

1. At 300 K, the forward rate constant,  $k_f$ , is  $1.50 \times 10^{-5} \text{ s}^{-1}$  for the reaction  

$$2 \text{NOCl(g)} \rightleftharpoons 2 \text{NO(g)} + \text{Cl}_2(\text{g}) \quad \Delta H = +75.2 \text{ kJ mol}^{-1}$$
The activation energy,  $E_a$ , for the forward reaction at 300 K is  $90.2 \text{ kJ mol}^{-1}$ .
- (a) The reaction follows the second-order kinetics with rate law:  
 $\text{rate} = k_f [\text{NOCl}]^2$ . **TRUE / FALSE**
- (b) A linear plot of  $\ln k$  versus  $T^{-1}$  yields a slope of  $+E_a / R$ . **TRUE / FALSE**
- (c) The activation energy at 300 K for the reverse reaction is: \_\_\_\_\_
- (d) A decrease in temperature will shift the equilibrium to the right. **TRUE / FALSE**
- (e) In the presence of a catalyst at 320 K, the activation energy is altered by  $38.6 \text{ kJ mol}^{-1}$ .
- (i) The  $E_{a(\text{cat})}$  for the catalyzed reaction is: \_\_\_\_\_
- (ii) The  $K_c$  for the catalyzed reaction will be increased. **TRUE / FALSE**
2. In a closed vessel at 2000 K,  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO(g)}$   $K_p = 2.5 \times 10^{-4}$   
However,  $\text{NO(g)}$  rapidly reacts with oxygen to produce  $\text{NO}_2(\text{g})$ .  

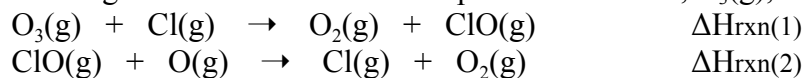
$$2 \text{NO(g)} + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g}) \quad K_p = 1.6 \times 10^{-4}$$
The net reaction of  $\text{NO}_2(\text{g})$  formation is:  

$$\text{N}_2(\text{g}) + 2 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g}) \quad \Delta H^\circ = +68 \text{ kJ mol}^{-1}$$
- (a)  $K_p$  expression for the net reaction is written as: \_\_\_\_\_
- (b)  $K_p$  for the overall reaction (with units) is: \_\_\_\_\_
- (c) Compressing the vessel volume shifts the equilibrium forward. **TRUE / FALSE**
- (d) Removing  $\text{NO}_2(\text{g})$  causes the reaction to the right. **TRUE / FALSE**
- (e) The  $K_p$  for  $\text{NO}_2(\text{g}) \rightleftharpoons \frac{1}{2} \text{N}_2(\text{g}) + \text{O}_2(\text{g})$  is: \_\_\_\_\_
- (f) The maximum conversion from  $\text{NO}_2(\text{g})$  to  $\text{N}_2(\text{g})$  and  $\text{O}_2(\text{g})$  is favoured by:  
( low / high ) pressure and ( low / high ) temperature
3. A 2.00-L container is filled with 1.00 mol  $\text{N}_2\text{O}_5(\text{g})$  at 400 K. At equilibrium, 40.0% of  $\text{N}_2\text{O}_5(\text{g})$  has dissociated according to the equation:  $2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
- (a) The equilibrium constant expression,  $K_c$ , is written as: \_\_\_\_\_
- (b) The equilibrium concentration of  $\text{N}_2\text{O}_5(\text{g})$  is: \_\_\_\_\_
- (c) The equilibrium concentration of  $\text{NO}_2(\text{g})$  is: \_\_\_\_\_
- (d) The equilibrium concentration of  $\text{O}_2(\text{g})$  is: \_\_\_\_\_
- (e) At 400 K,  $K_c$  (with units) is equal to: \_\_\_\_\_
- (f) At 400 K,  $K_p$  (with units) is equal to: \_\_\_\_\_

- (g) If the initial pressures of  $\text{N}_2\text{O}_5(\text{g})$ ,  $\text{NO}_2(\text{g})$  and  $\text{O}_2(\text{g})$  are 6.00 atm, 9.00 atm and 10.0 atm, respectively, the reaction quotient,  $Q_p$ , is equal to:
- \_\_\_\_\_

Since  $Q_p$  is ( less / greater ) than  $K_p$ , the reaction proceeds to the ( left / right ).

4. Given the following mechanism for the decomposition of ozone,  $\text{O}_3(\text{g})$ , in the stratosphere.

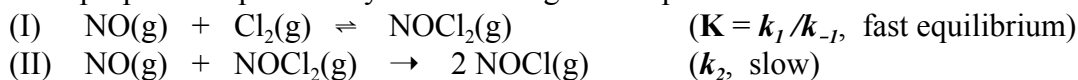


Thermochemical data provided:  $\Delta H_f^\circ [\text{O}_3] = +148 \text{ kJ mol}^{-1}$   $\text{BE} (\text{O}-\text{O}) = +498 \text{ kJ mol}^{-1}$   
 $\Delta H_f^\circ [\text{ClO}] = +102 \text{ kJ mol}^{-1}$   $\text{BE} (\text{Cl}-\text{Cl}) = +244 \text{ kJ mol}^{-1}$

- (a) Write the equation for the overall reaction. \_\_\_\_\_
- (b) The intermediate is \_\_\_\_\_ and the catalyst is \_\_\_\_\_.
- (c)  $\Delta H_{\text{rxn}(1)}$  equals to \_\_\_\_\_ and  $\Delta H_{\text{rxn}(2)}$  equals to \_\_\_\_\_.
- (d) The enthalpy change for the overall reaction is: \_\_\_\_\_
- (e) The decomposition of  $\text{O}_3(\text{g})$  is favoured by low temperature. **TRUE** / **FALSE**
- (f) Increase in the pressure of  $\text{O}_3(\text{g})$  favours the reverse reaction. **TRUE** / **FALSE**

5. The reaction of nitric oxide and chlorine is:  $2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{NOCl}(\text{g})$

It has been proposed to proceed by the following two-step mechanism:



- (a) The intermediate is: \_\_\_\_\_
- (b) The rate-determining step is: \_\_\_\_\_
- (c) The rate law for the rate-determining step is: \_\_\_\_\_
- (d) Show that the proposed mechanism is consistent with the experimentally obtained rate law,  
 $\text{rate} = k_{\text{exp}} [\text{NO}]^2 [\text{Cl}_2]$   
 (i) Using the Equilibrium Constant (**K**) method to eliminate concentration of an intermediate  
 (ii) Using the Steady-State approach to eliminate concentration of an intermediate
- (e) The  $k_{\text{exp}}$  equals to: \_\_\_\_\_ in Equilibrium Constant method, and  
 \_\_\_\_\_ in Steady State approach.
- (f) State, under what conditions, the rate law derived using the Equilibrium Constant method would be the same as that derived from the Steady-State method.

6. Given that  $K_f$  for water is  $1.86^\circ\text{C kg mol}^{-1}$ , the freezing point of a solution made by adding 0.0200 moles of  $\text{Na}_3\text{PO}_4$  to 200.0 g water is:
- \_\_\_\_\_

7. The concentration of  $\text{K}_2\text{SO}_4$  solution, which is isotonic with that of blood, with osmotic pressure of 6.5 atm at  $37^\circ\text{C}$  is:
- \_\_\_\_\_  $\text{mol L}^{-1}$

8. A 0.200 L sample of hard water containing 84.5 ppm of  $\text{Ca}^{2+}$  ( $40.08 \text{ g mol}^{-1}$ ) is titrated against unknown EDTA solution to the Eriochrome Black endpoint. It requires 24.62 mL of the EDTA to reach the endpoint. The concentration of EDTA used is:
- \_\_\_\_\_

**Data Information**

$$\Delta T = k_f m$$

$$\pi = c R T \quad (0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1})$$

$$k = A \times e^{-\frac{E_a}{R T}}$$

**ANSWERS**

1. (a) FALSE  
(b) FALSE  
(c) +15 kJ mol<sup>-1</sup>  
(d) FALSE  
(e) (i) 51.6 kJ mol<sup>-1</sup>  
(ii) FALSE
2. (a)  $K_p = p(\text{NO})^2 / p(\text{N}_2) p(\text{O}_2)^2$   
(b)  $4.0 \times 10^{-8} \text{ atm}^{-1}$   
(c) TRUE  
(d) TRUE  
(e)  $5.0 \times 10^3 \text{ atm}^{1/2}$   
(f) low pressure and low temperature
3. (a)  $K_c = [\text{NO}_2]^4 [\text{O}_2] / [\text{N}_2\text{O}_5]^2$   
(b) 0.300 M  
(c) 0.400 M  
(d) 0.100 M  
(e) 0.0284 M<sup>3</sup>  
(f)  $1.00 \times 10^3 \text{ atm}^3$   
(g)  $1.82 \times 10^3 \text{ atm}^3$ ; greater; left
4. (a)  $\text{O}_3(\text{g}) + \text{O}(\text{g}) \rightarrow 2 \text{O}_2(\text{g})$   
(b) intermediate: ClO(g); catalyst: Cl(g)  
(c)  $\Delta H_{\text{rxn}}(1): -168 \text{ kJ mol}^{-1}$        $\Delta H_{\text{rxn}}(2): -229 \text{ kJ mol}^{-1}$   
(d)  $-397 \text{ kJ mol}^{-1}$   
(e) TRUE  
(f) FALSE
5. (a) NOCl<sub>2</sub>(g)  
(b)  $\text{NO}(\text{g}) + \text{NOCl}_2(\text{g}) \rightarrow 2 \text{NOCl}(\text{g})$   
(c) rate =  $k_2 [\text{NO}] [\text{NOCl}_2]$   
(e) For Equilibrium Constant method:  $k_{\text{exp}} = K k_2$  (or  $k_1 k_2 / k_{-1}$ )  
For Steady State approach:  $k_{\text{exp}} = k_1 k_2 / k_{-1} + k_2 [\text{NO}]$   
(f)  $k_{-1} \gg k_2 [\text{NO}]$
6.  $\ominus 0.744 \text{ }^\circ\text{C}$
7.  $0.085 \text{ mol L}^{-1}$
8. 0.0171 M