55.9%

# 2. (6 marks) The solubility of  $H_2S(g)$  in water at STP (1 atm,  $0^\circ C$ ) is 0.195 M. What mass of  $H_2S$  would be dissolved in a 1.5 L solution at  $0^\circ C$  if the air above the solution contains 0.0055 % (by mole)  $H_2S$  at a total pressure of 765 mm Hg?

1.5 Solubility at  $P_{H_2S} = 1 \text{ atm}$ :  $C = k P_{H_2S} \Rightarrow k = \frac{0.195 \text{ mol/L}}{1 \text{ atm } H_2S}$   
 gives Henry's law constant

Now use Henry's law:  $C = k P_{H_2S}$  for air with low %  $H_2S$   
 [where  $P_{H_2S} = \left(\frac{0.0055}{100}\right) (765 \text{ mm}) \times \left(\frac{1 \text{ atm}}{760 \text{ mm}}\right) = 5.536 \times 10^{-5} \text{ atm } H_2S$

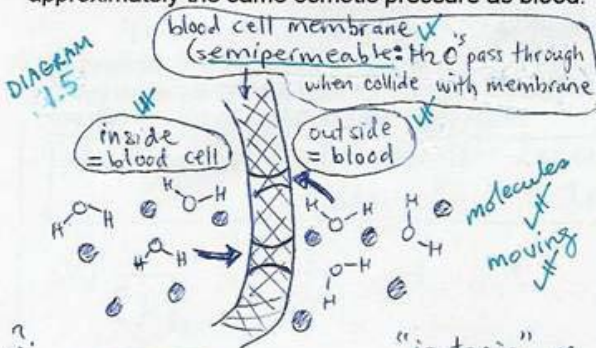
So,  $C = \left(\frac{0.195 \text{ mol/L}}{\text{atm } H_2S}\right) (5.536 \times 10^{-5} \text{ atm } H_2S)$   
 $= 1.0795 \times 10^{-5} \text{ M dissolved } H_2S$

Thus: in a 1.5 L solution

$$m_{H_2S} = (1.0795 \times 10^{-5} \frac{\text{mol}}{\text{L}}) (1.5 \text{ L}) (34.0225 \frac{\text{g}}{\text{mol } H_2S})$$

$\therefore m_{H_2S} = 5.5 \times 10^{-4} \text{ g}$  not very much, but not much  $H_2S$  in the air

# 3. (5 marks) Explain on a molecular level why it is essential that fluids used in intravenous injections have approximately the same osmotic pressure as blood. Include relevant diagrams.



Normal situation: "isotonic" or "isocosmetic"

- same solute concentration (salts, etc.) inside blood cell as in blood
- $\Rightarrow$  same fraction of molecules in each solution are solvent ( $H_2O$ ),  $\therefore$  can pass through cell membrane at equal rates both ways
- $\Rightarrow$  zero net flow of  $H_2O$  in vs. out
- $\Rightarrow$  same osmotic pressure in vs. out  $\Rightarrow$  stable cell volumes.

osmosis definition? flow of  $H_2O$  down its own conc. gradient (x)  
 $\pi = \frac{n}{V} RT$  explained (x)

If inject a solution into blood:

- ① if hypertonic (concentrated c.f. blood)
  - higher [solute] in blood after injection
  - $\Rightarrow$  lower  $[H_2O]$  in blood than cell
  - $\Rightarrow$   $H_2O$  flow: NET leaving cell ( $T_{cell} \downarrow$ )
  - $\Rightarrow$  cells can shrivel
- ② if hypotonic (dilute c.f. blood)
  - lower [solute] in blood after injection
  - $\Rightarrow$  higher  $[H_2O]$  in blood than cell
  - $\Rightarrow$   $H_2O$  flow: NET into cell ( $T_{cell} \uparrow$ )
  - $\Rightarrow$  cell can burst
- ③ if isotonic (same [solute] as blood)
  - no change in osmotic pressure compared to normal situation
  - $\Rightarrow$  cells remain healthy

# 4. (10 marks) Think about the gas-phase decomposition of nitrogen dioxide:  $2 \text{NO}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$ .

- a) (4 marks) Determine the rate law (including the numerical value of the rate constant, and its units) for this reaction. Explain your reasoning.

Kinetics data (at 600 K) for: $2 \text{NO}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$		
Expt.	$[\text{NO}_2]_0$ (M)	Initial rate (M/s)
1 (x2)	0.0010	$5.4 \times 10^{-7}$
2	0.0020	$2.2 \times 10^{-6}$

Expt 1 vs 2:  $[\text{NO}_2]_0 \times 2 \Rightarrow \text{rate} \times 2^2 (=4)$   
 work shown ✓  
 conclude ✓ second order in  $[\text{NO}_2]$

$\Rightarrow \text{rate} = k [\text{NO}_2]^2$  ✓ because rate responds to changes in  $[\text{NO}_2]$  with a square dependence, not linearly

4 1.5  $k = \frac{\text{rate}_0}{[\text{NO}_2]_0^2} = \frac{5.4 \times 10^{-7} \text{ M s}^{-1}}{(0.0010 \text{ M})^2} \doteq 0.54 \text{ M}^{-1} \text{ s}^{-1}$  from expt ①  
 and  $0.55 \text{ M}^{-1} \text{ s}^{-1}$  from expt ②  
 $0.545 \text{ M}^{-1} \text{ s}^{-1}$  average of ①+②

$\Rightarrow k = 0.55 \text{ M}^{-1} \text{ s}^{-1}$  ✓ second order rate constant

- b) (2 marks) Does your result from part (a) give you any insight into the mechanism of the reaction? Explain.

2 The stoichiometric equation shows 2 molecules of  $\text{NO}_2$  are required overall. The observed rate law is second order in  $\text{NO}_2$  ✓, which suggests that the rate-limiting step is bimolecular involving 2 molecules of  $\text{NO}_2$  ✓.  
 The mechanism may simply be a single, bimolecular step ✓.

- c) (4 marks) If 0.0050 mol of  $\text{NO}_2$  is placed into a 1.0 L flask and allowed to decompose at 600 K, how many seconds does it take for the  $\text{NO}_2$  concentration to drop to 0.0010 M? If you could not do part (a), use a rate constant of "5.0" to solve this problem.

2nd order: for time-dependence of conc, use 2<sup>nd</sup> order integrated rate law.

4 ✓  $\frac{1}{[\text{A}]_t} = \frac{1}{[\text{A}]_0} + kt$

$\Rightarrow t = \left( \frac{1}{[\text{NO}_2]_t} - \frac{1}{[\text{NO}_2]_0} \right) \div k$

$t = \left( \frac{1}{0.0010 \text{ M}} - \frac{1}{0.0050 \text{ M}} \right) \div 0.545 \text{ M}^{-1} \text{ s}^{-1}$

10  $t = \frac{800 \text{ M}^{-1}}{0.545 \text{ M}^{-1} \text{ s}^{-1}} = 1468 \text{ s} \left( \doteq 1500 \text{ seconds} \right)$

where  $[\text{A}]$  is  $[\text{NO}_2]$ .

and  $[\text{NO}_2]_t = 0.0010 \text{ M}$

and ✓  $[\text{NO}_2]_0 = \frac{0.0050 \text{ mol}}{1.0 \text{ L}} = 0.0050 \text{ M}$

and  $k_{\text{book}} = 0.545 \text{ M}^{-1} \text{ s}^{-1}$  from (a) (extra SF)

if used  $k = 5.0$ ,  
 $t = 160 \text{ s}$

#5. (10 marks) Ethanol is made industrially by the hydration of ethylene:  $\text{CH}_2=\text{CH}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_3\text{CH}_2\text{OH}(\text{l})$

a) (7 marks) Is this reaction product-favoured at 25°C? Include brief explanatory comments at each step of your calculation.

- Product-favoured if spontaneous,  $\Delta G^\circ < 0$ .
- To use  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ , must first calculate  $\Delta H^\circ$  &  $\Delta S^\circ$  for reaction.

Thermodynamic data at 298 K		
Substance	$\Delta H_f^\circ$ (kJ/mol)	$S_f^\circ$ (J/mol·K)
$\text{CH}_2=\text{CH}_2(\text{g})$ (x1)	+52.3	219.5
$\text{H}_2\text{O}(\text{l})$ (x1)	-285.8	69.9
$\text{CH}_3\text{CH}_2\text{OH}(\text{l})$ (x1)	-277.7	161

$\Delta H_{\text{rxn}}^\circ = \sum n \Delta H_f^\circ \text{ products} - \sum n \Delta H_f^\circ \text{ reactants}$  ✓ ← Hess's law.

$= [(1 \text{ mol})(-277.7 \frac{\text{kJ}}{\text{mol}})] - [(1 \text{ mol})(+52.3 \frac{\text{kJ}}{\text{mol}}) + (1 \text{ mol})(-285.8 \frac{\text{kJ}}{\text{mol}})]$

$= -277.7 - (-233.5) \text{ kJ}$  ✓

$= -44.2 \text{ kJ}$  ✓ ∴ exothermic, releases heat (favourable) to surroundings

2.0

$\Delta S_{\text{univ}}^\circ = \frac{-\Delta H^\circ}{T}$   
 $\approx 0.148 \frac{\text{kJ}}{\text{K}}$

$\Delta S_{\text{rxn}}^\circ = \sum n S_f^\circ \text{ products} - \sum n S_f^\circ \text{ reactants}$  ✓

$= [(1 \text{ mol})(161 \frac{\text{J}}{\text{mol}\cdot\text{K}})] - [(1 \text{ mol})(219.5 \frac{\text{J}}{\text{mol}\cdot\text{K}}) + (1 \text{ mol})(69.9 \frac{\text{J}}{\text{mol}\cdot\text{K}})]$

$= 161 - 289.4 \text{ J/K}$  ✓

$= -128.4 \text{ J/K}$  ✓ ∴ disorder of system decreases (unfavourable)

2.0

Overall: rxn is enthalpically favourable but entropically unfavourable  
 ∴ must calculate  $\Delta G^\circ$  to determine overall favourability.  
 → or,  $\Delta S_{\text{universe}}$ , either is fine ...

$\Delta G^\circ = -44.2 \text{ kJ} - (298 \text{ K})(-0.1284 \text{ kJ/K})$  ✓ ← units match.  
 $= -44.2 \text{ kJ} - (-38.26 \text{ kJ})$

3.0

∴  $\Delta G^\circ = -5.9 \text{ kJ} < 0$  ∴ spontaneous forward, ✓

OR,  $\Delta S_{\text{univ}}^\circ = \Delta S_{\text{rxn}}^\circ + \Delta S_{\text{surv}}^\circ = 0.020 \frac{\text{kJ}}{\text{K}}$

product-favoured, ✓  
 although driving force is not large.

b) (3 marks) Why does this reaction become non-spontaneous at high temperatures? Explain in words.  
 Do not include calculations. → BE SPECIFIC.

The reaction is entropically unfavourable, because the system becomes more ordered during the course of the reaction. This occurs because 1 mol of gas (high disorder) and 1 mol of liquid (moderate disorder) are converted to 1 mol of liquid (moderate disorder).

Disorder itself scales with temperature because of thermal motions, so this unfavourability is larger as temperature increases.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  tells us this... for as  $T \uparrow$ ,  $-T\Delta S^\circ$  becomes a larger positive number that eventually will overwhelm the -ve  $\Delta H^\circ$ .

logic of mathematical  
1.5

10