

This set of review questions is designed to help you in preparation of the *second* midterm exam, which will include the following three topics: (1) **thermochemistry** (Hess's law, bond dissociation energies and calorimetry); (2) **gases and the atmosphere** (ideal gas law, atmosphere constituents, greenhouse gases and global warming) and (3) **chemical kinetics** (rate of reaction, order of reaction, rate constant, first-, second- and pseudo-first order reaction, lifetimes, residence times and half-lives). These questions are intended to provide you with practice at solving quantitative problems. It is in your best interests to work through **all** these questions independently *before the exam*.

Complete answers to these review questions are placed in a binder which is available at the Reserve Desk in the MacLaughlin Library. Remember that photocopying the answers to the questions **in no way** substitutes for working through the questions on your own!

## PART A Thermochemistry (II)

1. Calculate the average O-H bond energy from the following data:
- |  |          |                               |         |
|--|----------|-------------------------------|---------|
| $\Delta H_f^\circ [\text{H}_2\text{O}(\text{R})]$      | ! 286 kJ | Bond Energy (O <sub>2</sub> ) | +495 kJ |
| $\Delta H_{\text{vap}} [\text{H}_2\text{O}(\text{R})]$ | +44 kJ   |                               |         |
| $\Delta H_f^\circ [\text{H}(\text{g})]$                | +218 kJ  |                               |         |

2. Calculate the heat of formation of  $\text{NH}_3(\text{g})$  from the bond energies of:

BE(H-H)	436 kJ mol <sup>-1</sup>
BE(N-N)	946 kJ mol <sup>-1</sup>
BE(N-H)	391 kJ mol <sup>-1</sup>

3. Calculate  $\Delta H^\circ$  for the reaction:  $\text{N}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{NO}(\text{g})$

given that: $\Delta H_f^\circ [\text{NO}(\text{g})]$	90.25 kJ mol <sup>-1</sup>
$\Delta H_f^\circ [\text{O}(\text{g})]$	249.2 kJ mol <sup>-1</sup>
BE(N-N)	946 kJ mol <sup>-1</sup>

4. Given the following heats of formation of:

H(g)	218 kJ mol <sup>-1</sup>
Cl(g)	121 kJ mol <sup>-1</sup>
HCl(g)	! 92 kJ mol <sup>-1</sup>

Calculate the H-Cl bond energy.

5. Given:

<b>Substance:</b>	H(g)	Br(g)	HBr(g)	Br <sup>l</sup> (aq)	Br <sub>2</sub> (g)
<b><math>\Delta H_f^\circ</math> (kJ mol<sup>-1</sup>):</b>	217	111.8	! 36.2	! 120.9	30.7

Give values in kJ mol<sup>-1</sup> for each of the following quantities:

- (a)  $\Delta H^\circ$  for the reaction:  $\text{H}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{HBr}(\text{g})$   
 (b) the molar (H-Br) bond energy  
 (c) the molar (Br-Br) bond energy

6. Given the following data:

<b>Bond Energies (kJ mol<sup>-1</sup>)</b>		<b>Enthalpies of Formation (kJ mol<sup>-1</sup>)</b>	
(O-H)	464	OH <sup>l</sup> (aq)	! 229.9
(H-H)	435	H <sub>2</sub> O(l)	! 285.8
		H <sub>2</sub> O(g)	! 241.8

Calculate  $\Delta H$  for each of the following reactions:

- |  |   |
|--|---|
| (a) $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{R})$ | (d) $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{R})$ |
| (b) $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$ | (e) $2 \text{H}(\text{g}) \rightarrow \text{H}_2(\text{g})$                                   |
| (c) $2 \text{H}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$               | (f) $2 \text{H}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{R})$      |

7. When 2.50 g sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$ , was burned in excess  $\text{O}_2(\text{g})$  in a bomb calorimeter surrounded by 1.00 kg water, the temperature rose from 18.22°C to 22.73°C. The heat capacity of the calorimeter was given as 4.98 kJ K<sup>-1</sup>. Calculate the amount of energy which would be released (in MJ) on combustion of 1.00 mole sucrose under these conditions.
8. In a calorimetry experiment, 50.0 g of HCl whose concentration is 2.04 mol kg<sup>-1</sup> is mixed with 50.0 g of NaOH solution whose concentration is 2.13 mol kg<sup>-1</sup>. The specific heat of the resulting solution is 3.90 J °C<sup>-1</sup> g<sup>-1</sup>. The temperature of the mixture rises from 22.1°C to 37.0°C. Calculate the enthalpy change for the reaction.
9. Our bodies can use glucose,  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$  (180.2 g mol<sup>-1</sup>), as a fuel. The heat of combustion of glucose is ! 2.820 × 10<sup>3</sup> kJ mol<sup>-1</sup>. The human body has a specific heat of 4.18 J deg<sup>-1</sup> g<sup>-1</sup>.
- (a) How many grams of glucose would an 80.0 kg person need to consume to raise the body temperature from 36.00 to 39.0°C? (Assume that all the energy goes to warm the body.)  
 (b) Use the answer from Part (a), calculate how much CO<sub>2</sub>(g) will be released to the atmosphere as a result of the glucose metabolism in the body. (Assume glucose metabolism to be a combustion reaction.)
10. (a) Calculate  $\Delta H^\circ$  for the reaction:  $\text{CO}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{O}(\text{g})$ .  
 (b) Estimate the maximum wavelength of light capable of causing this reaction.  
 (c) To what part of electromagnetic spectrum does light of this wavelength belong?  
 (d) Do you expect this reaction to be possible in the troposphere or stratosphere?

**PART B Gases and the Atmosphere**

- Express  $2.0 \times 10^{14}$  atm of hydroxyl radical at 25°C in units of:
  - ppmv
  - $\text{mol L}^{-1}$
  - $\text{molec cm}^{-3}$
- What mass of benzene,  $\text{C}_6\text{H}_6$ , must be burned to produce 5.42 L of gaseous  $\text{CO}_2$  measured at  $9.75 \times 10^4$  Pa and 22°C?
- A brownish gas has density  $3.67 \text{ g L}^{-1}$  at 22.7°C and 98 kPa. Chemical analysis showed that the gas is a dinitrogen-containing oxide. What is the molar mass and the molecular formula of the gas?
- The vapour pressure of water at 27°C is 3.57 kPa. Calculate the mass of water in a room which measures  $10.0 \text{ ft} \times 12.0 \text{ ft} \times 8.00 \text{ ft}$  when the vapour pressure of water is 72.0%. (1 foot = 12 inches, 1 inch = 2.54 cm)
- Calculate the maximum mass of quicklime, CaO, which reacts completely with excess ammonium chloride solution to yield 25.0 L of ammonia gas at 0.850 atm and 21°C.
 
$$\text{CaO(s)} + 2 \text{NH}_4\text{Cl(aq)} \div 2 \text{NH}_3(\text{g}) + \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O(l)}$$
- Potassium permanganate and hydrogen chloride react in aqueous solution according to the equation
 
$$2 \text{KMnO}_4(\text{aq}) + 16 \text{HCl(aq)} \div 2 \text{KCl(aq)} + 2 \text{MnCl}_2(\text{aq}) + 8 \text{H}_2\text{O(l)} + 5 \text{Cl}_2(\text{g})$$
 What volume of  $\text{Cl}_2(\text{g})$  measured at 25.0°C and 202.3 kPa would be produced by reaction of 50.0 mL of 1.00 M  $\text{KMnO}_4$  solution and 100.0 mL of 5.00 M HCl?
- $\text{CCl}_4(\text{l})$  is produced from  $\text{CS}_2(\text{l})$  by reaction with  $\text{Cl}_2(\text{g})$ :
 
$$4 \text{CS}_2(\text{l}) + 8 \text{Cl}_2(\text{g}) \div 4 \text{CCl}_4(\text{l}) + \text{S}_8(\text{s})$$
 When 10.0 kg of  $\text{CS}_2(\text{l})$  react with  $10^4$  L of  $\text{Cl}_2(\text{g})$  at 1 atm and 400 K, 15.0 kg of  $\text{CCl}_4(\text{l})$  are produced. What is the percent yield in this preparation?
- Calculate the volume of  $\text{H}_2(\text{g})$  measured at STP which will be produced by reaction of 0.954 g LiH(s) with 1.26 g of  $\text{H}_2\text{O(l)}$  according to the reaction:
 
$$\text{LiH(s)} + \text{H}_2\text{O(l)} \div \text{LiOH(s)} + \text{H}_2(\text{g})$$
- Discuss fossil and biomass fuels (so called "dirty" fuel). Reason?
  - Discuss hydrogen gas as a source of "clean" (?) fuel.
  - Explain the processes that cause the natural greenhouse effect. What atmospheric gases are responsible for the greenhouse effect? What gases are involved in the enhanced greenhouse effect? Explain the phenomenon and its possible consequences.

**PART C Chemical Kinetics (I)**

- The rate equation for the reaction  $\text{A} \div \text{B} + \text{C}$  is expressed in terms of the concentration of A only. The rate of disappearance of A is  $0.0080 \text{ mol L}^{-1} \text{ s}^{-1}$  when  $[\text{A}]$  is  $0.20 \text{ mol L}^{-1}$ . Calculate a value for the rate constant  $k$  if the reaction is:
  - first order in A
  - second order in A
- For the reaction  $2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \div 2 \text{NOCl}(\text{g})$ , the rate equation is second-order in  $[\text{NO}]$ , first-order in  $[\text{Cl}_2]$  and third order overall. Compare the initial rate of reaction of a mixture of  $0.020 \text{ mol NO}(\text{g})$ , and  $0.020 \text{ mol Cl}_2(\text{g})$  with:
  - the rate when half the  $\text{NO}(\text{g})$  has been consumed
  - the rate when half the  $\text{Cl}_2(\text{g})$  has been consumed
  - the rate when two-thirds the  $\text{NO}(\text{g})$  has been consumed
- For the reaction  $\text{A} + \text{B} \div \text{products}$ , the initial rates of reaction at various concentrations ( $\text{mol L}^{-1}$ ) of A and B are:
 

	$[\text{A}]$	$[\text{B}]$	rate ( $\text{mol L}^{-1} \text{ s}^{-1}$ )
(1)	0.20	0.020	$1.6 \times 10^{13}$
(2)	0.30	0.020	$2.4 \times 10^{13}$
(3)	0.30	0.030	$3.6 \times 10^{13}$

  - Calculate the order with respect to A and B, and determine the overall order.
  - Calculate a value for the rate constant.
- Thermal decomposition of acetone ( $\text{C}_3\text{H}_6\text{O}$ ) is first-order, with a half-life of 80 seconds at 600°C. In what time will 1/10 of an acetone sample decompose at 600°C?
- A reaction:  $\text{A} \rightarrow \text{B}$  is first-order in A and first-order overall. It requires 60.0 min for 75.0% of A to react. The rate constant for this process in units of  $\text{min}^{-1}$  is:
  - $4.79 \times 10^{13}$
  - $1.00 \times 10^{13}$
  - $1.16 \times 10^{12}$
  - $1.73 \times 10^{12}$
  - $2.31 \times 10^{12}$
- The decomposition of  $\text{N}_2\text{O}_5(\text{g})$  is a first-order reaction with  $k = 1.45 \times 10^{13} \text{ s}^{-1}$ .

- (a) Calculate the half-life,  $t_{1/2}$ , of  $\text{N}_2\text{O}_5(\text{g})$ .  
 (b) Calculate the percent of the original  $\text{N}_2\text{O}_5(\text{g})$  which has decomposed after 10.0 minutes.  
 (c) How long will it take for the concentration of  $\text{N}_2\text{O}_5(\text{g})$  to drop from the initial value of  $8.90 \times 10^{14} \text{ mol L}^{-1}$  to  $6.90 \times 10^{14} \text{ mol L}^{-1}$ ?
7. (a) Consider the first-order reaction:  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$ .  
 The initial concentration of  $\text{N}_2\text{O}_4(\text{g})$  is  $0.88 \text{ mol L}^{-1}$ .  
 (i) Calculate the rate constant,  $k$ , when the initial rate is  $1.14 \times 10^{12} \text{ mol L}^{-1} \text{ s}^{-1}$ .  
 (ii) How long will it take to form  $0.22 \text{ mol L}^{-1} \text{NO}_2$ ?  
 (iii) Calculate the concentration of  $\text{NO}_2(\text{g})$ , in  $\text{mol L}^{-1}$ , after 45 seconds.  
 (b) Solve the above question this time assuming that it is a second-order reaction.
8. For the decomposition of  $\text{NOCl}$ , the following data were obtained at  $100^\circ\text{C}$ .

<u>time (s)</u>	<u>[NOCl] (mol L<sup>-1</sup>)</u>
0	0.500
10	0.357
20	0.278
30	0.227

From these data,

- (a) determine if the reaction is first or second order  
 (b) determine the rate constant
9. The hydrolysis of ethyl acetate (EA) by hydroxide ion is a second-order reaction (first-order in each reactant), having  $k = 0.84 \text{ L mol}^{-1} \text{ s}^{-1}$  at  $54^\circ\text{C}$ .  
 $\text{EA} + \text{OH}^- = \text{Products}$   
 (a) Calculate the pseudo-first order rate constant if  $[\text{OH}^-]$  is constant at  $0.015 \text{ mol L}^{-1}$ .  
 (b) Calculate the half-life of ethyl acetate under the conditions of Part (a).
10. Calculate the rate constant and half-life corresponding to residence time  $2.3 \times 10^2 \text{ s}$ .
11. Excited oxygen atoms suffer two fates in the atmosphere  
 (i)  $\text{O}^* \rightleftharpoons \text{O}(\text{ground state})$   $k_1 = 7.2 \times 10^8 \text{ s}^{-1}$   
 (ii)  $\text{O}^* + \text{H}_2\text{O} \rightleftharpoons 2 \text{OH}$   $k_2 = 2.2 \times 10^{10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
- Both rate constants are given at  $25^\circ\text{C}$ , at which temperature the saturated vapour pressure of water is 3.2 kPa. If the relative humidity is 75%, calculate the lifetime of the excited oxygen atom.
12. In the first-order reaction:  $2 \text{A} \rightleftharpoons \text{B} + \text{C}$ , it was observed that the initial concentration of **A** decreases to 80% of its original concentration in 175 min. How much time would be needed for it to decrease to 20% of its original value?
13. For the first-order reaction:  $\text{A} \rightleftharpoons 3 \text{B} + \text{C}$ , when  $[\text{A}_0] = 0.015 \text{ mol L}^{-1}$ , the concentration of **B** increases to  $0.020 \text{ mol L}^{-1}$  in 3.0 min.  
 (a) What is the rate constant for the reaction?  
 (b) How much more time would be needed for the concentration of **B** to increase to  $0.040 \text{ mol L}^{-1}$ ?
14. In a second-order reaction, it takes 30.0 min for the concentration of reactant **A** to drop to 0.30 M. The half-life of **A** is 90.0 min.  
 (a) Calculate the rate constant for the reaction.  
 (b) Determine the initial concentration of **A**.

## ANSWERS

## PART A Thermochemistry (II)

6. +463 kJ  
 7. ! 46 kJ mol<sup>-1</sup>  
 8. ! 632 kJ mol<sup>-1</sup>  
 9. +431 kJ mol<sup>-1</sup>  
 10. (a) +84.7 kJ mol<sup>-1</sup> (b) +365 kJ mol<sup>-1</sup> (c) +192.9 kJ mol<sup>-1</sup>  
 11. (a) ! 285.8 kJ mol<sup>-1</sup> (b) +241.8 kJ mol<sup>-1</sup> (c) ! 928 kJ mol<sup>-1</sup>  
 (d) ! 55.9 kJ mol<sup>-1</sup> (e) ! 435 kJ mol<sup>-1</sup> (f) ! 972 kJ mol<sup>-1</sup>  
 12. ! 5.66 MJ heat evolved  
 13. ! 57.0 kJ mol<sup>-1</sup>  
 14. (a) 64.1 g (b) 93.9 g  
 15. (a) 532.154 kJ mol<sup>-1</sup> (b) 230 nm (c) UV spectrum (d) stratosphere

## PART B Gases and the Atmosphere

1. (a)  $2.0 \times 10^8$  ppmv (b)  $8.2 \times 10^{16}$  mol L<sup>-1</sup> (c)  $4.9 \times 10^5$  molec cm<sup>-3</sup>  
 2. 2.81 g  
 3. 92 g mol<sup>-1</sup>; N<sub>2</sub>O<sub>4</sub>  
 4. 505 g  
 5. 24.7 g  
 6. 1.53 L  
 7. 74.2%  
 8. 1.57 L

## PART C Chemical Kinetics (I)

1. (a) 0.040 s<sup>-1</sup> (b) 0.20 L mol<sup>-1</sup> s<sup>-1</sup>  
 2. (a) 3/16 (b) 0 (c) 2/27  
 3. (a) rate %[A]; rate %[B]; rate =  $k[A][B]$  (second-order overall) (b) 0.40 L mol<sup>-1</sup> s<sup>-1</sup>  
 4. 12 s  
 5. e  
 6. (a) 478 s (b) 58.1% (c) 176 s  
 7. (a) (i)  $1.3 \times 10^{12}$  s<sup>-1</sup> (ii) 10 s (iii) 0.78 mol L<sup>-1</sup>  
 (b) (i)  $1.5 \times 10^{12}$  L mol<sup>-1</sup> s<sup>-1</sup> (ii) 11 s (iii) 0.65 mol L<sup>-1</sup>  
 8. (a) second order (b)  $8.01 \times 10^{12}$  L mol<sup>-1</sup> s<sup>-1</sup>  
 9. (a)  $1.3 \times 10^{12}$  s<sup>-1</sup> (b) 55 s  
 10. 43 s<sup>-1</sup>;  $1.6 \times 10^{12}$  s  
 11.  $1.2 \times 10^9$  s  
 12.  $1.26 \times 10^3$  min  
 13. (a) 0.20 min<sup>-1</sup> (b) an additional 8 min is needed  
 14.  $k = 2.8 \times 10^{12}$  M<sup>-1</sup> min<sup>-1</sup>; [A<sub>0</sub>] = 0.40 M