

F09

LAST NAME: Rogers
FIRST NAME: marking scheme
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!**

Mark breakdown:

Page 2. / 12
Page 3. / 9
Page 4. / 7
Page 5. / 8
Page 6. / 8

TOTAL: / 43 (max. = 44)

PERCENT: %

EARNED toward
FINAL GRADE: / 15

1. (6 marks) CIRCLE THE CORRECT WORDS (in capitals) to make the following statements true.

a) Consider the reaction: $A \rightarrow B + C$. If $[A]_0$ is ^{x2} doubled and the reaction's ^{x4 = 2²} rate quadruples, the reaction is described as being (FIRST ORDER / SECOND ORDER) with respect to reactant A.

b) When a process does not involve work, the first law of thermodynamics requires that the heat flow according to the system is equal in (SIGN / MAGNITUDE) to the heat flow according to the surroundings.

$$q_{\text{sys}} = -q_{\text{surr}} \quad \text{ie: } |q_{\text{sys}}| = |q_{\text{surr}}| \text{ but opposite signs.}$$

c) By comparing their Henry's law constants, k , we can see that helium gas ($k = 3.7 \times 10^{-4} \text{ M/atm}$) is (LESS SOLUBLE / MORE SOLUBLE) water at 30°C than nitrogen gas ($k = 6.0 \times 10^{-4} \text{ M/atm}$). $S_{\text{gas}} = k P_{\text{gas}}$

d) When a temperature decrease causes a solution to contract in volume, its concentration expressed in (MOLALITY / MOLARITY) can increase significantly.

$$\text{molality} = \frac{n_{\text{solute}}}{\text{kg solvent}} \quad \text{vs} \quad \text{molarity} = \frac{n_{\text{solute}}}{V_{\text{solution}}}$$

e) When a car's air bag is activated during an accident, a chemical reaction occurs that rapidly produces gas. Defining this reaction as the system: work is done (BY THE SYSTEM / ON THE SYSTEM).

\hookrightarrow system expands, $\Delta V \uparrow \therefore w = 0$ pushes away surroundings.

f) A 1.0 m aqueous solution of CaCl_2 will have a (LOWER / HIGHER) freezing point than a 1.0 m aqueous solution of KCl .

$$i=2 \quad i=3$$

$$\Delta T_f = i K_f m$$

\uparrow depression \therefore lower if [solute] \uparrow

2. (6 marks) Phosphorus trichloride (PCl_3) is more volatile than arsenic trichloride (AsCl_3) at 25°C .

Note: for this question, point-form explanations are acceptable.

a) Both PCl_3 and AsCl_3 are trigonal pyramidal molecules, and As and P have nearly identical electronegativities. So, what causes AsCl_3 to have stronger intermolecular forces? Explain briefly.

As atoms are larger \therefore more polarizable than P atoms.

\uparrow
below P
on periodic
table...

\therefore larger induced-dipoles can form
 \therefore exaggerates polarity of molecule (transiently)
 \therefore stronger intermolecular forces

b) Define vapour pressure. Which substance has the higher vapour pressure at 25°C ? Explain briefly.

$\checkmark P_{\text{vap}}$ = pressure of vapour that exists above a liquid at equilibrium (in a closed container; rate evaporation = rate condensation).

\checkmark If "more volatile", \Rightarrow more easily vaporized \Rightarrow higher vapour P (weaker intermol. forces)

$\therefore \text{PCl}_3$ higher P_{vap}

c) Define normal boiling point. Which substance has the higher boiling point? Explain your choice.

\checkmark b.p. = temperature at which liquid's vapour P = P_{external} .

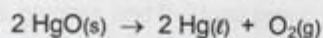
(1 atm for "normal" bp)

Higher bp \Rightarrow require more energy to achieve $P_{\text{vap}} = P_{\text{external}}$

\Rightarrow less volatile (stronger intermol. forces)

$\therefore \text{AsCl}_3$

3. (9 marks) The reaction used by Joseph Priestley to prepare (and discover!) elemental oxygen was:



- a) (6 marks) Is this reaction thermodynamically favourable at 298 K? Include full calculations and brief comments about the meaning of each quantity you calculate.

Thermodynamic data at 298 K		
Substance	ΔH_f° (kJ/mol)	S_f° (J/mol·K)
R HgO(s)	-90.83	70.29
P Hg(l)	0	76.02
P O ₂ (g)	0	205.07

Thermodynamically favourable = spontaneous.
i.e. find $\Delta G^\circ_{\text{rxn}}$ at 298 K.

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}} \quad \text{where calculate } \Delta H^\circ_{\text{rxn}} \text{ \& } \Delta S^\circ_{\text{rxn}} \text{ via Hess' law.}$$

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= [2 \text{ mol}(0 \text{ kJ/mol Hg}) + 1 \text{ mol}(0 \text{ kJ/mol O}_2)] - [2 \text{ mol}(-90.83 \text{ kJ/mol HgO})] \\ &= 0 - (-181.66) \text{ kJ} \\ &= +181.66 \text{ kJ} \Rightarrow \text{endothermic reaction} \end{aligned}$$

prod. - reactants ✓
mole scaling ✓
math ✓

$$\begin{aligned} \Delta S^\circ_{\text{rxn}} &= [2 \text{ mol}(76.02 \text{ J/mol·K}) + 1 \text{ mol}(205.07 \text{ J/mol·K})] - [2 \text{ mol}(70.29 \text{ J/mol·K})] \\ &= 357.11 - 140.58 \text{ J/K} \\ &= +216.53 \text{ J/K} \Rightarrow \text{disorder increases in system} \end{aligned}$$

P-R ✓
n ✓
math ✓

$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &= +181.66 \text{ kJ} - (298 \text{ K})(0.21653 \text{ kJ/K}) \\ &= 181.66 - 64.526 \text{ kJ} \\ &= +117.13 \text{ kJ} \Rightarrow \text{NOT SPONTANEOUS at this temperature} \\ &\quad \text{NOT thermodynamically favourable} \\ &\quad \text{(i.e. low product yield)} \end{aligned}$$

units ✓
equation ✓
math ✓

- b) (1 mark) Is the reaction driven by enthalpy, by entropy, or by neither?

must match (a)

but not at 298 K..

- c) (2 marks) Did Mr. Priestley need to heat up or cool down his reaction mixture in order to obtain a high yield of oxygen gas? Explain. Assume the values of ΔH_{rxn} & ΔS_{rxn} are unaffected by temperature changes.

To get high yield: ideally need $\Delta G^\circ_{\text{rxn}} < 0$! i.e. product-fav'd = spont.

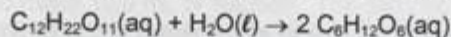
For this reaction: entropically favourable: if $T \uparrow$, yield \uparrow

$$\text{i.e. when } \Delta G = 0, T = \frac{\Delta H_{\text{rxn}}}{\Delta S_{\text{rxn}}} = 839 \text{ K} \approx 566^\circ \text{C}$$

above this T, $\Delta G < 0$ high yield of O₂
below this T, $\Delta G > 0$ low yield of O₂

NOTE: In equilibrium chapter (16), we'll see that if the gas could escape, that would drive the reaction forward to...

4. (7 marks) Sucrose ($C_{12}H_{22}O_{11}$), commonly known as table sugar, breaks down in dilute acid solution into two simpler sugars, glucose and fructose (each with formula $C_6H_{12}O_6$):



aqueous i.e. H₂O present in excess

The data in the first graph were collected for the disappearance of sucrose in 0.50 M aqueous HCl at 23°C. To analyze the reaction kinetics, the other two graphs were plotted and fitted to linear trends (see equations).

a) (1 mark) What is the order of the reaction with respect to sucrose? How did you decide?

✓ • First order: rate = $k[H_2O]^n[sucrose]^1$

✓ • data fits well (linear, $R \approx 1$) to the $\ln[]$ plot i.e. $\ln[]_t = \ln[]_0 - kt$

b) (1 mark) What is the value of the rate constant?

Here, H₂O is in excess, so graph yields an effective rate constant $k_{eff} = k[H_2O]^n$.
slope = $-k_{eff} \Rightarrow k_{eff} = 0.0037 \text{ min}^{-1}$

c) (5 marks) How long will it take for 75% of the sucrose in a 0.075 M acidic sucrose solution to be broken down into glucose and fructose? If you could not solve parts a-b, use the following assumptions (possibly wrong...): 1st order, $k = 5 \text{ s}^{-1}$.

Use 1st order integrated rate law: ✓

check the numbers:

$$\ln[sucrose]_t = \ln[sucrose]_0 - kt$$

amount remaining once 75% broken down i.e. 25% of 0.075 M ✓
initial concentration i.e., 0.075 M = all.

$$\ln(0.25) = \ln(1.0) - k_{eff} t$$

$$\ln 0.25 - \ln 1 = -k_{eff} t$$

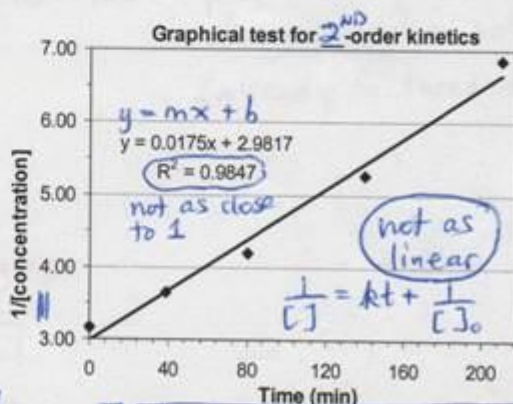
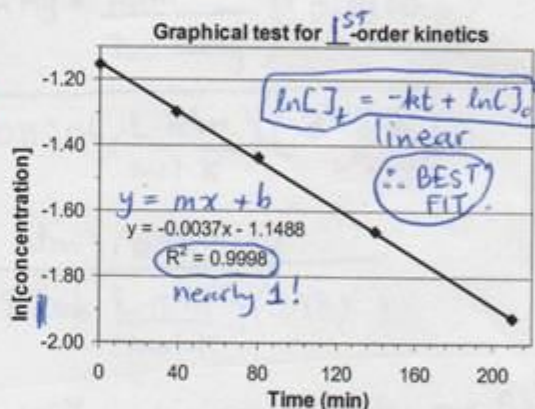
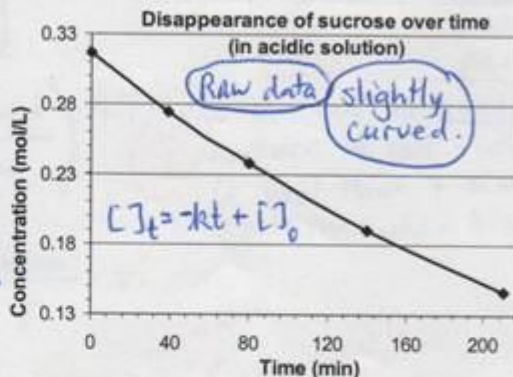
$$\ln\left(\frac{0.25}{1}\right) = -k_{eff} t$$

$$-1.3863 = -(0.0037 \text{ min}^{-1}) t$$

$$\therefore t = 374.67$$

$$\therefore t \approx 370 \text{ min (2SF)}$$

It will take approximately 370 min. = 6.2 h



Using the "wrong" data: $t = 0.28 \text{ s}$

but should then be 1SF (k...)
 $\therefore t = 0.3 \text{ s}!$

5. (8 marks) Imagine you are working in a lab that studies the active ingredients in herbal medicines. You take 53.0 mg of an electrolyte (previously determined to have $i = 2$) isolated from throat lozenges and dissolve it in enough water to make 10.0 mL of solution. The osmotic pressure of the resulting solution at 25°C was 1034 mm Hg. What is the molar mass of this compound?

Provide full calculations and brief explanatory comments. (worth 1)

+275
+273
298 K
now 3SF!

Osmotic pressure $\Pi = \left(\frac{n_{\text{solute}}}{V_{\text{solution}}} \right) RT$ where $n_{\text{solute}} = \frac{\text{total dissolved particles}}$

i.e. $\Pi = \left(i \frac{n_{\text{compound}}}{V_{\text{solution}}} \right) RT$ to correct for "electrolyte" nature of our solute i.e. fact that it dissociates into ions when dissolved.

APPROACH:

Find moles of compound so can relate to its mass, + find MM!

$$\begin{aligned} n_{\text{compound}} &= \frac{\Pi \cdot V_{\text{solution}}}{i \cdot R T} \\ &= \frac{(1034 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}) (0.0100 \text{ L})}{(2) (0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}) (298 \text{ K})} \\ &= \frac{(1.3605 \text{ atm}) (0.0100 \text{ L})}{(2) (0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}) (298 \text{ K})} \end{aligned}$$

$\therefore n_{\text{compound}} = 2.782 \times 10^{-4} \text{ mol}$ provided by our 53.0 mg of compound in solution. (already factored out i)

Thus: since $n = \frac{m}{\text{MM}}$,

$\text{MM} = \frac{m}{n}$

$= \frac{0.0530 \text{ g}}{2.782 \times 10^{-4} \text{ mol}}$

$= 190.51 \text{ g/mol}$

NOTE: accepted 1SF too, since $i=2$ given in question is implied to be an experimental measurement too!

$\therefore \text{MM} \approx 191 \text{ g/mol}$ (3SF, from m & V data)

(math/logical answer) feasible MM?

-0.25 if use 2SF... NOTE: 25°C used as 298 K = 3SF!!

8

6. (8 marks) Chlorofluorocarbons (CFCs, tradename *freon*) have long been used as heat transfer fluids in air conditioners, but they will be banned as of 2010 because they are known to damage the ozone layer. However, if your air conditioner is more than 10 years old, it may contain the chlorofluorocarbon CCl_2F_2 .

Data for CCl_2F_2 : boiling point $\text{b.p.} = -29.8^\circ\text{C}$ PHASE CHANGES DURING OUR WARMING EXPERIMENT.
 heat of vaporization $\Delta H^\circ_{\text{vap}} = +20.11 \text{ kJ/mol}$
 molar heat capacity $C_m = 117.2 \text{ J/mol}\cdot\text{K}$ for $\text{CCl}_2\text{F}_2(\text{g})$ & $72.3 \text{ J/mol}\cdot\text{K}$ for $\text{CCl}_2\text{F}_2(\text{l})$.

How much heat is absorbed when 20.0 g of CCl_2F_2 is warmed from -35°C to $+35^\circ\text{C}$?

Provide full calculations with brief explanatory comments at each step.



1.5 Our warming experiment involves 3 stages:

- ✓ ① warming liquid -35° to -29.8°C $+5.2^\circ\text{C}$ change
- ✓ ② boiling liquid at -29.8°C
- ✓ ③ warming vapour -29.8°C to $+35^\circ\text{C}$ $+64.8^\circ\text{C}$ change

✓ mole calc. 0.1654 mol

Thus, total heat absorbed is the sum over all 3 stages:

$$\checkmark q_{\text{total}} = q_{\text{①}} + q_{\text{②}} + q_{\text{③}}$$

For clarity, I will calculate each q separately, then add them.

WARM UP LIQUID $q_{\text{①}} = C_{m(\text{l})} \times n_{(\text{l})} \times \Delta T_{(\text{l})} = \left(72.3 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) \left(\frac{20.0 \text{ g}}{120.91 \text{ g/mol}}\right) (+5.2 \text{ K}) = 62.19 \text{ J}$

BOIL LIQUID $q_{\text{②}} = \Delta H^\circ_{\text{vap}} \times n_{(\text{l})} = \left(+20.11 \frac{\text{kJ}}{\text{mol}} \times 1000 \frac{\text{J}}{\text{kJ}}\right) (0.1654 \text{ mol}) = 3326.44 \text{ J}$

WARM UP VAPOUR $q_{\text{③}} = C_{m(\text{g})} \times n_{(\text{g})} \times \Delta T_{(\text{g})} = \left(117.2 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right) (0.1654 \text{ mol}) (+64.8 \text{ K}) = 1256.14 \text{ J}$

$$\begin{aligned} q_{\text{TOTAL}} &= 62.19 + 3326.44 + 1256.14 \text{ J} \\ &= 4644.77 \text{ J} \\ &= 4.645 \text{ kJ} \end{aligned}$$

$$\therefore q_{\text{TOTAL}} = 4.6 \text{ kJ}$$

Thus, 4.6 kJ of heat was absorbed during this warming experiment.

8

2 SF due to ΔT of liquid...