

Rogers

Chem 206 Winter 2008 section 01

GENERAL CHEMISTRY II
MIDTERM EXAMINATION

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

This test paper includes 4 pages (both sides); some potentially useful information (look at it!) is given on back of the periodic table. Check that your paper is complete before starting. You can remove the periodic table if you wish. Answer all questions in the space provided. Calculators are permitted; cell phones and electronic dictionaries are not allowed. You have 75 min to complete the test. *70 min actually.*

I suggest you scan the whole test quickly before starting & do the 'easy' stuff first. **GOOD LUCK!**
Suggestion: spend 1 min / mark \Rightarrow 35 min left to finish uncertain problems & check.

LAST NAME: marking scheme FIRST NAME: _____

STUDENT NUMBER: _____

Mark breakdown:

			<u>Averages</u>		<u>%</u>
Concepts - All chapters mostly calculation	ch. 6/19	Page 2.	5.3	/ 10	53%
		Page 3.	7.3	/ 11	67%
	Ch. 14	Page 4.	5.8	/ 10	58%
	ch. 15	Page 5.	5.0	/ 10	50%

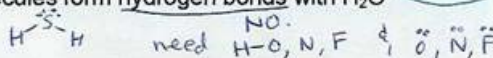
TOTAL: 23.5 / 40 (max. = 41)

PERCENT: 58.7 %

EARNED toward
FINAL GRADE: 11.7 / 20

1. (4 marks) TRUE OR FALSE? Circle T or F to describe the following three statements.

F (1) T / (F) When hydrogen sulfide gas dissolves in water, H₂S molecules form hydrogen bonds with H₂O molecules. Ch. 13

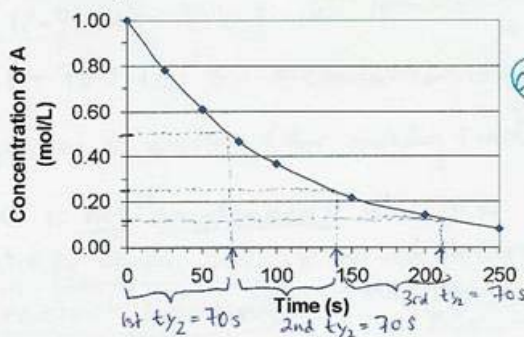


T (1) T / F When a reaction with $\Delta n_{\text{gases}} < 0$ takes place at constant pressure, the surroundings perform work on the system. Ch. 6

net loss of gas \therefore volume \downarrow
(compression by surroundings!)

Refer to the graph shown here for reaction 2 A \rightarrow B:

T (2) T / F The reaction 2 A \rightarrow B is first order with respect to the concentration of reactant A. constant $t_{1/2} \Rightarrow$ 1st order. Ch. 15



2. (6 marks) Complete the table: circle the substance/solution with the desired property & explain briefly.

Poor performance here!

Desired property	Substances to choose from (PURE unless given concentration...)	How you decided (briefly!)
(2) Highest vapour pressure at 25°C Ch. 13.5	Pure: CH ₄ ✓ CH ₃ CH ₃ CH ₃ CH ₂ CH ₃	Highest P_{vap} means <u>most volatile</u> . ie. weakest intermolecular forces (easiest to break away from). All substances here = nonpolar \therefore all have induced dipole-induced dipole forces ① atom types = same ② # points of contact = least for CH ₄ .
(2) Highest temperature after absorbing 100 kJ of heat Ch. 6	Pure: Ti(s) ✓ C _p = 0.52 Al(s) 0.90 SiO ₂ (s) 0.74 J/(g·°C)	$q = m C_p \Delta T$ for same q , and m (assume) $\Rightarrow \Delta T = \frac{q}{m C_p}$ ✓ so: <u>smallest specific heat capacity</u> means easiest to warm up ✓ \therefore will get the hottest.
(2) Highest osmotic pressure Ch. 14.4	Solutions: 1 M H ₂ SO ₄ ✓ $i = 3$? max really $2 < i < 3$ 1 M C ₆ H ₁₂ O ₆ $i = 1$ 1 M NaCl $i = 2$ ✓ i values	$\Pi V = nRT$ ✓ $\Rightarrow \Pi = \left(\frac{n}{V}\right) RT$ total conc. of solute particles Solute that releases most particles per unit dissolved will yield highest osmotic P \therefore compare i values

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3. (11 marks) Metallic tungsten (W) is produced on large scale by the reduction of WO_3 with hydrogen:



a) (4 marks) Is this reaction spontaneous at 25°C?

Show calculations and explain briefly.

Hess's law

Find: is $\Delta G_{rxn}^\circ < 0$? via $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$? (cont!)

Thermodynamic data at 298 K = 25°C.			
Substance	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	
$WO_3(s)$	-763.1	-839.9	x 1
$H_2O(g)$	-228.6	-241.8	x 3
for elements formation...	FREE E. = 0	ENTHALPY = 0	

1 Use: $\Delta G_{rxn}^\circ = \sum n \Delta G_f^\circ \text{ products} - \sum n \Delta G_f^\circ \text{ reactants}$ ✓

2 $= [1(0) + 3(-228.6)] - [1(-763.1) + 3(0)]$ ← each is (- mol)(- kJ/mol)

$= -685.8$ ✓ - (-763.1) ✓ kJ ← (moles cancelled!)

∴ $\Delta G_{rxn}^\circ = +77.3$ kJ ✓ for rxn equation as written (for making 1 mol W(s))

5 1 Since POSITIVE, rxn is not spontaneous at 298 K
i.e., overall, the entropy of the universe would decrease, not increase.
∴ rxn would be reactant-favoured. i.e. $\Delta S_{univ} < 0$.

b) (5 marks) Calculate the value of ΔS_{rxn}° at 25°C.

Find: ΔS_{rxn}° via $\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T\Delta S_{rxn}^\circ$

4 2 First: $\Delta H_{rxn}^\circ = [1(0) + 3(-241.8)] - [1(-839.9) + 3(0)]$ ← each is (- mol)(- kJ/mol)

$= -725.4$ ✓ - (-839.9) ✓

∴ $\Delta H_{rxn}^\circ = +114.5$ kJ ✓ ← endothermic (enthalpically unfav. ∴ ΔS_{sum} decreases)

2 So: $\Delta S_{rxn}^\circ = \frac{\Delta G_{rxn}^\circ - \Delta H_{rxn}^\circ}{-T} = \frac{(+77.3 - 114.5) \text{ kJ}}{-298 \text{ K}}$

$= +0.1248$ kJ/K disorder of sys increases

∴ $\Delta S_{rxn}^\circ = +125$ J/K ← entropically favourable according to SYSTEM

c) (2 marks) At higher temperatures, will this reaction have higher yield or lower yield? Explain briefly.

2 Entropically favoured reactions (according to system) are always more product-favoured at higher temperatures.

$\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T\Delta S_{rxn}^\circ$ → as $T \uparrow$, $-T\Delta S^\circ$ becomes a larger negative #, contributing to ΔG° becoming more negative (product-favoured if T high enough) ∴ higher yield as temperature increases.

Another view: products are more disordered (for this reaction) than reactants, which is favourable. This difference is exaggerated at higher temperatures due to ↑ motions, so products even more favoured!

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$12^{11}22^{11}$ } 22H: 22.174
 110: 175.596

MM = 342.26 g/mol

4. (10 marks) Ice cream is made by freezing a liquid mixture that (in a simplified view) can be considered a solution of sucrose ($C_{12}H_{22}O_{11}$) in water.

Calculate the temperature at which the first ice crystals begin to appear when you cool a mixture that consists of 34% (by mass) sucrose in water.

ie. Find melting point of solution: 34% sucrose, rest water

freezing point depression $\Delta T_f = K_f m$ $1.86 \frac{^\circ C}{m}$

total molality of solute particles

solute = $C_{12}H_{22}O_{11}$ molecules ($i=1$)

must specifically state this, here or in equation, as

$\Delta T_f = i K_f m$

- Plan: ① use mass % data to find molality
 ② sub into equation for f.p. depression (above)

Solution:

① In arbitrary 1 kg solution sample:
 $(0.34)(1kg) = 0.340$ kg sucrose AND 0.660 kg water

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Molality = $\frac{n_{solute}}{kg_{solvent}} = \frac{(0.340 \text{ kg sucrose} \times \frac{1000g}{1kg})}{342.26 \text{ g mol}^{-1} \times 0.660 \text{ kg H}_2\text{O}}$

= $\frac{0.9934 \text{ mol}}{0.660 \text{ kg}}$

= 1.505 mol/kg ← total solute particle (molecule!) concentration

2 above + 3

② $\Delta T_f = (1.86 \frac{^\circ C}{mol/kg}) (1.505 \text{ mol/kg})$

= $2.7996 \text{ }^\circ C$ but 2SF based on mass % data (& all x and ÷...)

$\therefore \Delta T_f \approx 2.8 \text{ }^\circ C$ ← depression relative to pure solvent's freezing point of $0.00 \text{ }^\circ C$

CONCLUSION: The sucrose/water mixture will begin to freeze at $-2.8 \text{ }^\circ C$.

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5. (10 marks) In basic solution, chlorine dioxide yields chlorate ions and chlorite ions:



To investigate the reaction's kinetics, the initial reaction rate was measured in three separate experiments (data shown in table):

Kinetic data at 298 K			
Run	$[\text{ClO}_2]_0$ mol·L ⁻¹	$[\text{OH}^-]_0$ mol·L ⁻¹	Initial rate mol·L ⁻¹ ·s ⁻¹
1	0.060	0.030	0.0248
2	0.020	0.030	0.00276
3	0.020	0.090	0.00828

a) (6 marks) Determine the rate law and the value of the rate constant at this temperature. Show your work.

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- Run 2 vs. 1: $[\text{ClO}_2]_0 \times 3 \Rightarrow \text{rate} \frac{0.0248 \text{ M s}^{-1}}{0.00276 \text{ M s}^{-1}} = \frac{9}{1} = \frac{3^2}{1}$ 2nd order in $[\text{ClO}_2]$
- Run 2 vs. 3: $[\text{OH}^-]_0 \times 3 \Rightarrow \text{rate} \frac{0.00828 \text{ M s}^{-1}}{0.00276 \text{ M s}^{-1}} = \frac{3}{1} = \frac{3^1}{1}$ 1st order in $[\text{OH}^-]$

\Rightarrow Thus: rate law is: $\text{Rate} = k [\text{OH}^-] [\text{ClO}_2]^2$ 3rd order overall.

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Find rate constant: $k = \frac{\text{rate}_0}{[\text{OH}^-]_0 [\text{ClO}_2]_0^2}$ ✓ for any run (best if average)

$$= \frac{0.0248 \text{ M s}^{-1}}{(0.030 \text{ M})(0.060 \text{ M})^2} \text{ using run 1 data}$$

$$= 229.63 \text{ M}^{-2} \text{ s}^{-1}$$

$\therefore k \approx 230 \text{ M}^{-2} \text{ s}^{-1}$ (2SF)

units must be consistent with rate law.

b) (4 marks) Compare the reaction equation to your experimentally determined rate law. What conclusions (if any) can you make about the mechanism of this reaction? Explain briefly.

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- Reaction equation: If one step, the reaction would be quatermolecular involving 4 molecules simultaneously colliding. This is statistically improbable (in other words, we can rule out a 1-step mechanism already!)
- Experimental rate law: 3rd order (suggests perhaps a termolecular RLS) This does not match a quatermolecular reaction, so we can conclusively say that the reaction must proceed via a multistep mechanism (otherwise it would match the net reaction's stoichiometry). Beyond this, we cannot say much else. The mechanism MIGHT involve an initial, rate-limiting, termolecular step $\text{OH}^- + \text{ClO}_2 + \text{ClO}_2 \rightarrow ?$ but other mechanisms could also yield the observed rate law. more expts needed!

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