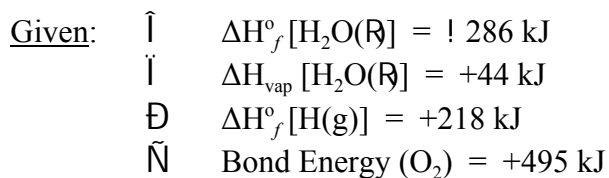
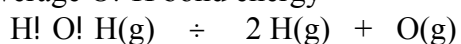


**PART A**  
**QUESTION 1**

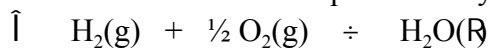


To find: the average O! H bond energy

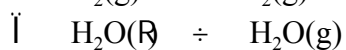


$$\Delta H^\circ_{\text{rxn}} = 2 \times \text{BE}(\text{O! H}) = ?$$

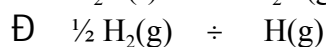
The above data can be represented by the following thermochemical equations:



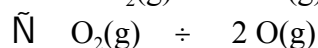
$$\Delta H_f^\circ [\text{H}_2\text{O}(\text{R})] = -286 \text{ kJ}$$



$$\Delta H_{\text{vap}} [\text{H}_2\text{O}(\text{R})] = +44 \text{ kJ}$$

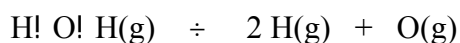
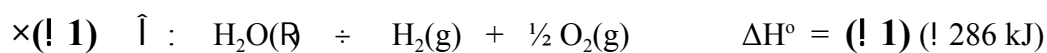


$$\Delta H_f^\circ [\text{H}(\text{g})] = +218 \text{ kJ}$$



$$\text{BE}(\text{O! O}) = +495 \text{ kJ}$$

Using Hess's Law:



$$\Delta H^\circ_{\text{rxn}} = +925.5 \text{ kJ}$$

$$\Delta H^\circ_{\text{rxn}} = 2 \times \text{BE}(\text{O! H})$$

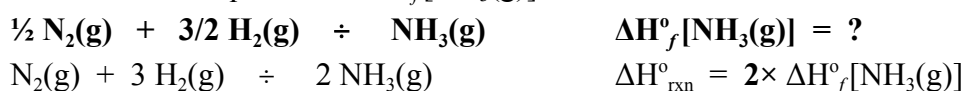
$$\begin{aligned} \text{BE}(\text{O! H}) &= \frac{1}{2} \Delta H^\circ_{\text{rxn}} \\ &= \frac{1}{2} (+925.5 \text{ kJ}) \\ &= +462.75 \text{ kJ} \\ &= \underline{\underline{+463 \text{ kJ}}} \end{aligned}$$

**PART A**  
**QUESTION 2**

Given: 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>

To find: the heat of formation of NH<sub>3</sub>(g),  $\Delta H_f^\circ[\text{NH}_3(\text{g})] = ?$

The thermochemical equation of  $\Delta H_f^\circ[\text{NH}_3(\text{g})]$  is written as:

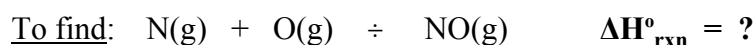
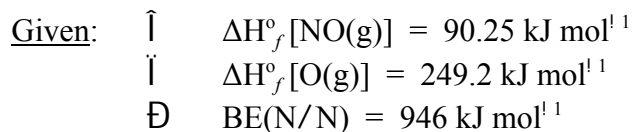


$\text{N}_2(\text{g})$	+	$3 \text{H}_2(\text{g})$	$\div$	$2 \text{NH}_3(\text{g})$	$\Delta H_{\text{rxn}}^\circ = 2 \times \Delta H_f^\circ[\text{NH}_3(\text{g})] = ?$
2 N(g)		$3 \times 2 \text{H}(\text{g})$		$2 \times 3 \text{BE}(\text{N! H})$	
BE(N/N)		$3 \times \text{BE}(\text{H! H})$		$6 \times \text{BE}(\text{N! H})$	
946 kJ mol <sup>-1</sup>		$3 \times (436 \text{ kJ mol}^{-1})$		$6 \times (391 \text{ kJ mol}^{-1})$	

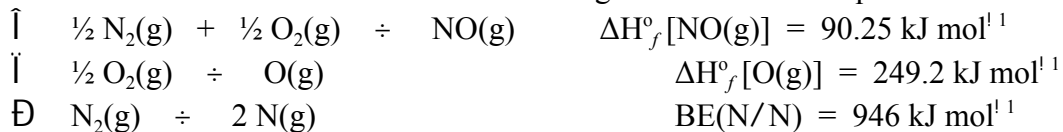
$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= 3 \text{ n BE(reactants)} - 3 \text{ n BE(products)} \\ &= \{\text{BE}(\text{N/N}) + 3 \times \text{BE}(\text{H! H})\} - \{6 \times \text{BE}(\text{N! H})\} \\ &= \{(946 \text{ kJ mol}^{-1}) + 3 \times (436 \text{ kJ mol}^{-1})\} - \{6 \times (391 \text{ kJ mol}^{-1})\} \\ &= -92 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta H_{\text{rxn}}^\circ = 2 \times \Delta H_f^\circ[\text{NH}_3(\text{g})]$$

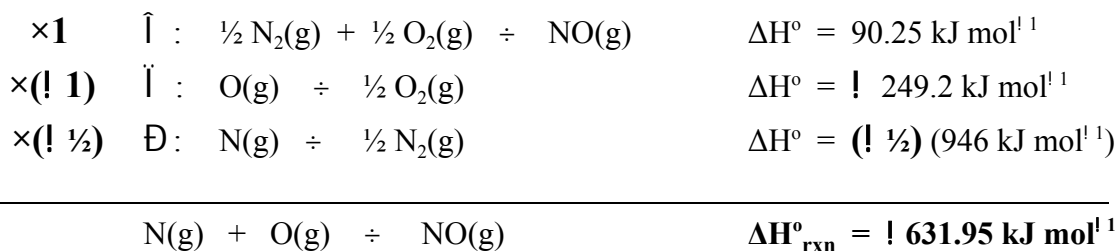
$$\begin{aligned} \Delta H_f^\circ[\text{NH}_3(\text{g})] &= \frac{1}{2} \Delta H_{\text{rxn}}^\circ \\ &= \frac{1}{2} (-92 \text{ kJ mol}^{-1}) \\ &= \underline{\underline{-46 \text{ kJ mol}^{-1}}} \end{aligned}$$

**PART A**  
**QUESTION 3**


The above data can be written as the following thermochemical equations:

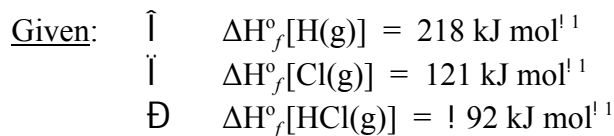


Using Hess's Law:



$\Delta H^\circ$  for the reaction:  $\text{N}(\text{g}) + \text{O}(\text{g}) \div \text{NO}(\text{g})$  is **! 632 kJ mol<sup>-1</sup>**.

**PART A  
QUESTION 4**

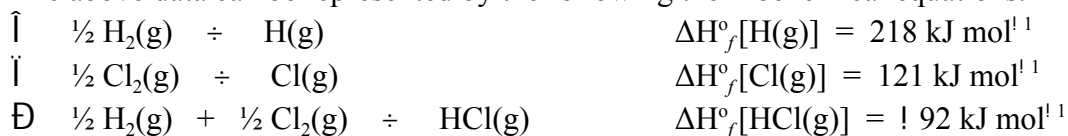


To find: **BE(H-Cl) = ?**

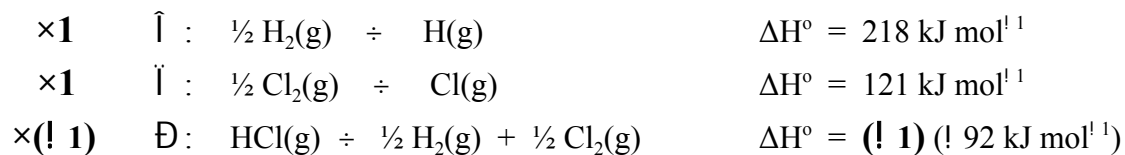
The thermochemical equation of BE(H-Cl) is written as:



The above data can be represented by the following thermochemical equations:



Using Hess's Law:



**OR**

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= 3 n \Delta H_f^\circ(\text{products}) - 3 n \Delta H_f^\circ(\text{reactants}) \\ &= \{\Delta H_f^\circ[\text{H(g)}] + \Delta H_f^\circ[\text{Cl(g)}]\} - \{\Delta H_f^\circ[\text{HCl(g)}]\} \\ &= \{(218 \text{ kJ mol}^{-1}) + (121 \text{ kJ mol}^{-1})\} - \{(-92 \text{ kJ mol}^{-1})\} \\ &= \underline{\underline{+431 \text{ kJ mol}^{-1}}} \end{aligned}$$

**PART A**  
**QUESTION 5**

Given:	$\Delta H_f^\circ[\text{H}(\text{g})] = 217 \text{ kJ mol}^{-1}$	$\Delta H_f^\circ[\text{Br}_2(\text{g})] = 30.7 \text{ kJ mol}^{-1}$
	$\Delta H_f^\circ[\text{Br}(\text{g})] = 111.8 \text{ kJ mol}^{-1}$	$\Delta H_f^\circ[\text{Br}^\cdot(\text{aq})] = 120.9 \text{ kJ mol}^{-1}$
	$\Delta H_f^\circ[\text{HBr}(\text{g})] = 36.2 \text{ kJ mol}^{-1}$	$\Delta H_f^\circ[\text{H}^+(\text{aq})] = 0$

(a)  $\Delta H^\circ$  for the reaction:  $\text{H}^+(\text{aq}) + \text{Br}^\cdot(\text{aq}) \rightarrow \text{HBr}(\text{g})$

$$\begin{aligned}
 \Delta H_{\text{rxn}}^\circ &= \sum n \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants}) \\
 &= \{\Delta H_f^\circ[\text{HBr}(\text{g})]\} - \{\Delta H_f^\circ[\text{H}^+(\text{aq})] + \Delta H_f^\circ[\text{Br}^\cdot(\text{aq})]\} \\
 &= \{36.2 \text{ kJ mol}^{-1}\} - \{0 + 120.9 \text{ kJ mol}^{-1}\} \\
 &= \underline{\underline{+84.7 \text{ kJ mol}^{-1}}}
 \end{aligned}$$

(b) the molar (H-Br) bond energy



$$\begin{aligned}
 \text{BE}(\text{H-Br}) &= \Delta H_{\text{rxn}}^\circ \\
 &= \sum n \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants}) \\
 &= \{\Delta H_f^\circ[\text{H}(\text{g})] + \Delta H_f^\circ[\text{Br}(\text{g})]\} - \{\Delta H_f^\circ[\text{HBr}(\text{g})]\} \\
 &= \{(217 \text{ kJ mol}^{-1}) + (111.8 \text{ kJ mol}^{-1})\} - \{36.2 \text{ kJ mol}^{-1}\} \\
 &= \underline{\underline{+365 \text{ kJ mol}^{-1}}}
 \end{aligned}$$

(c) the molar (Br-Br) bond energy

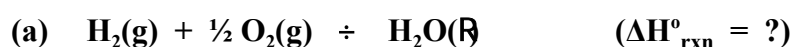


$$\begin{aligned}
 \text{BE}(\text{Br-Br}) &= \Delta H_{\text{rxn}}^\circ \\
 &= \sum n \Delta H_f^\circ(\text{products}) - \sum n \Delta H_f^\circ(\text{reactants}) \\
 &= \{2 \times \Delta H_f^\circ[\text{Br}(\text{g})]\} - \{\Delta H_f^\circ[\text{Br}_2(\text{g})]\} \\
 &= \{(2)(111.8 \text{ kJ mol}^{-1})\} - \{30.7 \text{ kJ mol}^{-1}\} \\
 &= \underline{\underline{+192.9 \text{ kJ mol}^{-1}}}
 \end{aligned}$$

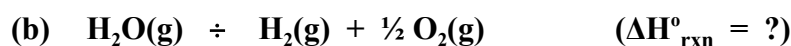
**PART A**  
**QUESTION 6**

At standard states,  
 $\Delta H_f^\circ[\text{H}_2(\text{g})] = 0$   
 $\Delta H_f^\circ[\text{O}_2(\text{g})] = 0$   
 $\Delta H_f^\circ[\text{H}^+(\text{aq})] = 0$

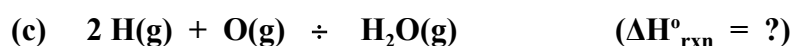
Given:  $\text{BE}(\text{O! H}) = 464 \text{ kJ mol}^{-1}$   $\Delta H_f^\circ[\text{OH}^-(\text{aq})] = -229.9 \text{ kJ mol}^{-1}$   
 $\text{BE}(\text{H! H}) = 435 \text{ kJ mol}^{-1}$   $\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] = -285.8 \text{ kJ mol}^{-1}$   
 $\Delta H_f^\circ[\text{H}_2\text{O}(\text{g})] = -241.8 \text{ kJ mol}^{-1}$



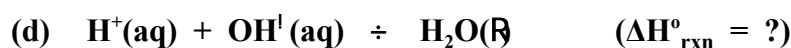
$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] = \underline{\underline{-285.8 \text{ kJ mol}^{-1}}}$$



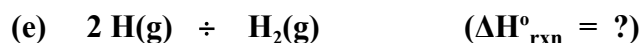
$$\Delta H_{\text{rxn}}^\circ = -\Delta H_f^\circ[\text{H}_2\text{O}(\text{g})] = -(-241.8 \text{ kJ mol}^{-1}) = \underline{\underline{+241.8 \text{ kJ mol}^{-1}}}$$



$$\Delta H_{\text{rxn}}^\circ = -2 \text{ BE}(\text{O! H}) = -2 (464 \text{ kJ mol}^{-1}) = \underline{\underline{-928 \text{ kJ mol}^{-1}}}$$



$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= 3 n \Delta H_f^\circ(\text{products}) - 3 n \Delta H_f^\circ(\text{reactants}) \\ &= \{\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})]\} - \{\Delta H_f^\circ[\text{H}^+(\text{aq})] + \Delta H_f^\circ[\text{OH}^-(\text{aq})]\} \\ &= \{-285.8 \text{ kJ mol}^{-1}\} - \{0 + (-229.9 \text{ kJ mol}^{-1})\} \\ &= \underline{\underline{-55.9 \text{ kJ mol}^{-1}}} \end{aligned}$$



$$\Delta H_{\text{rxn}}^\circ = -\text{BE}(\text{H! H}) = -(435 \text{ kJ mol}^{-1}) = \underline{\underline{-435 \text{ kJ mol}^{-1}}}$$



From (a):	$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	$\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})]$	$-285.8 \text{ kJ mol}^{-1}$
From (b):	$\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$	$-\Delta H_f^\circ[\text{H}_2\text{O}(\text{g})]$	$-(-241.8 \text{ kJ mol}^{-1})$
From (c):	$2 \text{H}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$	$-2 \text{ BE}(\text{O! H})$	$-2 (464 \text{ kJ mol}^{-1})$

---


$$2 \text{H}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H_{\text{rxn}}^\circ = \underline{\underline{-972 \text{ kJ mol}^{-1}}}$$

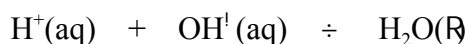


**PART A  
QUESTION 8**

Given: 50.0 g of HCl,  $2.04 \text{ mol kg}^{-1}$   
 50.0 g of NaOH,  $2.13 \text{ mol kg}^{-1}$   
 the specific heat of the resulting solution =  $3.90 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}$   
 $\Delta T = (37.0^\circ\text{C} - 22.1^\circ\text{C}) = +14.9^\circ\text{C} = +14.9 \text{ K}$  ( *exothermic* reaction)

To find: the enthalpy change for the reaction ( $\Delta H_{\text{rxn}}$ )

The NIE for the neutralization reaction of strong acid (HCl) and strong base (NaOH) is written as:



$$n(\text{HCl}) = (50.0 \times 10^{-3} \text{ kg}) (2.04 \text{ mol kg}^{-1}) = 0.102 \text{ mol}$$

$$n(\text{NaOH}) = (50.0 \times 10^{-3} \text{ kg}) (2.13 \text{ mol kg}^{-1}) = 0.1065 \text{ mol}$$

- Notes:
1. HCl is the *limiting reactant*.
  2. total mass of solution = (50.0 g HCl + 50.0 g NaOH) = 100.0 g

$$\begin{aligned} q_{\text{surr}} &= \text{mass} \times \Delta T \times \text{specific heat of solution} \\ &= (100.0 \text{ g}) (+14.9^\circ\text{C}) (3.90 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}) \\ &= +5.811 \times 10^3 \text{ J} \\ &= +5.811 \text{ kJ} \end{aligned}$$

$$q_{\text{rxn}} = q_{\text{surr}} = -5.811 \text{ kJ} \text{ (total heat evolved in the reaction)}$$

$$\begin{aligned} \Delta H_{\text{rxn}} &= -5.811 \text{ kJ} \div 0.102 \text{ mol} \\ &= -56.97 \text{ kJ mol}^{-1} \\ &= \underline{\underline{-57.0 \text{ kJ mol}^{-1}}} \end{aligned}$$

**PART A**  
**QUESTION 9**

Given:  $M(\text{glucose, C}_6\text{H}_{12}\text{O}_6) = 180.2 \text{ g mol}^{-1}$   
 specific heat of human body =  $4.18 \text{ J deg}^{-1} \text{ g}^{-1}$   
 heat of combustion of glucose =  $2.820 \times 10^3 \text{ kJ mol}^{-1}$  (*exothermic* reaction)  
 80.0 kg ( $80.0 \times 10^3 \text{ g}$ ) person  
 $\Delta T = (39.0^\circ\text{C} - 36.0^\circ\text{C}) = +3.0^\circ\text{C} = +3.0 \text{ K} = 3.0 \text{ deg}$  (*exothermic* reaction)

**(a) grams of glucose needed**

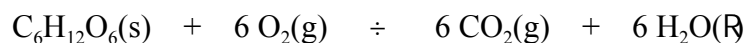
$$\begin{aligned} \text{heat required by the body} &= \text{mass} \times \Delta T \times \text{specific heat of human body} \\ &= (80.0 \times 10^3 \text{ g}) (+3.0 \text{ deg}) (4.18 \text{ J deg}^{-1} \text{ g}^{-1}) \\ &= +1.0032 \times 10^6 \text{ J} \\ &= +1.0032 \times 10^3 \text{ kJ} \\ \text{heat *released* by the body} &= -1.0032 \times 10^3 \text{ kJ} \\ &= \text{total heat generated by the glucose metabolism} \end{aligned}$$

$$\begin{aligned} n(\text{glucose}) &= (\text{total heat generated by the glucose metabolism}) \div (\text{heat of combustion of glucose}) \\ &= (-1.0032 \times 10^3 \text{ kJ}) \div (-2.820 \times 10^3 \text{ kJ mol}^{-1}) \\ &= 0.355745 \times 10^1 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{mass}(\text{glucose}) &= (0.355745 \times 10^1 \text{ mol}) \times (180.2 \text{ g mol}^{-1}) \\ &= 64.105 \text{ g} \\ &= \underline{\underline{64.1 \text{ g}}} \end{aligned}$$

**(b) mass of CO<sub>2</sub>(g) released to the atmosphere as a result of the glucose metabolism in the body**

The combustion reaction of glucose is:



**1 mole** of  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$  produces **6 moles** of  $\text{CO}_2(\text{g})$

$$\begin{aligned} n(\text{CO}_2) &= n(\text{glucose}) \times (6 \text{ moles CO}_2 \div 1 \text{ mole glucose C}_6\text{H}_{12}\text{O}_6) \\ &= (0.355745 \times 10^1 \text{ mol}) (6) \\ &= 2.13447 \text{ mol} \end{aligned}$$

$$\begin{aligned} M(\text{CO}_2) &= [12.011 + 2(15.999)] \text{ g mol}^{-1} = 44.009 \text{ g mol}^{-1} \\ \text{mass}(\text{CO}_2) &= n(\text{CO}_2) \times M(\text{CO}_2) = (2.13447 \text{ mol}) (44.009 \text{ g mol}^{-1}) \\ &= 93.9359 \text{ g} \\ &= \underline{\underline{93.9 \text{ g}}} \end{aligned}$$

**PART A**  
**QUESTION 10**

Given: Thermodynamics data from the textbook  
 $\Delta H_f^\circ[\text{CO}_2(\text{g})] = -393.509 \text{ kJ mol}^{-1}$   
 $\Delta H_f^\circ[\text{CO}(\text{g})] = -110.525 \text{ kJ mol}^{-1}$   
 $\Delta H_f^\circ[\text{O}(\text{g})] = 249.17 \text{ kJ mol}^{-1}$

**(a)  $\Delta H^\circ$  for the reaction**


$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \\ &= \{\Delta H_f^\circ[\text{CO}(\text{g})] + \Delta H_f^\circ[\text{O}(\text{g})]\} - \{\Delta H_f^\circ[\text{CO}_2(\text{g})]\} \\ &= \{(-110.525 \text{ kJ mol}^{-1}) + (249.17 \text{ kJ mol}^{-1})\} - \{(-393.509 \text{ kJ mol}^{-1})\} \\ &= \underline{\underline{+532.154 \text{ kJ mol}^{-1}}} \end{aligned}$$

**(b) Estimate the maximum wavelength of light ( $\lambda_{\text{max}}$ )**

$$\Delta E \text{ (kJ mol}^{-1}\text{)} \cdot \frac{1.2 \times 10^5 \text{ kJ mol}^{-1} \text{ nm}}{\lambda \text{ (nm)}}$$

Assume  $\Delta H_{\text{rxn}}^\circ \cdot \Delta E = +532.154 \text{ kJ mol}^{-1}$

$$\begin{aligned} \lambda_{\text{max}} \text{ (nm)} &= (1.2 \times 10^5 \text{ kJ mol}^{-1} \text{ nm}) \div \Delta E \\ &= (1.2 \times 10^5 \text{ kJ mol}^{-1} \text{ nm}) \div (+532.154 \text{ kJ mol}^{-1}) \\ &= \underline{\underline{225.5 \text{ nm}}} \\ &= \underline{\underline{230 \text{ nm}}} \quad (2 \text{ s.f.}) \end{aligned}$$

**(c) To what part of the electromagnetic spectrum does light of this wavelength belong?**

Light of 230 nm belongs to the UV spectrum.

**(d) Do you expect this reaction to be possible in the troposphere or stratosphere?**

This reaction is possible to occur only in the stratosphere. The wavelength range absorbed by the reaction is  $\lambda < 230 \text{ nm}$ , which is available in the stratosphere, but not in the troposphere. Note that the tropospheric solar spectrum extends from  $\approx 300 \text{ nm}$  to longer wavelength.

**PART B**  
**QUESTION 1**

Given:  $2.0 \times 10^{14}$  atm of hydroxyl radical (OH)  
 $T = 25^\circ\text{C} = (273 + 25) \text{ K} = 298 \text{ K}$

$$\begin{aligned} R &= 8.314 \text{ kPa L K}^{-1} \text{ mol}^{-1} \\ &= 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} \\ &= \mathbf{0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1}} \\ &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

(a) in units of ppmv

$$p(\text{OH}) = (2.0 \times 10^{14} \text{ atm}) (10^6 \text{ ppmv atm}^{-1})$$

$$10^6 \text{ ppmv at 1 atm}$$

$$\begin{aligned} &= \underline{2.0} \times 10^{18} \text{ ppmv} \\ &= \underline{\mathbf{2.0 \times 10^{18} \text{ ppmv}}} \end{aligned}$$

(b) in units of mol L<sup>-1</sup>

$$\mathbf{P = c R T}$$

$$\begin{aligned} 2.0 \times 10^{14} \text{ atm} &= c(\text{OH}) (0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1}) (298 \text{ K}) \\ c(\text{OH}) \text{ in } \underline{\mathbf{mol L}^{-1}} &= \underline{8.175 \times 10^{16} \text{ mol L}^{-1}} \\ &= \underline{\mathbf{8.2 \times 10^{16} \text{ mol L}^{-1}}} \end{aligned}$$

(c) in units of molec cm<sup>-3</sup>

$$\text{Avogadro's number} = 6.022 \times 10^{23} \text{ molec mol}^{-1}$$

$$1 \text{ L} = 10^3 \text{ mL} \quad \& \quad 1 \text{ cm}^3 = 1 \text{ mL}$$

$$(8.175 \times 10^{16} \text{ mol L}^{-1}) (6.022 \times 10^{23} \text{ molec mol}^{-1}) \left(\frac{\text{L}}{10^3 \text{ mL}}\right) \left(\frac{\text{mL}}{\text{cm}^3}\right) = 4.9 \times 10^5 \text{ molec cm}^{-3}$$

**PART B**  
**QUESTION 2**

Given:  $V(\text{CO}_2, \text{g})$  produced = 5.42 L  
 $P = 9.75 \times 10^4 \text{ Pa}$   
 $T = 22^\circ\text{C} = (273 + 22) \text{ K} = 295 \text{ K}$   
 $R = 8.314 \times 10^3 \text{ Pa L K}^{-1} \text{ mol}^{-1}$

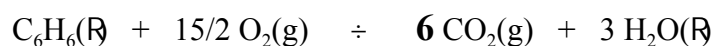
To find: mass of benzene,  $\text{C}_6\text{H}_6$ , required

$$P V = n R T$$

For  $\text{CO}_2(\text{g})$ ,

$$\begin{aligned} (9.75 \times 10^4 \text{ Pa}) (5.42 \text{ L}) &= n(\text{CO}_2) (8.314 \times 10^3 \text{ Pa L K}^{-1} \text{ mol}^{-1}) (295 \text{ K}) \\ n(\text{CO}_2) &= \underline{0.21546 \text{ mol}} \end{aligned}$$

The complete combustion of  $\text{C}_6\text{H}_6(\text{R})$  is:



**1 mole**  $\text{C}_6\text{H}_6(\text{R})$  produces **6 moles** of  $\text{CO}_2(\text{g})$

$$\begin{aligned} n(\text{C}_6\text{H}_6) &= n(\text{CO}_2) \times (1 \text{ mole } \text{C}_6\text{H}_6 \div 6 \text{ moles } \text{CO}_2) \\ &= (0.21546 \text{ mol}) \times (1/6) \\ &= \underline{0.035910 \text{ mol}} \end{aligned}$$

$$M(\text{C}_6\text{H}_6) = [6 (12.011) + 6 (1.0079)] \text{ g mol}^{-1} = 78.1134 \text{ g mol}^{-1}$$

$$\begin{aligned} \hat{\text{mass}}(\text{C}_6\text{H}_6) &= n(\text{C}_6\text{H}_6) \times M(\text{C}_6\text{H}_6) \\ &= (0.035910 \text{ mol}) \times (78.1134 \text{ g mol}^{-1}) \\ &= \underline{2.8051 \text{ g}} \\ &= \underline{\mathbf{2.81 \text{ g}}} \quad (3 \text{ s.f.}) \end{aligned}$$

**PART B**  
**QUESTION 3**

Given: brownish gas  $N_2O_x$   
 density (d) =  $3.67 \text{ g L}^{-1}$   
 $P = 98 \text{ kPa}$   
 $T = 22.7^\circ\text{C} = (273 + 22.7) \text{ K} = 295.7 \text{ K}$   
 $R = 8.314 \text{ kPa L K}^{-1} \text{ mol}^{-1}$

To find: the molar mass and the molecular formula of  $N_2O_x$

$$P V = n R T$$

$$n = \frac{\text{mass}}{M}$$

$$d = \frac{\text{mass}}{V}$$

$$P = \frac{n}{V} R T = \frac{\text{mass}}{M V} R T = \frac{d}{M} R T$$

$$M = \frac{d R T}{P}$$

$$M = \frac{(3.67 \text{ g L}^{-1}) (8.314 \text{ kPa L K}^{-1} \text{ mol}^{-1}) (295.7 \text{ K})}{98 \text{ kPa}} = 92.066 \text{ g mol}^{-1}$$

^ The molar mass of  $N_2O_x = 92.066 \text{ g mol}^{-1} = \underline{92 \text{ g mol}^{-1}}$  (2 s.f.)

$$\begin{aligned} M(N_2O_x) &= [2(14.007) + x(15.999)] \text{ g mol}^{-1} \\ \underline{92.066 \text{ g mol}^{-1}} &= [(28.014) + (15.999x)] \text{ g mol}^{-1} \\ \hat{x} &= \underline{4.003} \text{ (. 4)} \end{aligned}$$

^ The molecular formula of the brownish gas is:



**PART B**  
**QUESTION 4**

Given:

$$p(\text{H}_2\text{O},\text{g}) = 3.57 \text{ kPa}$$

$$R = 8.314 \text{ kPa L K}^{-1} \text{ mol}^{-1}$$

$$T = 27^\circ\text{C} = (273 + 27) \text{ K} = 300 \text{ K}$$

$$V = 10.0 \text{ ft} \times 12.0 \text{ ft} \times 8.00 \text{ ft}$$

$$= 960 \text{ ft}^3 \quad (1 \text{ foot} = 12 \text{ inches})$$

$$= 960 (12 \text{ inches})^3$$

$$= \underline{1.65888} \times 10^6 \text{ in}^3 \quad (1 \text{ inch} = 2.54 \text{ cm})$$

$$= \underline{1.65888} \times 10^6 (2.54 \text{ cm})^3$$

$$= \underline{2.7184} \times 10^7 \text{ cm}^3 \quad (1 \text{ cm}^3 = 1 \text{ mL})$$

$$= \underline{2.7184} \times 10^7 \text{ mL} \quad (10^3 \text{ mL} = 1 \text{ L})$$

$$= \underline{2.7184} \times 10^4 \text{ L}$$

To find: mass of water when  $p(\text{H}_2\text{O},\text{g}) = 72.0\%$

When the vapour pressure of water is 72%

$$p(\text{H}_2\text{O},\text{g}) = (3.57 \text{ kPa}) \times 72\% = \underline{2.5704} \text{ kPa}$$

$$\boxed{P V = n R T}$$

For  $\text{H}_2\text{O}(\text{g})$ ,

$$\frac{(2.5704 \text{ kPa}) (2.7184 \times 10^4 \text{ L})}{n(\text{H}_2\text{O})} = \frac{n(\text{H}_2\text{O}) (8.314 \text{ kPa L K}^{-1} \text{ mol}^{-1}) (300 \text{ K})}{n(\text{H}_2\text{O})}$$

$$= \underline{28.014} \text{ mol}$$

$$M(\text{H}_2\text{O}) = [2 (1.0079) + (15.999)] \text{ g mol}^{-1} = 18.0148 \text{ g mol}^{-1}$$

$$\hat{\text{mass}}(\text{H}_2\text{O}) \text{ occupied in the room} = n(\text{H}_2\text{O}) \times M(\text{H}_2\text{O})$$

$$= (28.014 \text{ mol}) (18.0148 \text{ g mol}^{-1})$$

$$= \underline{504.67} \text{ g}$$

$$= \underline{505} \text{ g} \quad (3 \text{ s.f.})$$

**PART B**  
**QUESTION 5**

Given: CaO (*limiting reactant*)  
 ammonium chloride, NH<sub>4</sub>Cl (*in excess*)  
 V(NH<sub>3</sub>,g) = 25.0 L  
 P = 0.850 atm  
 T = 21°C = (273 + 21) K = 294 K  
 R = 0.0821 atm L K<sup>-1</sup> mol<sup>-1</sup>

To find: *maximum* mass of quicklime, CaO

$$P V = n R T$$

For NH<sub>3</sub>(g),

$$\begin{aligned} (0.850 \text{ atm}) (25.0 \text{ L}) &= n(\text{NH}_3) (0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1}) (294\text{K}) \\ n(\text{NH}_3) &= \underline{0.88037 \text{ mol}} \end{aligned}$$

From the reaction:



**1 mole** CaO(s) yields **2 moles** of NH<sub>3</sub>(g)

$$\begin{aligned} n(\text{CaO}) &= n(\text{NH}_3) \times (1 \text{ mole CaO} \div 2 \text{ moles NH}_3) \\ &= (0.88037 \text{ mol}) \times (1/2) \\ &= \underline{0.440185 \text{ mol}} \end{aligned}$$

$$M(\text{CaO}) = [40.08 + 15.999] \text{ g mol}^{-1} = 56.079 \text{ g mol}^{-1}$$

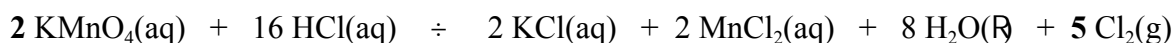
$$\begin{aligned} \hat{\quad} \textit{maximum} \text{ mass(CaO) required} &= n(\text{CaO}) \times M(\text{CaO}) \\ &= (0.440185 \text{ mol}) \times (56.079 \text{ g mol}^{-1}) \\ &= \underline{24.685 \text{ g}} \\ &= \underline{\underline{24.7 \text{ g}}} \quad (3 \text{ s.f.}) \end{aligned}$$

**PART B**  
**QUESTION 6**

Given: 50.0 mL of 1.00 M  $\text{KMnO}_4(\text{aq})$   
 100.0 mL of 5.00 M  $\text{HCl}(\text{aq})$   
 $T = 25.0^\circ\text{C} = (273 + 25.0) \text{ K} = 298 \text{ K}$   
 $P = 202.3 \text{ kPa}$   
 $R = 8.314 \text{ kPa L K}^{-1} \text{ mol}^{-1}$

To find: volume of  $\text{Cl}_2(\text{g})$

According to the reaction:



$$\begin{aligned} (1) \quad n(\text{KMnO}_4) &= c(\text{KMnO}_4) \times V(\text{KMnO}_4) \\ &= (1.00 \text{ mol L}^{-1}) (50.00 \times 10^{-3} \text{ L}) \\ &= \underline{5.00} \times 10^{-2} \text{ mol} \end{aligned}$$

$$\begin{aligned} (2) \quad n(\text{HCl}) &= c(\text{HCl}) \times V(\text{HCl}) \\ &= (5.00 \text{ mol L}^{-1}) (100.0 \times 10^{-3} \text{ L}) \\ &= \underline{5.00} \times 10^{-1} \text{ mol} \end{aligned}$$

**2 moles** of  $\text{KMnO}_4(\text{aq})$  reacts with **16 moles** of  $\text{HCl}(\text{aq})$   
 $\text{ratio}(\text{KMnO}_4) = (5.00 \times 10^{-2} \text{ mol}) \div 2 \text{ mol} = \underline{2.50} \times 10^{-2}$   
 $\text{ratio}(\text{HCl}) = (5.00 \times 10^{-1} \text{ mol}) \div 16 \text{ mol} = \underline{3.125} \times 10^{-2}$   
 $\text{KMnO}_4$  is the *limiting reactant* and  $\text{HCl}$  is *in excess*.

**2 moles** of  $\text{KMnO}_4(\text{aq})$  produces **5 moles** of  $\text{Cl}_2(\text{g})$

$$\begin{aligned} n(\text{Cl}_2) &= n(\text{KMnO}_4) \times (5 \text{ moles Cl}_2 \div 2 \text{ moles KMnO}_4) \\ &= (5.00 \times 10^{-2} \text{ mol}) \times (5/2) \\ &= \underline{0.125} \text{ mol} \end{aligned}$$

$$\boxed{P V = n R T}$$

For  $\text{Cl}_2(\text{g})$ ,

$$\begin{aligned} (202.3 \text{ kPa}) V(\text{Cl}_2, \text{g}) &= (0.125 \text{ mol}) (8.314 \text{ kPa L K}^{-1} \text{ mol}^{-1}) (298 \text{ K}) \\ V(\text{Cl}_2, \text{g}) &= \underline{1.5308} \text{ L} \\ &= \underline{\underline{1.53}} \text{ L} \quad (3 \text{ s.f.}) \end{aligned}$$

**PART B**  
**QUESTION 7**

Given: 10.0 kg (*or*  $10.0 \times 10^3$  g)  $\text{CS}_2(\text{R})$   
 15.0 kg (*or*  $15.0 \times 10^3$  g)  $\text{CCl}_4(\text{R})$  produced  
 $V(\text{Cl}_2, \text{g}) = 10^4$  L  
 $P = 1$  atm  
 $T = 400$  K

To find: % yield of  $\text{CCl}_4(\text{R})$

$$M(\text{CS}_2) = [12.011 + 2(32.06)] \text{ g mol}^{-1} = 76.131 \text{ g mol}^{-1}$$

(1) For  $\text{CS}_2(\text{R})$ :

$$\begin{aligned} n(\text{CS}_2) &= \text{mass}(\text{CS}_2) \div M(\text{CS}_2) \\ &= (10.0 \times 10^3 \text{ g}) \div (76.131 \text{ g mol}^{-1}) \\ &= \underline{1.3135 \times 10^2} \text{ mol} \end{aligned}$$

(2) For  $\text{Cl}_2(\text{g})$ :

$$\boxed{P V = n R T}$$

$$\begin{aligned} (1 \text{ atm}) (10^4 \text{ L}) &= n(\text{Cl}_2) (0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1}) (400 \text{ K}) \\ n(\text{Cl}_2) &= \underline{3.045 \times 10^2} \text{ mol} \end{aligned}$$

According to the reaction:  $4 \text{CS}_2(\text{R}) + 8 \text{Cl}_2(\text{g}) \div 4 \text{CCl}_4(\text{R}) + \text{S}_8(\text{s})$

**4 moles** of  $\text{CS}_2(\text{R})$  reacts with **8 moles** of  $\text{Cl}_2(\text{g})$   
 $\text{ratio}(\text{CS}_2) = (1.3135 \times 10^2 \text{ mol}) \div 4 \text{ moles} = \underline{32.838}$   
 $\text{ratio}(\text{Cl}_2) = (3.045 \times 10^2 \text{ mol}) \div 8 \text{ moles} = \underline{38.063}$   
 $\text{CS}_2(\text{R})$  is the *limiting reactant*.

**4 moles** of  $\text{CS}_2(\text{R})$  yields **4 moles** of  $\text{CCl}_4(\text{R})$

$$n(\text{CCl}_4) = n(\text{CS}_2) \times (4 \text{ moles CCl}_4 \div 4 \text{ moles CS}_2) = \underline{1.3135 \times 10^2} \text{ mol}$$

$$M(\text{CCl}_4) = [12.011 + 4(35.453)] \text{ g mol}^{-1} = 153.823 \text{ g mol}^{-1}$$

$$\begin{aligned} \text{theoretical mass}(\text{CCl}_4) \text{ produced} &= n(\text{CCl}_4) \times M(\text{CCl}_4) \\ &= (1.3135 \times 10^2 \text{ mol}) (153.823 \text{ g mol}^{-1}) \\ &= \underline{2.0204 \times 10^4} \text{ g} \\ &= \underline{20.204} \text{ kg} \end{aligned}$$

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{15.0 \text{ kg}}{20.204 \text{ kg}} \times 100\% = 74.2\%$$

**PART B**  
**QUESTION 8**

Given: 0.954 g LiH(s)  
1.26 g of H<sub>2</sub>O(l)

At STP, molar volume of real gas = **22.4 L mol<sup>-1</sup>**

To find: volume of H<sub>2</sub>(g) produced **at STP**

$$M(\text{LiH}) = [6.941 + 1.0079] \text{ g mol}^{-1} = 7.9489 \text{ g mol}^{-1}$$

$$M(\text{H}_2\text{O}) = [2(1.0079) + 15.999] \text{ g mol}^{-1} = 18.0148 \text{ g mol}^{-1}$$

	LiH(s)	+	H <sub>2</sub> O(l)	÷	LiOH(s)	+	H <sub>2</sub> (g)
mass(x):	0.954 g		1.26 g				
M(x):	7.9489 g mol <sup>-1</sup>		18.0148 g mol <sup>-1</sup>				
n(x):	<u>0.1200</u> mol		<b>0.06994</b> mol				
ratio:	0.1200 mol ÷ 1 mol = <u>0.1200</u> ^ <b>in excess</b>		0.06994 mol ÷ 1 mol = <u>0.06994</u> ^ <b>L.R.</b>				

Based on the above reaction,

**1 mole** of H<sub>2</sub>O(l) produces **1 mole** of H<sub>2</sub>(g)

$$\begin{aligned} n(\text{H}_2) &= n(\text{H}_2\text{O}) \times (1 \text{ mole H}_2 \div 1 \text{ mole H}_2\text{O}) \\ &= (0.06994 \text{ mol}) (1) \\ &= 0.06994 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{At STP, } V[\text{H}_2(\text{g})] &= n(\text{H}_2) \times (\text{molar volume of real gas}) \\ &= (0.06994 \text{ mol}) (22.4 \text{ L mol}^{-1}) \\ &= \underline{1.5666 \text{ L}} \\ &= \underline{\underline{1.57 \text{ L}}} \quad (3 \text{ s.f.}) \end{aligned}$$

For molar volume of real gas,

$$P V = n R T$$

$$\frac{V}{n} = \frac{R T}{P} = \frac{(8.314 \text{ kPa L K}^{-1} \text{ mol}^{-1}) (273 \text{ K})}{101.3 \text{ kPa}} = 22.4 \text{ L mol}^{-1}$$

### Characteristics of ZERO, FIRST and SECOND ORDER Reactions

$a A(g) \rightarrow \text{products}$

(where  $[A]$  and  $[A_0]$  = concentrations of A at  $t$  and  $t=0$ , respectively)

Order	Rate Expression	Concentration/ Time Relationship	Linear Plot	Slope	$k$ (units)	y-intercept	$t_{1/2}$
zero	rate = $k$	$[A] = -kt + [A_0]$	$[A]$ vs $t$	$-k$	$M s^{-1}$	$[A_0]$	$\frac{[A_0]}{2k}$
first	rate = $k[A]$	$\ln[A] = -kt + \ln[A_0]$	$\ln[A]$ vs $t$	$-k$	$s^{-1}$	$\ln[A_0]$	$\frac{\ln 2}{k}$
second	rate = $k[A]^2$	$\frac{1}{[A]} = kt + \frac{1}{[A_0]}$	$\frac{1}{[A]}$ vs $t$	$k$	$M^{-1} s^{-1}$	$\frac{1}{[A_0]}$	$\frac{1}{k[A_0]}$

#### First-Order Kinetics:

$$\ln[A] = -kt + \ln[A_0] \quad \text{or} \quad \ln\left(\frac{[A]}{[A_0]}\right) = -kt$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

#### Second-Order Kinetics:

$$\frac{1}{[A]} = kt + \frac{1}{[A_0]}$$

$$t_{1/2} = \frac{1}{k[A_0]}$$

**PART C**  
**QUESTION 1**

Given: Reaction studied:  $A \rightarrow B + C$   
 $[A] = 0.20 \text{ mol L}^{-1}$

$$\text{rate} = -\frac{d[A]}{dt} = 0.0080 \text{ mol L}^{-1} \text{ s}^{-1}$$

To find: rate constant  $k$

(a) first order in A

$$\text{rate} = k [A]$$

$$(0.0080 \text{ mol L}^{-1} \text{ s}^{-1}) = k (0.20 \text{ mol L}^{-1})$$

$$k = \underline{\underline{0.040 \text{ s}^{-1}}} \quad (1^{\text{st}} \text{ order rate constant units})$$

(b) second order in A

$$\text{rate} = k [A]^2$$

$$(0.0080 \text{ mol L}^{-1} \text{ s}^{-1}) = k (0.20 \text{ mol L}^{-1})^2$$

$$k = \frac{0.0080 \text{ mol L}^{-1} \text{ s}^{-1}}{(0.20 \text{ mol L}^{-1})^2} = \underline{\underline{0.20 \text{ L mol}^{-1} \text{ s}^{-1}}} \quad (2^{\text{nd}} \text{ order rate constant units})$$

**PART C**  
**QUESTION 2**

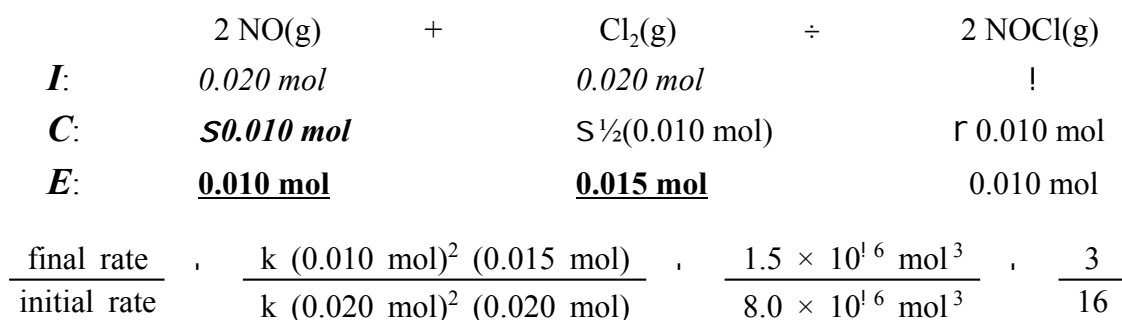
Given: Reaction studied:  $2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \div 2 \text{NOCl}(\text{g})$   
 (third order overall)

$$\text{rate} = k [\text{NO}]^2 [\text{Cl}_2]$$

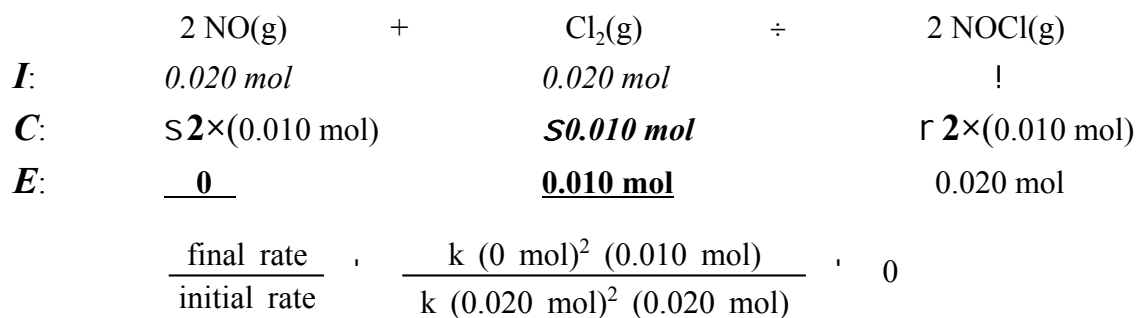
*initial*  $\text{NO}(\text{g}) = 0.020 \text{ mol}$

*initial*  $\text{Cl}_2(\text{g}) = 0.020 \text{ mol}$

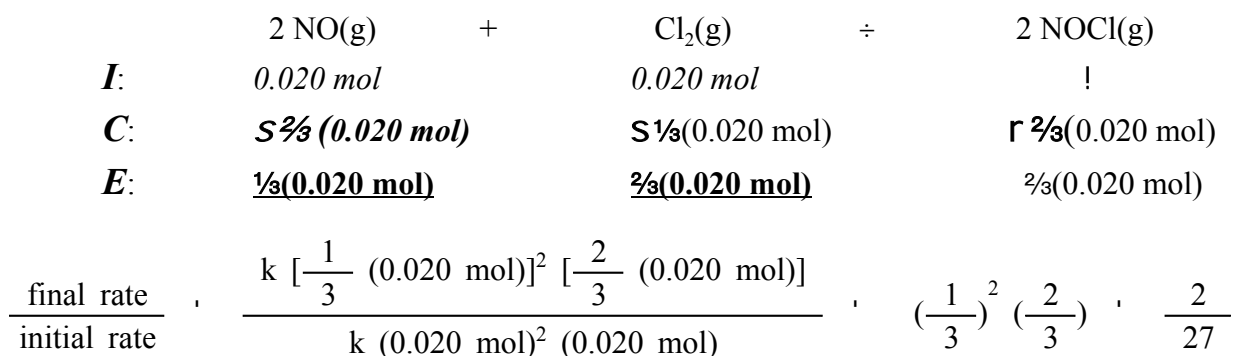
(a) when half the  $\text{NO}(\text{g})$  has been consumed (*i.e.*  $\text{NO}(\text{g})$  consumed = 0.010 mol)



(b) when half the  $\text{Cl}_2(\text{g})$  has been consumed (*i.e.*  $\text{Cl}_2(\text{g})$  consumed = 0.010 mol)



(c) when two-thirds the  $\text{NO}(\text{g})$  has been consumed (*i.e.*  $\text{NO}(\text{g})$  consumed =  $2/3(0.020 \text{ mol})$ )



**PART C**  
**QUESTION 3**

Given: Reaction:  $A + B \rightarrow \text{products}$

(a) the order with respect to A and B, and determine the overall order

(i) **Compare (1) and (2)**

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

[B] is constant,

$$\frac{\text{Rxn (2)}}{\text{Rxn (1)}} : \frac{[A] \text{ (2)}}{[A] \text{ (1)}} = \frac{0.30 \text{ mol L}^{-1}}{0.20 \text{ mol L}^{-1}} = \frac{1.5}{1}$$

$$\frac{\text{rate (2)}}{\text{rate (1)}} = \frac{2.4 \times 10^{13} \text{ mol L}^{-1} \text{ s}^{-1}}{1.6 \times 10^{13} \text{ mol L}^{-1} \text{ s}^{-1}} = \frac{1.5}{1}$$

$\hat{=}$  **rate % [A]** (*first order* with respect to A)

(ii) **Compare (2) and (3)**

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

[A] is constant,

$$\frac{\text{Rxn (3)}}{\text{Rxn (2)}} : \frac{[B] \text{ (3)}}{[B] \text{ (2)}} = \frac{0.030 \text{ mol L}^{-1}}{0.020 \text{ mol L}^{-1}} = \frac{1.5}{1}$$

$$\frac{\text{rate (3)}}{\text{rate (2)}} = \frac{3.6 \times 10^{13} \text{ mol L}^{-1} \text{ s}^{-1}}{2.4 \times 10^{13} \text{ mol L}^{-1} \text{ s}^{-1}} = \frac{1.5}{1}$$

$\hat{=}$  **rate % [B]** (*first order* with respect to B)

**Rate Law:**  $\text{rate} = k [A] [B]$  (**second order overall**)

**(b) a value for the rate constant**

From Rxn (1),  $[A] = 0.20 \text{ mol L}^{-1}$   
 $[B] = 0.020 \text{ mol L}^{-1}$   
 $\text{rate} = 1.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$

$$\begin{aligned} \text{rate} &= k [A] [B] \\ 1.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} &= k (0.20 \text{ mol L}^{-1}) (0.020 \text{ mol L}^{-1}) \\ k &= \underline{\underline{0.40 \text{ L mol}^{-1} \text{ s}^{-1}}} \end{aligned}$$

**PART C  
QUESTION 4**

Given: thermal decomposition indicates **1<sup>st</sup> order kinetics**  
 $t_{1/2} = 80 \text{ seconds at } 600^\circ\text{C}$

To find: at what time when 1/10 of an acetone sample *decomposed* at  $600^\circ\text{C}$   
*(i.e. acetone [A] remained = 9/10 [A<sub>0</sub>])*

$$\left( \frac{[A]}{[A_0]} = \frac{9}{10} \right)$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{80 \text{ s}} = \underline{\underline{8.66 \times 10^{-3} \text{ s}^{-1}}}$$

$$\ln [A] = -k t + \ln [A_0] \quad \text{or} \quad \ln \left( \frac{[A]}{[A_0]} \right) = -k t$$

$$\ln \left( \frac{9}{10} \right) = -(8.66 \times 10^{-3}) \times (t)$$

$$t = \underline{\underline{12.17 \text{ s}}} = \underline{\underline{12 \text{ s}}}$$

**PART C  
QUESTION 5**

Given: Reaction: **A → B**

$$\text{Rate Law: } \text{rate} = k [A]$$

(first-order overall)

$$[A]_{\text{reacted}} = 75.0\% [A_0] \quad (\text{at } t = 60.0 \text{ min})$$

$$(\text{i.e. } [A]_{\text{remained}} = 25.0\% [A_0])$$

$$\left( \frac{[A]}{[A_0]} = 25.0\% = 0.250 \right)$$

To find:  $k$  in  $\text{min}^{-1}$

$$\ln [A] = -k t + \ln [A_0] \quad \text{or} \quad \ln \left( \frac{[A]}{[A_0]} \right) = -k t$$

$$\ln (0.250) = -k (60.0 \text{ min})$$

$$k = \frac{2.310}{60.0} \times 10^2 \text{ min}^{-1} = \underline{\underline{2.31 \times 10^2 \text{ min}^{-1}}}$$

**PART C  
QUESTION 6**

Given:

$$\text{rate} = k [N_2O_5]$$

(first-order reaction)

$$k = 1.45 \times 10^{-3} \text{ s}^{-1}$$

Let  $[A]$  be  $[N_2O_5(g)]$

(a) the half-life,  $t_{1/2}$ , of  $N_2O_5(g)$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

$$t_{1/2} = \frac{0.693}{1.45 \times 10^{-3} \text{ s}^{-1}} = \underline{\underline{4.779 \times 10^2 \text{ s}}} = 478 \text{ s}$$

**PART C**  
**QUESTION 6**

(b) the percent of the original  $\text{N}_2\text{O}_5(\text{g})$  which has decomposed after 10.0 minutes

Given:  $k = 1.45 \times 10^{-3} \text{ s}^{-1}$   
 $t = 10.0 \text{ min} = 10.0 \times 60 \text{ s} = 600 \text{ s}$

$$\ln [A] = -kt + \ln [A_0] \quad \text{or} \quad \ln \left( \frac{[A]}{[A_0]} \right) = -kt$$

$$\ln \left( \frac{[A]}{[A_0]} \right) = -(1.45 \times 10^{-3} \text{ s}^{-1})(600 \text{ s})$$

$$\frac{[A]}{[A_0]} = 0.419 \quad (\text{N}_2\text{O}_5 \text{ remained})$$

$$\% \text{ N}_2\text{O}_5 \text{ decomposed} = (1 - 0.419) = 0.581 \quad (\text{or } \underline{\underline{58.1\%}})$$

(c) time required of  $[\text{N}_2\text{O}_5]$  to drop from  $[A_0]$  of  $8.90 \times 10^{-4} \text{ mol L}^{-1}$  to  $[A]$  of  $6.90 \times 10^{-4} \text{ mol L}^{-1}$

Given:  $[A_0] = 8.90 \times 10^{-4} \text{ mol L}^{-1}$   
 $[A] = 6.90 \times 10^{-4} \text{ mol L}^{-1}$   
 $k = 1.45 \times 10^{-3} \text{ s}^{-1}$

$$\ln [A] = -kt + \ln [A_0] \quad \text{or} \quad \ln \left( \frac{[A]}{[A_0]} \right) = -kt$$

$$\ln \left( \frac{6.90 \times 10^{-4} \text{ mol L}^{-1}}{8.90 \times 10^{-4} \text{ mol L}^{-1}} \right) = -(1.45 \times 10^{-3} \text{ s}^{-1})(t)$$

$$t = \frac{175.54 \text{ s}}{1} = \underline{\underline{176 \text{ s}}} \quad (\text{. } \underline{\underline{3 \text{ min}}})$$

**PART C  
QUESTION 7**

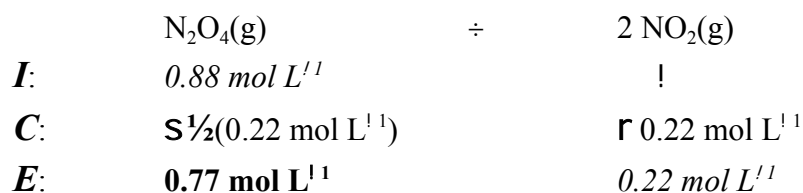
(a) Rate Law:  $\text{rate} = k [\text{N}_2\text{O}_4]$  (first order reaction)

(i) the rate constant ( $k$ )

Given:  $[\text{A}_0] = [\text{N}_2\text{O}_4(\text{g})] = 0.88 \text{ mol L}^{-1}$   
*initial* rate =  $1.14 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$

$$\begin{aligned} \text{rate} &= k [\text{N}_2\text{O}_4] \\ 1.14 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1} &= k (0.88 \text{ mol L}^{-1}) \\ k &= 0.01295 \text{ s}^{-1} = \underline{1.3 \times 10^{-2} \text{ s}^{-1}} \end{aligned}$$

(ii) time required to form  $0.22 \text{ mol L}^{-1} \text{ NO}_2$



$$\ln \left( \frac{[\text{A}]}{[\text{A}_0]} \right) = -k t$$

$$\ln \left( \frac{0.77 \text{ mol L}^{-1}}{0.88 \text{ mol L}^{-1}} \right) = -(1.3 \times 10^{-2} \text{ s}^{-1}) (t)$$

$$t = \underline{10.27 \text{ s}} = \underline{10 \text{ s}}$$

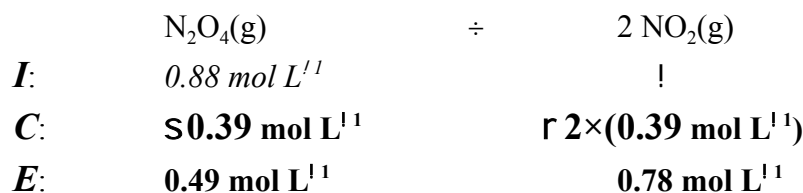
(iii) the concentration of  $\text{NO}_2(\text{g})$  after 45 seconds

- first calculate  $[\text{N}_2\text{O}_4]$  ( $[\text{A}]$ ) after 45 seconds

$$\ln \left( \frac{[\text{A}]}{[\text{A}_0]} \right) = -k t$$

$$\ln \left( \frac{[\text{A}]}{0.88 \text{ mol L}^{-1}} \right) = -(1.3 \times 10^{-2} \text{ s}^{-1}) (45 \text{ s})$$

$$[\text{A}] = 0.49 \text{ mol L}^{-1} \text{ (N}_2\text{O}_4 \text{ *remained* )}$$



$$\begin{aligned} [\text{NO}_2] \text{ after } 45 \text{ s} &= [\text{N}_2\text{O}_4] \text{ consumed} \times (2 \text{ moles NO}_2 \div 1 \text{ mole N}_2\text{O}_4) \\ &= (0.88 \text{ mol L}^{-1} - 0.49 \text{ mol L}^{-1}) \times (2) = \underline{0.78 \text{ mol L}^{-1}} \end{aligned}$$

**PART C  
QUESTION 7**

(b) Rate Law:  $\text{rate} = k [\text{N}_2\text{O}_4]^2$  (second order reaction)

(i) the rate constant ( $k$ )

Given:  $[\text{A}_0] = [\text{N}_2\text{O}_4(\text{g})] = 0.88 \text{ mol L}^{-1}$   
*initial* rate =  $1.14 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$

$$\begin{aligned} \text{rate} &= k [\text{N}_2\text{O}_4]^2 \\ 1.14 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1} &= k (0.88 \text{ mol L}^{-1})^2 \\ k &= 0.01472 \text{ L mol}^{-1} \text{ s}^{-1} = \underline{\underline{1.5 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}}} \end{aligned}$$

(ii) time required to form  $0.22 \text{ mol L}^{-1} \text{ NO}_2$

	$\text{N}_2\text{O}_4(\text{g})$	$\div$	$2 \text{ NO}_2(\text{g})$
<i>I:</i>	$0.88 \text{ mol L}^{-1}$		!
<i>C:</i>	$\text{S} \frac{1}{2}(0.22 \text{ mol L}^{-1})$		$\text{r} 0.22 \text{ mol L}^{-1}$
<i>E:</i>	<u><math>0.77 \text{ mol L}^{-1}</math></u>		$0.22 \text{ mol L}^{-1}$

$$\frac{1}{[\text{A}]} - k t = \frac{1}{[\text{A}_0]}$$

$$\frac{1}{0.77 \text{ mol L}^{-1}} - (1.47 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}) (t) = \frac{1}{0.88 \text{ mol L}^{-1}}$$

$$t = 11.04 \text{ s} = \underline{\underline{11 \text{ s}}}$$

(iii) the concentration of  $\text{NO}_2(\text{g})$  after 45 seconds

- first calculate  $[\text{N}_2\text{O}_4]$  ( $[\text{A}]$ ) after 45 seconds

$$\frac{1}{[\text{A}]} - (1.47 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}) (45 \text{ s}) = \frac{1}{0.88 \text{ mol L}^{-1}}$$

$$[\text{A}] = 0.556 \text{ mol L}^{-1} \text{ (N}_2\text{O}_4 \text{ *remained*)}$$

	$\text{N}_2\text{O}_4(\text{g})$	$\div$	$2 \text{ NO}_2(\text{g})$
<i>I:</i>	$0.88 \text{ mol L}^{-1}$		!
<i>C:</i>	$\text{S} 0.324 \text{ mol L}^{-1}$		$\text{r} 2 \times (0.324 \text{ mol L}^{-1})$
<i>E:</i>	<u><math>0.556 \text{ mol L}^{-1}</math></u>		<u><math>0.648 \text{ mol L}^{-1}</math></u>

$$\begin{aligned} [\text{NO}_2] \text{ after } 45 \text{ s} &= [\text{N}_2\text{O}_4] \text{ consumed} \times (2 \text{ moles NO}_2 \div 1 \text{ mole N}_2\text{O}_4) \\ &= (0.88 \text{ mol L}^{-1} - 0.556 \text{ mol L}^{-1}) \times (2) = 0.648 \text{ mol L}^{-1} = \underline{\underline{0.65 \text{ mol L}^{-1}}} \end{aligned}$$

**PART C  
QUESTION 8**

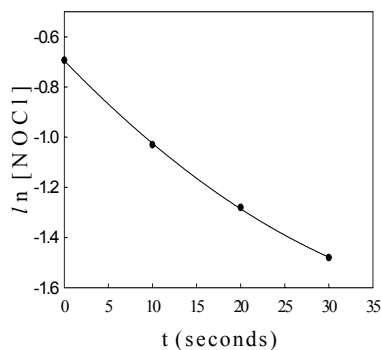
The rate constant ( $k$ ) for a first and second order reaction can be determined from the slope of the straight line.

**First Order Kinetics**

$$\ln [A] = -kt + \ln [A_0]$$

Plot  $\ln [A]$  vs  $t$

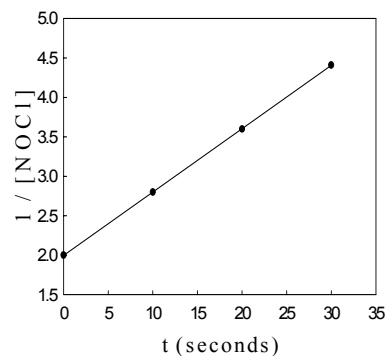
time (s)	[NOCl] (mol L <sup>-1</sup> )	$\ln [NOCl]$
0	0.500	-0.693
10	0.357	-1.03
20	0.278	-1.28
30	0.227	-1.48


**Second Order Kinetics**

$$\frac{1}{[A]} = kt + \frac{1}{[A_0]}$$

Plot  $\frac{1}{[A]}$  vs  $t$

time (s)	[NOCl] (mol L <sup>-1</sup> )	1/[NOCl]
0	0.500	2.00
10	0.357	2.80
20	0.278	3.60
30	0.227	4.41



(a) determine if the reaction is first or second order

Plotting  $\frac{1}{[NOCl]}$  vs  $t$  gives a straight line.

It is a second-order reaction.

(b) determine the rate constant

At 10 seconds,  $[A_0] = \text{initial} [NOCl] = 0.500 \text{ mol L}^{-1}$

$[A] = \text{final} [NOCl] = 0.357 \text{ mol L}^{-1}$

$$\frac{1}{0.357 \text{ mol L}^{-1}} = k(10 \text{ s}) + \frac{1}{0.500 \text{ mol L}^{-1}}$$

$$k = 8.0112 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1} = \underline{\underline{8.01 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}}}$$

**PART C**  
**QUESTION 9**

Given: EA + OH<sup>-</sup> = Products

$$\text{rate} = k [\text{EA}] [\text{OH}^-]$$

(second-order reaction, first order in each reactant)

$$k = 0.84 \text{ L mol}^{-1} \text{ s}^{-1} \text{ (second-order units)}$$

(a) the pseudo-first order rate constant

$$\text{Given: } [\text{OH}^-] = 0.015 \text{ mol L}^{-1}$$

$$\text{rate} = k' [\text{EA}] \quad (\text{where } k' = \text{pseudo-first order rate constant} = k [\text{OH}^-])$$

$$\begin{aligned} k' &= k [\text{OH}^-] \\ &= (0.84 \text{ L mol}^{-1} \text{ s}^{-1}) (0.015 \text{ mol L}^{-1}) \\ &= \underline{1.26 \times 10^2 \text{ s}^{-1}} \\ &= \underline{\underline{1.3 \times 10^2 \text{ s}^{-1}}} \end{aligned}$$

(b) the half-life of ethyl acetate

From Part (a):

$$k' = \underline{1.26 \times 10^2 \text{ s}^{-1}}$$

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{0.693}{k'}$$

$$t_{1/2} = \frac{0.693}{1.26 \times 10^2 \text{ s}^{-1}} = \underline{55.0 \text{ s}} = 55 \text{ s}$$

**PART C**  
**QUESTION 10**

Given: residence time ( $\tau$ ) =  $2.3 \times 10^{12}$  s

To find: rate constant ( $k$ ) and half-life ( $t_{1/2}$ )

$$\tau = \frac{1}{k}$$

(where  $k$  = rate constant)

$$k = \frac{1}{\tau} = \frac{1}{2.3 \times 10^{12} \text{ s}} = 43.48 \text{ s}^{-1} = 43 \text{ s}^{-1}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

$$t_{1/2} = \frac{0.693}{43.48 \text{ s}^{-1}} = 1.594 \times 10^{12} \text{ s} = 1.6 \times 10^{12} \text{ s}$$

**PART C**  
**QUESTION 11**

Given: (i)  $O^* \div O$  (ground state)  $k_1 = 7.2 \times 10^8 \text{ s}^{-1}$

$$\text{rate} = k_1 [O^*]$$

(ii)  $O^* + H_2O \div 2 OH$   $k_2 = 2.2 \times 10^{10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$

$$\text{rate} = k_2 [O^*] [H_2O]$$

$T = 25^\circ\text{C} = (273 + 25) \text{ K} = 298 \text{ K}$

standard vapour pressure of water ( $p(H_2O, g)$ ) = 3.2 kPa

‡ the relative humidity = 75%

^  $p(H_2O, g) = (3.2 \text{ kPa}) (75\%) = 2.4 \text{ kPa}$

Note that this vapour pressure of water is much greater than concentration of excited oxygen atoms ( $O^*$ ), and we can safely assume that  $[H_2O] \gg [O^*]$

To find: the lifetime ( $\tau$ ) of the excited oxygen atom ( $O^*$ )

$$\text{rate} = k_2 [O^*] [H_2O] = k_2' [O^*] \quad (\text{where } k_2' = k_2 [H_2O])$$

$$P V = n R T$$

or

$$c = \frac{P}{R T} \quad (\text{where } c = \frac{n}{V})$$

$$c = \frac{2.4 \text{ kPa}}{(8.314 \text{ kPa L K}^{-1} \text{ mol}^{-1}) (298 \text{ K})} = 9.687 \times 10^{14} \text{ mol L}^{-1}$$

Express  $[H_2O]$  in  $\text{molec cm}^3$

$$(9.687 \times 10^{14} \text{ mol L}^{-1}) (6.022 \times 10^{23} \text{ molec mol}^{-1}) \left(\frac{1 \text{ L}}{10^3 \text{ cm}^3}\right) = 5.833 \times 10^{17} \text{ molec cm}^{-3}$$

$$\begin{aligned} k_2' &= k_2 [H_2O] = (2.2 \times 10^{10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}) (5.833 \times 10^{17} \text{ molec cm}^{-3}) \\ &= 1.283 \times 10^8 \text{ s}^{-1} \end{aligned}$$

$$\tau = \frac{1}{k_1 + k_2'}$$

$$\tau = \frac{1}{(7.2 \times 10^8 \text{ s}^{-1}) + (1.283 \times 10^8 \text{ s}^{-1})} = 1.179 \times 10^{-9} \text{ s} \approx 1.2 \times 10^{-9} \text{ s}$$

**PART C**  
**QUESTION 12**

Given: First-order reaction:  $2 A \rightarrow B + C$

$$\text{rate} = k[A]$$

$$[A_0] = 100\% \quad (\text{at } t = 0)$$

$$[A] = 80\% \quad (\text{at } t = 175 \text{ min})$$

To find: time when  $[A] = 20\%$

**(1) When  $[A] = 80\%$  in 175 min**

$$\ln\left(\frac{[A]}{[A_0]}\right) = -kt$$

$$\ln\left(\frac{80\%}{100\%}\right) = -k(175 \text{ min})$$

$$k = 1.275 \times 10^{-3} \text{ min}^{-1}$$

**(2) When  $[A] = 20\%$  in ? min**

$$\ln\left(\frac{20\%}{100\%}\right) = -(1.2751 \times 10^{-3} \text{ min}^{-1})(t)$$

$$\begin{aligned} t &= 1.2622 \times 10^3 \text{ min} \\ &= \underline{1.26 \times 10^3 \text{ min}} \\ &= \underline{21.0 \text{ hrs}} \end{aligned}$$

**PART C**  
**QUESTION 13**

Given: First-order reaction:  $A \div 3 B + C$

$$\text{rate} = k[A]$$

$$[A_0] = 0.015 \text{ mol L}^{-1} \quad (\text{at } t = 0)$$

$$[B] = 0.020 \text{ mol L}^{-1} \quad (\text{at } t = 3.0 \text{ min})$$

(a) the rate constant ( $k$ ) for the reaction

	A	÷	3 B	+	C
<b>I:</b>	$0.015 \text{ mol L}^{-1}$		!		
<b>C:</b>	$3 \times (0.020 \text{ mol L}^{-1})$		$0.020 \text{ mol L}^{-1}$		$3 \times (0.020 \text{ mol L}^{-1})$
<b>E:</b>	<u><math>0.00833 \text{ mol L}^{-1}</math></u>		$0.020 \text{ mol L}^{-1}$		$0.0067 \text{ mol L}^{-1}$

$$\ln \left( \frac{[A]}{[A_0]} \right) = -k t$$

$$\ln \left( \frac{0.00833 \text{ mol L}^{-1}}{0.015 \text{ mol L}^{-1}} \right) = -k (3.0 \text{ min})$$

$$k = 0.1961 \text{ min}^{-1}$$

$$= \underline{\underline{0.20 \text{ min}^{-1}}}$$

(b) additional time needed for [B] to increase to  $0.040 \text{ mol L}^{-1}$

	A	÷	3 B	+	C
<b>I:</b>	$0.015 \text{ mol L}^{-1}$		!		
<b>C:</b>	$3 \times (0.040 \text{ mol L}^{-1})$		$0.040 \text{ mol L}^{-1}$		$3 \times (0.040 \text{ mol L}^{-1})$
<b>E:</b>	<u><math>0.00167 \text{ mol L}^{-1}</math></u>		$0.040 \text{ mol L}^{-1}$		$0.0133 \text{ mol L}^{-1}$

$$\ln \left( \frac{[A]}{[A_0]} \right) = -k t$$

$$\ln \left( \frac{0.00167 \text{ mol L}^{-1}}{0.015 \text{ mol L}^{-1}} \right) = -(0.20 \text{ min}^{-1}) (t)$$

$$t = 10.976 \text{ min} = \underline{\underline{11 \text{ min}}}$$

An additional **8 min** (11 min - 3.0 min) is needed.

**PART C**  
**QUESTION 14**

Given: **Second-order reaction:**

$$\frac{1}{[A]} = k t + \frac{1}{[A_0]}$$

$$t_{1/2} = \frac{1}{k [A_0]}$$

$$[A] = 0.30 \text{ M at } 30.0 \text{ min}$$

$$t_{1/2} = 90.0 \text{ min}$$

To find: rate constant ( $k$ ) and  $[A_0]$

First generate an arithmetic expression for  $[A_0]$  at  $t = 0$  in terms of  $k$

Ĥ At 30.0 min,

$$\frac{1}{0.30 \text{ M}} = k (30.0 \text{ min}) + \frac{1}{[A_0]}$$

Ï  $t_{1/2} = 90.0 \text{ min}$ ,

$$90.0 \text{ min} = \frac{1}{k [A_0]}$$

$$[A_0] = \frac{1}{k (90.0 \text{ min})}$$

(a) Substitute Ï into Ĥ:

$$\frac{1}{0.30 \text{ M}} = k (30.0 \text{ min}) + \frac{1}{\frac{1}{k (90.0 \text{ min})}}$$

$$\frac{1}{0.30 \text{ M}} = k (30.0 \text{ min}) + k (90.0 \text{ min})$$

$$\frac{1}{0.30 \text{ M}} = k (120.0 \text{ min})$$

$$k = \frac{2.7778 \times 10^{12} \text{ M}^{-1} \text{ min}^{-1}}{120.0 \text{ min}} = \underline{\underline{2.8 \times 10^{12} \text{ M}^{-1} \text{ min}^{-1}}}$$

(b) From Ï:

$$[A_0] = \frac{1}{k (90.0 \text{ min})} = \frac{1}{(2.8 \times 10^{12} \text{ M}^{-1} \text{ min}^{-1}) (90.0 \text{ min})} = 0.40 \text{ M}$$