W09 DAY

LAST NAME:	Rogers
FIRST NAME:	answer key
STUDENT ID:	

Chem 206 - GENERAL CHEMISTRY II

MIDTERM EXAMINATION

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

- This test includes 4 pages (both sides). Read over the whole test quickly before starting.
- Calculators are permitted; cell phones and other electronic devices are not allowed.
- Potentially useful information (look at it...) is given on back of the periodic table.
- You can remove the periodic table if you wish.
- Answer all questions in the space provided.
- You have 70 min to complete the test.

- **GOOD LUCK!**

NOTE: you must show comments/explanations even for calculations
① to show that you understand what you did
AND② to guide the reader through (especially important if you
make an error!!)

Mark breakdown:

Averages

Page 2.	7.3	/ 11 =	66.7 %
Page 3.	4.6	/ 8 =	57.9 % ← review!!
Page 4.	5.0	/ 8 =	62.7 %
Page 5.	3.1	/ 5 =	62.7 %
Page 6.	6.7	/ 9 =	74.0 %

TOTAL: 26.8 / 40 (max. = 41)

PERCENT: 67 %

EARNED toward
FINAL GRADE: / 20

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$\checkmark = 1$, $\checkmark' = 0.5$, $\checkmark^x = 0.25$ points

1. (5 marks) TRUE OR FALSE? Circle T or F to describe each of the following statements.
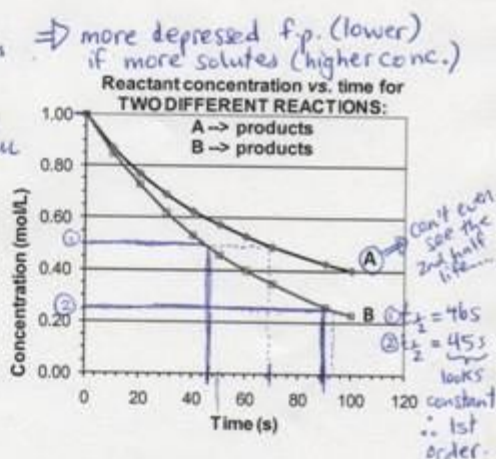
T / (F) If a solution of a gas-phase solute is suddenly exposed to a higher partial pressure of the gas, the concentration of dissolved gas will begin to decrease. ✗ $C_{gas} = k P_{gas}$

T / (F) A proposed mechanism is *consistent with experiment* if the experimentally observed rate law is the same as the rate law predicted for the first step in the mechanism.
      no, the slow (rate-limiting) step

(T)/ F The rate-limiting step of a reaction is the elementary step with the largest activation energy.

           solutes
(T)/ F The freezing point of s̶a̶l̶t̶ water is lower than the
      freezing point of fresh water. $\Delta T_f = K m_{solutes}$ ⟹ more depressed f.p. (lower)
         few solutes   if more solutes (higher conc.)

T / (F) From the graph, curve A corresponds to a first-order reaction whereas curve B does not.,
      ← NOT TRUE   NOT LIKELY
                               BUT CAN'T TELL
      $t_{1/2}$ constant for B ∴ first order

Reactant concentration vs. time for
TWO DIFFERENT REACTIONS:
A → products
B → products

can't even see the 2nd half life...

B ⊙ $t_1 = 46s$
  ② $t_2 = 45s$
      looks constant
      ∴ 1st order.

2. (6 marks) In the table, circle the substance with the desired property and provide a brief explanation.

Desired property	Choices (= pure substances!)	Brief explanation (in point form – key words only)
Higher boiling point	H–N̈–H H–P̈–H (NH₃) vs. PH₃ both polar both polar	Higher bp ⟹ stronger intermolecular forces. NH₃ : hydrogen bonding ← stronger forces PH₃ : dipole–dipole interactions
Higher vapour pressure When polarity is similar, size effects dominate.	(H₂S) vs. H₂Se ⊛Recall: electronegativity is NOT most important feature when SIZES are different too ⊛except when hydrogen-bonding is possible...	Higher vapour pressure = more volatile = WEAKER intermolecular forces H₂S: d–d ← weaker forces H₂Se: d–d but larger atom ∴ more polarizable too (Se>S) ∴ stronger forces...
Higher solubility in water	I₂ vs. (NaNO₃) :Ï–Ï: Na O N̈ O O	Higher solubility in water ⟹ more polar, or at least stronger interactions with polar H₂O molecules I₂: non-polar ∴ id–d NaNO₃: ionic ∴ ion-dipole ← stronger forces

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2

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3. (8 marks) Zinc metal reacts with hydrochloric acid according to the following balanced equation:

$$Zn(s) + 2\,HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

⟹ $m_{TOTAL} = 50.103\,g$ including the Zn

a) (7 marks) When 0.103 g of Zn(s) is combined with enough HCl to make 50.0 mL of solution in a perfectly insulated coffee-cup calorimeter, all of the zinc reacts. The temperature of the solution increases from 22.5 °C to 23.7 °C. Determine the enthalpy change for this reaction (per mole of zinc). [Note: assume the solution is dilute enough to be treated as "pure water" in your calculations.]

From 1st law of thermodynamics:

$\checkmark$ $q_{rxn} = -(q_{soln} + q_{calorimeter})$ ⟸ But no information given for calorimeter ∴ simplify...

⟹ $q_{rxn} = -q_{soln}$ ⟸ ≈ all heat lost by reaction is gained by the solution, which is treated here as "water"

$= -(m_{soln}\, C_{soln}\, \Delta T_{soln})$ must all match!

$= -\left(50.0\,mL \times 1.00\frac{g}{mL}\right)\left(4.184\,\frac{J}{g\cdot K}\right)\left(\underbrace{23.7 - 22.5\,°C}\right)$

or better, 50.103 g total...   final — initial

$\Delta T = +1.2°C = +1.2\,K$ since CHANGE

$= -(251.04\,J)$

∴ $q_{rxn} = -251.04\,J$ ⟸ the reaction is exothermic... and this much heat released for 0.103 g Zn.

How many moles?

$n_{Zn} = \dfrac{0.103\,g}{65.39\,g\cdot mol^{-1}}$ $\checkmark \doteq 1.575 \times 10^{-3}$ mol Zn

Enthalpy of reaction:

$\Delta H = \dfrac{q_p}{n}$ ⟵ constant pressure calorimeter (since cup is "open") so heat flow yields enthalpy information (by definition, $q_p = \Delta H$)

$= \dfrac{-251.04\,J}{1.575 \times 10^{-3}\,mol}$ $\checkmark$

⟹ $\Delta H \doteq -159390$ J/mol $\checkmark$ Thus: $\boxed{\Delta H_{rxn} \doteq -160\ kJ/mol}$

$\checkmark$ 2 SF from ΔT data

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b) (1 mark) Is work done on/by the system during this reaction? Explain with a few key words.

H_2 gas $^{\checkmark\checkmark}$ is released, thus volume $^{\checkmark\checkmark}$ expands ⟹ work is done (of system) $\checkmark$ BY SYSTEM.

1

To expand, the system must push against the atmosphere, thus it expends energy (performs work). $\boxed{W = -P\Delta V}$
i.e. $W < 0$

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See Kotz Ch 14 Example 14.9 ← analogous ΔTmp example.

**# 4. (8 marks)** Imagine you are studying a complex metal-containing compound with formula: $Co(NH_3)_6Cl_3$. You wish to learn if this compound is covalent (*i.e.*, nonelectrolyte) or if it contains ions (*i.e.*, electrolyte), so you perform the following experiment:

- You prepare an aqueous solution of well-defined concentration: 0.00207 M = $\frac{mol}{L}$ molarity of compound
- You carefully measure the solution's osmotic pressure at 298 K: 0.201 atm

Use this data and relevant reference data from the information page to:

(1) determine the osmotic pressure expected if the compound is a nonelectrolyte
(2) determine the observed van't Hoff factor, i, of this compound using the data above
(3) conclude whether the compound is covalent or if it contains ions.

Show all calculations and include brief explanatory comments.

$$Co(NH_3)_6Cl_3\ (aq) \longrightarrow \text{molecules}_{(aq)}\ ?\quad (i=1)$$
$$\text{compound} \qquad\qquad \text{ions}_{(aq)}\ ?\quad (i>1)$$
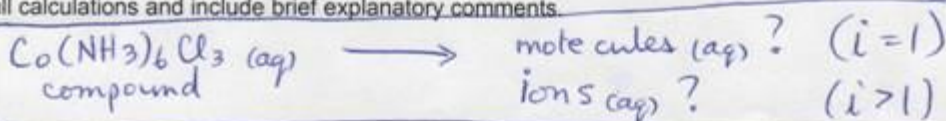
(1) If non-electrolyte : dissolved compound remains as intact molecules $(i=1)$

$$\pi V = i\,n\,R T$$

3.5 $\pi = i\left(\frac{n}{V}\right)RT \Rightarrow \pi = (1)\left(0.00207\ \frac{mol}{L}\right)\left(0.08206\ \frac{L\cdot atm}{mol\cdot K}\right)(298K)$

$$\therefore \pi = 0.05062\ atm$$

← expected osmotic pressure for non-electrolyte.

(2) Observed : higher osmotic pressure than this!

$$\frac{\pi_{obs}}{\pi_{non-el}} = \frac{0.201\ atm}{0.05062\ atm} \doteq 3.97 \approx 4\times \text{ higher than expected } (i=1)$$

3   thus, $i = 4$!

Alternate route (direct...)
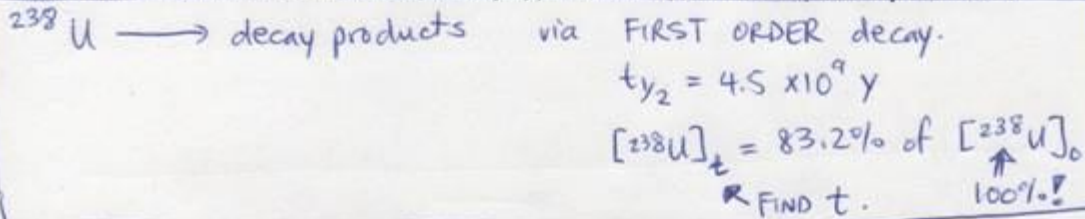$\pi = i\left(\frac{n}{V}\right)RT$ where n/V is compound concentration

$\therefore i = \dfrac{\pi}{\left(\frac{n}{V}\right)RT} = \dfrac{0.201\ atm}{\left(0.00207\ \frac{mol}{L}\right)\left(0.08206\ \frac{L\cdot atm}{mol\cdot K}\right)(298K)} \doteq 3.97 = 4$!

(3) Because the osmotic pressure was higher than a non-electrolyte would
1.5 yield at this concentration, the compound must actually dissociate into IONS when it dissolves. Four ions are produced per unit:

$$Co(NH_3)_6Cl_3\ (aq) \longrightarrow Co(NH_3)_6^{3+}\ _{(aq)} + 3\ Cl^-\ _{(aq)}$$

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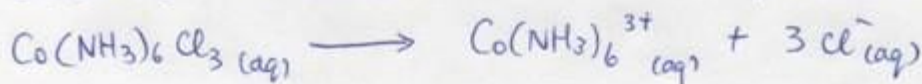
 # 5. (5 marks) Geologists can estimate the age of ancient rocks by their uranium-238 content. The radioactive U-238 is incorporated in the rock as it hardens and then decays with first-order kinetics and half-life of 4.5 billion years (*i.e.*, 4.5×10^9 years). The amount of U-238 present when the rock formed can be deduced by the quantities of U-238 decay products present in the rock; this original amount of U-238 is then compared to the amount currently contained in the rock to estimate the rock's age.

Suppose a rock is found to contain 83.2% of the U-238 it contained when it was formed. How old is the rock? Your answer must include calculations (not only approximations) and brief explanatory comments.

$^{238}U \longrightarrow$ decay products   via   FIRST ORDER decay.

$$t_{1/2} = 4.5 \times 10^9 \, y$$

$$[^{238}U]_t = 83.2\% \text{ of } [^{238}U]_o$$

$$\swarrow \text{FIND } t. \qquad 100\%!$$

For first order process $\ln [^{238}U]_t = \ln [^{238}U]_o - kt$

So: find k using $t_{1/2}$

$$t_{1/2} = \frac{\ln 2}{k} \checkmark$$

1.5

$$\therefore k = \frac{\ln 2}{4.5 \times 10^9 \, y} \checkmark \doteq 1.54 \times 10^{-10} \, y^{-1} \checkmark$$

units worth 0.25

derived from...
after $t_{1/2}$ has passed

$$\ln\left(\frac{[^{238}U]_o}{2}\right) = \ln [^{238}U]_o - kt_{1/2}$$

$$\ln\left(\tfrac{1}{2}\right) = -kt_{1/2}$$

$$\therefore t_{1/2} = \frac{\ln 2}{k}$$

Now: use integrated rate law

$$\checkmark \ln [^{238}U]_t = \ln [^{238}U]_o - (1.54 \times 10^{-10} \, y^{-1})t$$

$$\ln \frac{[^{238}U]_t}{[^{238}U]_o} = -(1.54 \times 10^{-10} \, y^{-1})t$$

3.5

$$\ln\left(\frac{83.2}{100}\right) = -1.54 \times 10^{-10} \, y^{-1} \, t$$

$$\therefore t = \frac{-0.18392}{1.54 \times 10^{-10} \, y^{-1}} \quad \checkmark \text{ math}$$

$$= 1194304144 \, y \quad (2SF)$$

$$t \doteq 1.2 \times 10^9 \, y \checkmark \Leftarrow \text{ age of rock} = 1.2 \text{ billion years!}$$

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similar to age of rocks = in the Laurentian typical Canadian Shield rocks: 540 million – 4.5 billion years old.

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✓ = 1   ✗ = 0.5   ✗ 0.25 points...

 # 6. (9 marks) Nitrogen dioxide, a pollutant in the atmosphere, can combine with water to form nitric acid. One of the possible reactions occurring in clouds is shown below.

$$3\,NO_2(g) + H_2O(\ell) \rightarrow 2\,HNO_3(aq) + NO(g)$$
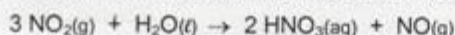
a) (7 marks) Calculate the Gibbs free energy change for this reaction at 298 K. Show full calculations. Is this reaction <u>spontaneous</u> at this temperature? Explain very briefly.

To be spontaneous: $\Delta G° = (\Delta H° - T\Delta S°) < 0$
free energy released.

SF limit by # decimal places

Thermodynamic data at 298 K			
Substance	$\Delta H_f°$ (kJ/mol)	$S°$ (J/mol·K)	
$NO_2(g)$	33.1	240.04	x 3
$H_2O(\ell)$	-285.83	69.95	x 1
$HNO_3(aq)$	-207.36	146.4	x 2
$NO(g)$	90.29	210.76	x 1

So, calculate $\Delta H°$ & $\Delta S°$ from data :

$\Delta H°_{rxn} = \sum n \Delta H_f°\ products - \sum n \Delta H_f°\ reactants$

2.25

$= \left[2\,mol\left(-207.36\,\tfrac{kJ}{mol}\right) + 1\,mol\left(90.29\,\tfrac{kJ}{mol}\right)\right] - \left[3\,mol\left(33.1\,\tfrac{kJ}{mol}\right) + 1\,mol\left(-285.83\,\tfrac{kJ}{mol}\right)\right]$

$= -324.43\ kJ - (-186.53\ kJ)$ ← SF: keep 1 decimal place (subtraction rules)

$= -137.90\ kJ$ ← exothermic rxn, releases heat to surroundings (enthalpically favourable)
   NOT per mol (cancels)

$\Delta S°_{rxn} = \left[2\,mol\left(146.4\,\tfrac{J}{mol·K}\right) + 1\,mol\left(210.76\,\tfrac{J}{mol·K}\right)\right] - \left[3\,mol\left(240.04\,\tfrac{J}{mol·K}\right) + 1\,mol\left(69.95\,\tfrac{J}{mol·K}\right)\right]$

2.25

$= +503.56\ J/K - (790.08\ J/K)$ ← SF keep 1 decimal place

$= -286.52\ J/K$ ← entropically unfavourable, disorder of system ↓
   NOT per mol (cancels)

Thus: $\Delta G°_{rxn} = \Delta H°_{rxn} - T\Delta S°_{rxn}$ energy unit MUST match (ΔH & ΔS ...) both kJ or both J

$= -137.90\ kJ - (298\,K)(-0.28652\ kJ/K)$

2.5

$= -137.9\ kJ + 85.383\ kJ$] SF: addition rules keep 1 decimal place

$= -52.5\ kJ$ not per mol

SF errors -0.25

thermodynamically favourable (spontaneous fwd) entropy of UNIVERSE increases if this rxn occurs

b) (2 marks) If the quantity of NO_2 that reaches the clouds is constant throughout the year (*not true...*), could the following statement be true? Explain briefly.

"Nitrogen dioxide contributes more to acid rain in the summer months."   REALLY not true

NOTE: ① this rxn is NOT the only source of acid rain
② more NO_2 is generated in summer, so more does reach clouds (higher temperatures)

2

If the same amount of NO_2 reaches the clouds, and the same amount of water (or, excess in any case) is available, then the reaction's product yield should be determined by the temperature: $\Delta G°_{rxn} = \Delta H°_{rxn} - T\Delta S°_{rxn}$. This reaction is entropically unfavourable ($\Delta S°_{rxn} < 0$), so it will be LESS product-favoured at higher temperatures, i.e. less acid rain via NO_2.

9

Why: $\Delta G°_{rxn} = \Delta H°_{rxn} - T\underline{\Delta S°_{rxn}}$ ⊖   ⟹ as T ↑, $-T\Delta S$ becomes ↑ ⊕ ∴ $\Delta G°_{rxn}$ becomes less ⊖.