THE UNIVERSITY OF ZAMBIA
SCHOOL OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY
ACADEMIC YEAR 2019/20
TERM 2
CHE1000: INTRODUCTION TO CHEMISTRY

Solved Examples:

1. Consider the reaction of nitrogen dioxide with fluorine to give nitryl fluoride, NO_2F.

   $$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

   How is the rate of formation of NO_2F related to the rate of reaction of fluorine?

   $$\textbf{Rate of reaction} = \frac{1}{2}\frac{\Delta[NO_2F]}{\Delta t} = \frac{\Delta[F_2]}{\Delta t}$$

2. The following data were obtained for the decomposition of N_2O_5 in CCl_4. The following data were collected.

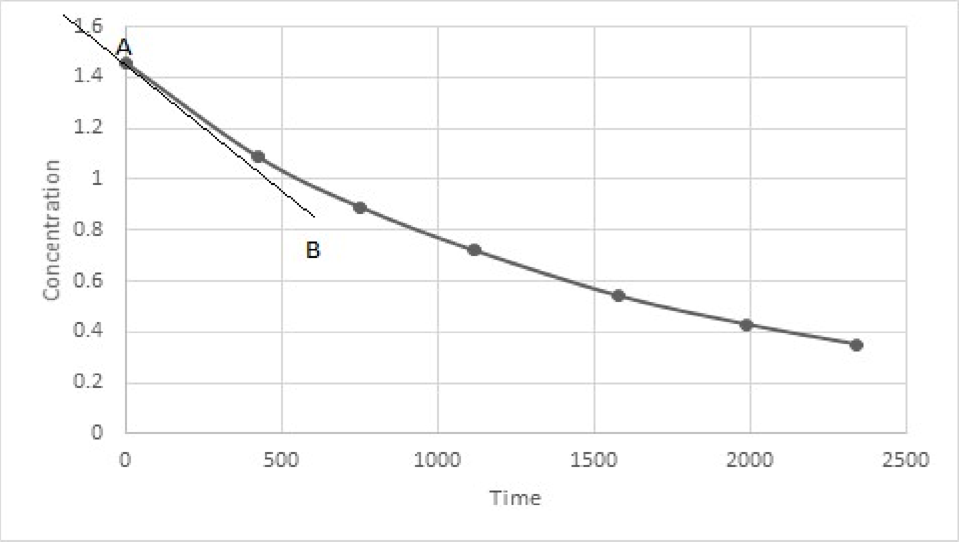
Time/ s	0	423	753	1116	1582	1986	2343
$[N_2O_5]$/ mol dm^{-3}	1.46	1.09	0.89	0.72	0.54	0.43	0.35

CCalculate:

(a) Average rate of reaction.

$$\textbf{Rate of reaction} = \frac{\Delta[N_2O_5]}{\Delta t} = \frac{(0.35-1.46)mol\ dm^3}{(2343-0)\ s} = 4.74\ \times 10^{-4} \qquad \textbf{[1 mark]}$$

(b) Initial instantaneous rate.



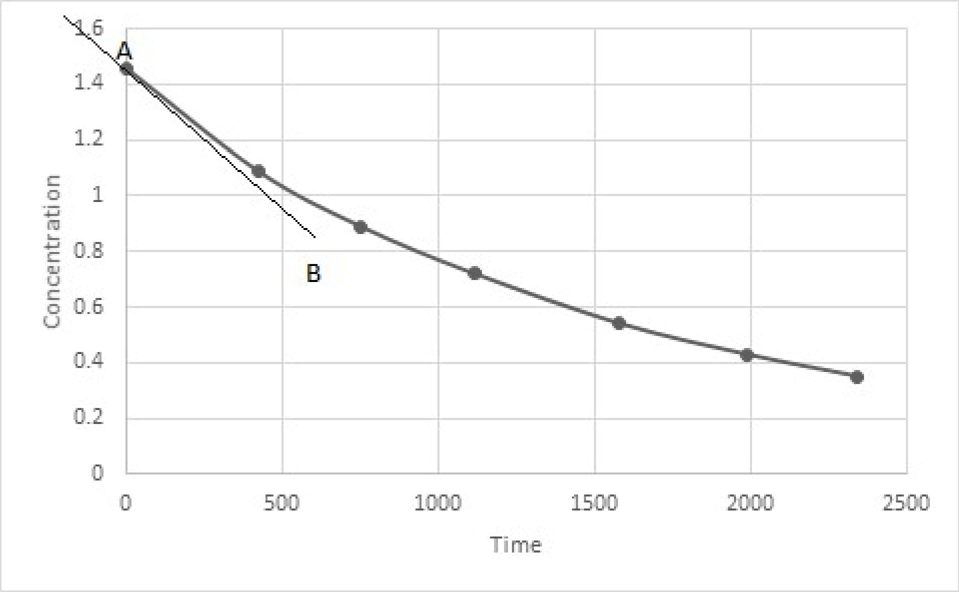
From the concentration time graph: slope of the line at AB = 0.00102 s^{-1}.

(c) Order with respect to N_2O_5

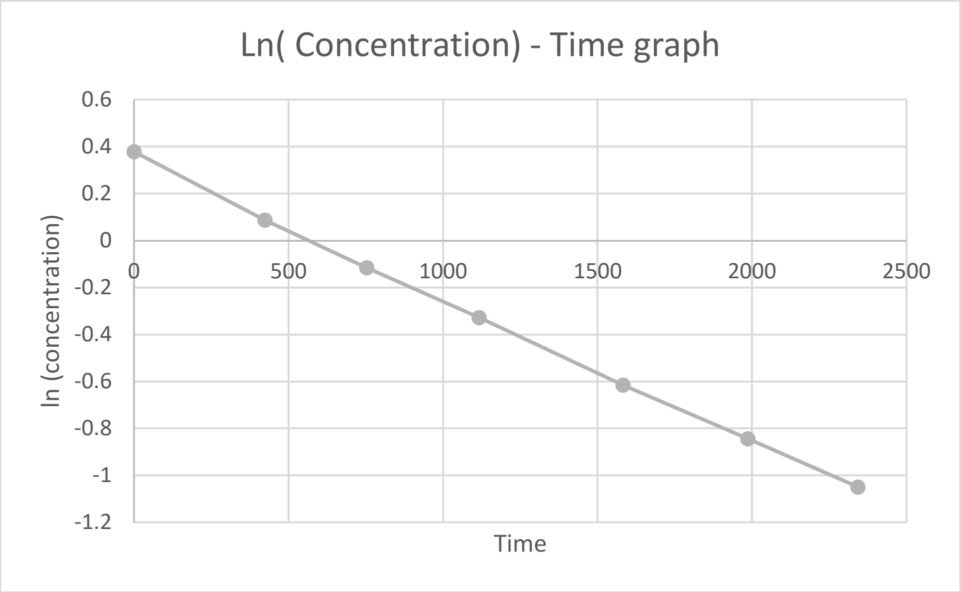
Time	$[N_2O_5]$	LN[N2O5]	1/[N2O5]
0	**1.46**	**0.378436**	**0.684932**
423	**1.09**	**0.086178**	**0.917431**
753	**0.89**	**-0.11653**	**1.123596**
1116	**0.72**	**-0.3285**	**1.388889**
1582	**0.54**	**-0.61619**	**1.851852**
1986	**0.43**	**-0.84397**	**2.325581**
2343	**0.35**	**-1.04982**	**2.857143**

Plot the graphs:

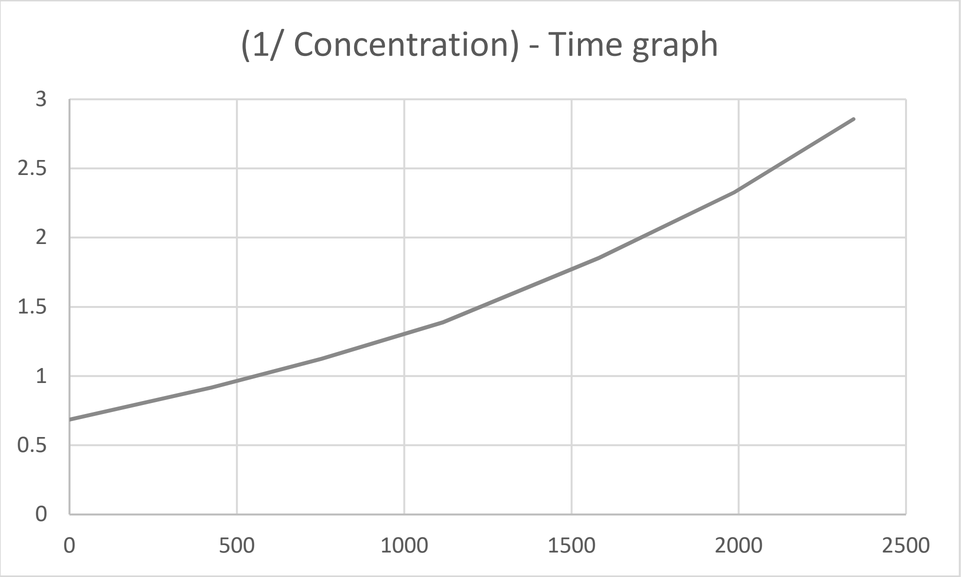
(i) If the graph is straight line, reaction is zero order:
Concentration time graph:



(i) If the graph is straight line, reaction is first order:



(iii) If the graph is straight line, reaction is second order:



Reaction is first order as the 2nd graph is a straight line. **[1 marks]**

(d) Rate law for this reaction:
Rate (R) = k [N_2O_5]

3. What is the rate constant k, and what is the order of reaction if k = 4 $dm^3\ mol^{-1}\ s^{-1}$.

   Rate constant is a rate of reaction when concentration of reactants is one mole dm^{-3}. From the units reaction is second order.

4. Consider the reaction: $SO_2 + O_3 \rightarrow SO_3 + O_2$.
   A rate study of this reaction was conducted at 298 K. The data that were obtained are shown in the table.

$[SO_2]$, mol dm^{-3}	0.25	0.25	0.75
$[O_3]$, mol dm^{-3}	0.40	0.20	0.20
Initial Rate, mol $dm^{-3}\ s^{-1}$	0.118	0.118	1.062

(a) What is the order with respect to: SO_2 and O_3

Compare column 1 and 2. No change in initial rate when concentration of ozone is reduced to half, hence zero order with respect to ozone.

Compare column 1 and 3. Concentration of Sulphur dioxide is tripled and rate become nine times, hence third order.

OR

Assume rate law is Rate (R) = k $[SO_2]^\alpha[O_3]^\beta$

Substitute the values from column 2 and 3 to get α

$0.118 = k\,(0.25)^\alpha(0.20)^\beta$ **(1)**

$1.062 = k\,(0.75)^\alpha(0.20)^\beta$ **(2)**

Divide equation 2 by equation 1

$$\frac{1.062}{0.118} = \left(\frac{0.75}{0.25}\right)^\propto$$

$$9 = (3)^\alpha$$

$\alpha = 2$

Substitute the values from column 1 and 2 to get α

$0.118 = k\,(0.25)^\alpha(0.20)^\beta$ **(3)**

$0.118 = k\,(0.25)^\alpha(0.40)^\beta$ **(4)**

Divide equation 4 by equation 3

$$\frac{0.118}{0.118} = \left(\frac{0.40}{0.20}\right)^\beta$$

$$1 = (2)^\beta$$

$\beta = 0$

(b) Write the rate law for this reaction.

Rate (R) = k $[SO_2]^2$

(c) Determine the value and units of the rate constant, k.

Rate (R) = k $[SO_2]^2$
0.118 mol dm^{-3} s^{-1} = k (0.25 mol dm^{-3})^2
k = 1.89 dm^3 mol^{-1} s^{-1}

5. Nitryl fluoride is an explosive compound that is made by the oxidation of nitrogen dioxide with fluorine.
$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$

	[NO_2] mol dm^{-3}	**[F_2] mol dm^{-3}**	**[NO_2F] mol dm^{-3}**	**Rate disappearance of NO (mol $dm^{-3}s^{-1}$)**
1	**0.0010**	**0.0050**	**0.0020**	**2.0×10^{-4}**
2	**0.0020**	**0.0050**	**0.0020**	**4.0×10^{-4}**
3	**0.0020**	**0.0020**	**0.0020**	**1.6×10^{-4}**
4	**0.0020**	**0.0020**	**0.0010**	**1.6×10^{-4}**

(a) What is the rate law for the reaction?

Compare rows 1 and 2 . Rate is doubled as the concentration of nitrogen dioxide is doubled while concentration of fluorine is kept constant, hence first order with respect to nitrogen dioxide.

Compare rows 2 and 3. Concentration of fluorine is decreased to 0.4 times while the concentration of nitrogen dioxide is kept constant and rate become 0.4 times, hence first order.

OR

Assume rate law is Rate (R) = k $[NO_2]^\alpha[F_3]^\beta$
Substitute the values from rows 1 and 2 to get α

$x\ 10^{-4} = k\ (0.0010)^\alpha(0.0050)^\beta$ (1)
$4\ x\ 10^{-4} = k\ (0.0020)^\alpha(0.0050)^\beta$ (2)

Divide equation 1 by equation 2

$$\frac{2}{4} = \left(\frac{0.0010}{0.0020}\right)^{\propto}$$

$$0.5 = (0.5)^\alpha$$

α = 1

Substitute the values from column 2 and 3 to get α
$4\ x\ 10^{-4} = k\ (0.0020)^\alpha(0.0050)^\beta$ (3)

$1.6 \times 10^{-4} = k\,(0.0020)^{\alpha}(0.0020)^{\beta}$ **(4)**

Divide equation 4 by equation 3

$$\frac{1.6}{4} = \left(\frac{0.0020}{0.0050}\right)^{\beta}$$

$$0.4 = (0.4)^{\beta}$$

$\beta = 1$

Rate (R) = k $[NO_2][F_3]$

(b) What is the order of the reaction with respect to each reactant and product?

First order with respect to both nitrogen dioxide and fluorine.

(c) Calculate the rate constant, k.

Rate (R) = k $[NO_2][F_3]$
1.6×10^{-4}mol dm^{-3} s^{-1} = k (0.0020 mol dm^{-3})(0.0020 mol dm^{-3})
K = 40 dm^{3} mol^{-1} s^{-1}

6. Ethyl chloride, CH_3CH_2Cl, used to produce tetraethyl lead gasoline additive, decomposes, when heated, to give ethylene and hydrogen chloride.

$CH_3CH_2Cl(g) \rightarrow C_2H_4(g) + HCl(g)$

The reaction is first order. In an experiment, the initial concentration of ethyl chloride was 0.00100 *mol dm^{-3}*. After heating at 500°C for 155 s, this was reduced to 0.00067 *mol dm^{-3}*. What was the concentration of ethyl chloride after a total of 256 s?

First order integrated rate law ln $[A]_t$ =ln $[A]_0$ – a k t

From the equation a = 1. Substitute the data:

ln $[A]_t$ =ln $[A]_0$ – a k t
ln (0.00067) = ln (0.00100) – 1 k 155
-7.31 = - 6.91 – 155k
- 0.40 = -155 k
k = 0.0026 s^{-1}

ln $[A]_t$ =ln $[A]_0$ – a k t
= ln (0.00100) – 1 x 0.0026 x 256 s
= -6.91 – 0.66 = -7.57
ln $[A]_t$ = -7.57
$[A]_t$ = 2.72

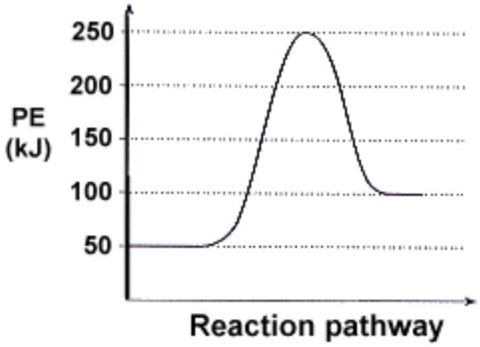
7. A reaction of the form *a*A → Products is second order with a rate constant of 0.413 *mol dm*$^{-3}$s^{-1}). What is the half-life, in seconds, of the reaction if the initial concentration of A is 5.25 x 10^{-3} *mol dm*$^{-3}$.?

   NOTE: Rate constant units should be *dm*^{3} *mol*$^{-1}$ s^{-1}

   For second order reaction half-life = $\frac{1}{ak[A]_0} = \frac{1}{a\times 0.413\ mol^{-1}\ dm^{3}\ s^{-1}\times 5.25\ x\ 10^{-3} mol\ dm^{-3}}$

   Half-life = a x 461 s.

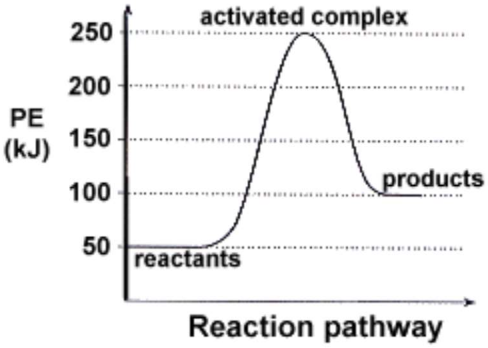
8. Answer the following questions based on the potential energy diagram shown here:



   (a) .Does the graph represent an endothermic or exothermic reaction?

   The graph represents an endothermic reaction.

   (b) Label the position of the reactants, products, and activated complex.



   (c) Determine the heat of reaction, ΔH, (enthalpy change) for this reaction.
   ΔH = 100 – 50 = 50 kJ/mol

   (d) Determine the activation energy, E_a for this reaction.
   E_a = 250 -50 = 200 kJ/ mol

   (e) How much energy is released or absorbed during the reaction?
   50 kJ/mol of energy is absorbed

   (f) How much energy is required for this reaction to occur?
   200 kJ of energy is required.

9. Consider the kinetic daa below for the reaction:

$2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$

T (K)	400.0	500.0	600.0
k ($M^{-1}s^{-1}$)	6.6 x10^{-4}	2.9 x10^{-1}	1.63 x10^{1}

Calculate activation energy, E_a, and A using Arrhenius equation

$2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$

$$\ln k = \ln A + -\frac{E_a}{R}\frac{1}{T}$$
$$y \;= a \;+ bx$$

T (K)	**400.0**	**500.0**	**600.0**
k ($M^{-1}s^{-1}$)	**6.6 x10^{-4}**	**2.9 x10^{-1}**	**1.63 x10^{1}**
1/T	**2.500 x10^{-3}**	**2.000 x10^{-3}**	**1.6667 x10^{-3}**
ln k	**-7.3232**	**-1.2379**	**2.7912**

a = 23.032 b = -1.2140 x104 r = 0.999998

$$b = -\frac{E_a}{R}$$

$$-1.214\text{x}10^4 = -\frac{E_a}{R}$$

$$E_a = 1.2140\,\text{x}10^4\,\text{K}\,\text{x}8.3145\,\text{J mol}^{-1}\text{K}^{-1} = 1.0094\,\text{x}10^5\,\text{J mol}^{-1} = 100.94\,\text{kJ mol}^{-1}$$

a =lnA

$$A = e^a = e^{23.032} = 1.006\,\text{x}10^{10}\,M^{-1}s^{-1}$$

OR Graphically

Use data point in the graph since the are on the straight line

$$b = \frac{y_2 - y_1}{x_2 - x_1} = \frac{2.7912 - (-1.2379}{(1.6667 = 2.000)\text{x}10^{-3}} = -1.2089\,\text{x}10^4$$

$$-1.2089\,\text{x}10^4 = -\frac{E_a}{R}$$

$$E_a = 1.2089\,\text{x}10^4\,\text{K}\,\text{x}8.3145\,\text{J mol}^{-1}\text{K}^{-1} = 1.0051\text{x}10^5\,\text{J mol}^{-1} = 100.51\text{kJ mol}^{-1}$$

Use a set of kinetic data to caluculate A

$$\ln 16.3 = \ln A - 1.2089 \text{x} 10^{4}\ \frac{1}{600}$$

$$2.791 = \ln A - 20.148$$

$$\ln A = 22.94$$

$$A = e^{22.94} = 9.17 \text{x} 10^{9}\ M^{-1}s^{-1}$$

10. Write the expression for the equilibrium constants for the following reactions:

(a) $Br_{2(g)} + H_{2\ (g)} \rightleftharpoons 2HBr_{(g)}$ $$K_p = \frac{[HBr]^2}{[Br_2][H_2]}$$

(b) $CS_{2(g)} + 4H_{2(g)} \rightleftharpoons CH_{4(g)} + 2H_2S_{(g)}$ $$K_p = \frac{[H_2S]^2[CH_4]}{[CS_2][H_2]^4}$$

(c) $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$ $$K_p = \frac{[H_2]}{[H_2O]}$$

11. Would either of the following reaction go almost completely to products?

$N_2 + 2O_2 \rightleftharpoons 2NO_2$ $K_c = 3 \text{ x } 10^{-17}$

$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3$ $K_c = 8 \text{ x } 10^{25}$

Explain.

Yes, the oxidation of sulphur dioxide would go almost to completion as equilibrium constant is high But the first one will not as the equilibrium constant is low.

12. A 6.0 L vessel contained 0.0222 mol of phosphorus trichloride, 0.0189 mol phosphorus pentachloride and 0.1044 mol 0f chlorine at 230 °C in an equilibrium mixture. Calculate the equilibrium constant K_c and K_p for the reaction.

$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

The reaction is	**$PCl_{3(g)}$ + $Cl_{2(g)}$**	$\rightleftharpoons$	**$PCl_{5(g)}$**
Equilibrium concentrations	$\frac{0.0222}{6}$	$\frac{0.1044}{6}$	$\frac{0.0189}{6}$
	0.0037	**0.0174**	**0.00315**

$$K_c = \frac{0.00315}{0.0037 \times 0.0174} = 48.9$$

$$\boldsymbol{K_p = K_c(RT)^{\Delta n}}$$

$$= \mathbf{48.9}\ (\mathbf{8.314} \times \mathbf{10^3}(\mathbf{230} + \mathbf{273}))^{-1}$$

$$= \mathbf{1.17} \times \mathbf{10^{-5}}$$

Note: R = 8.314 × 10^3 = Pa dm^3 mol^{-1} K^{-1}

13. At 77 °C 2 mol of nitrosyl bromide, NOBr, in a 1.0 L flask were allowed to reach equilibrium according to following equation:

$$2NOBr \rightleftharpoons 2NO + Br_2$$

If the NOBr is 9.4% dissociated at this temperature calculate the equilibrium constant.

	2NOBr	$\rightleftharpoons$	**2NO + Br$_2$**	
Initial concentration	**2**		**0**	**0**
Change	**- 2 x 9.4%**		**+9.4%**	**+4.7%**
	2 – (2x 9.4/100)		**(2x 9.4/100)**	**(2x 4.7/100)**

$$K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2}$$

$$= \frac{(0.188)^2(0.094)}{(1.812)^2} = 0.0010119 = 0.0010$$

14. Consider the equilibrium process :

$$C(s) \quad + CO_2(g) \rightleftharpoons 2CO(g)$$

At 700 °C the total pressure of the system is found to be 4.50 atm. If the equilibrium constant K_p is 1.52, calculate the equilibrium partial pressures of CO_2 and CO.

The equilibrium expression $K = \frac{(p_{CO})^2}{(p_{CO2})}$

Total pressure = Pco + P co$_2$ = 4.5 atm

Let us assume Pco = x

Then, Pco$_2$= (4.5-x) atm

$$K_p = \frac{P_{CO}{}^2}{P_{CO_2}} = \frac{x^2}{(4.50-x)} = 1.52$$

x^2 + 1.52x - 6.84 =0

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$$
$$= \frac{-1.52 \pm \sqrt{(1.52)^2 - 4\times 1\times(-6.84)}}{2\times 1}$$
$$= \frac{-1.52 \pm \sqrt{29.6704}}{2}$$
$$= \frac{-1.52 \pm 5.45}{2}$$
$$x = 1.96$$
$$or$$
$$x = -3.48$$

Only positive value has significance.

Hence, partial pressures are

Pco = 1.96 and Pco$_2$ = (4.50-1.96) = 2.54 atm

15. Consider the equilibrium:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)} \qquad H = 284kJ$$

What would be the effect on the position of equilibrium of

(a) increasing the total pressure on the system by decreasing its volume;
Increase in pressure favours the forward reaction as it decreases the number of moles. More O_3 is produced. OR Equilibrium shifts to right.

(b) adding O$_2$ to the system;

If the concentration of oxygen is increased the equilibrium is disturbed. System tries achieves new equilibrium by using up more oxygen Or OR Equilibrium shifts to right.

(c) decreasing the temperature?

The reaction is endothermic so decreasing the temperature shifts the equilibrium to left.

(d) What change would you expect in the value of equilibrium constant by increasing the temperature?

Equilibrium constant will increase.

16. At 200 °C $K_c = 1.4\text{x}10^{-10}$ for the reaction

$N_2O_{(g)} + NO_{2(g)} \rightleftharpoons 3NO_{(g)}$.

If 0.200 mol of N_2O and 0.400 mol of NO_2 are placed in a 4.00 L container, what would the concentration of NO be if this equilibrium were established?

The reaction is	**$N_2O_{(g)}$ +**	**$NO_{2(g)}$ $\rightleftharpoons$**	**$3NO_{(g)}$.**
Initial concentration	$\frac{0.200}{4}$	$\frac{0.400}{4}$	**0**
	0.0500	**0.100**	**0**
Change	**- x**	**- x**	**3x**
Equilibrium concentration	**(0.0500-x)**	**(0.100-x)**	**3x**

$$K_c = \frac{(3x)^3}{(0.0500 - x)(0.100 - x)} = 1.4 \times 10^{-10}$$

$$9x^3 = 1.4 \times 10^{-10} \times (0.05 - x)(0.1 - x)$$

Assume x is small as compared to 0.1 and 0.05.

Then $x^3 = (1.4 \times 10^{-10} \times 0.05 \times 0.1) / 9$

$x = 8.88 \times 10^{-5}$ mol dm^{-3}

17. At 25 °C Kc = 0.145 for the following reaction in the solvent CCl_4.

$2BrCl \rightleftharpoons Br_2 + Cl_2$

A solution was prepared with the following initial concentrations:

[BrCl] = 0.0400 mol dm^{-3}, [Cl$_2$] = 0.0200 mol dm^{-3}, [Br$_2$] = 0.0300 mol dm^{-3}. What will be their equilibrium concentration?

From the concentration Q =(0.03 x 0.02)/(0.04)^2 =0.375

Q is greater than equilibrium constant. Hence, the reaction would proceed in reverse direction or we can say concentration of BrCl would increase and of clorine and bromine decrease.

The reaction is	**$2BrCl \rightleftharpoons$**	**Br_2**	**+**	**Cl_2**
Initial concentration	**0.0400 M,**	**0.0300 M**		**0.0200 M.**
Change	**2x**	**x**		**x**
Equilibrium concentration	**(0.04 +2x)**	**(0.03 -x)**		**(0.02-x)**

K= 0.145= (0.03 -x) (0.02-x)/(0.04+2x)^2

0.145(0.04 + 2x)^2 = 0.0006 - 0.05 x + x^2

0.145(0.0016+4x^2 + 0.16x)= 0.0006 - 0.05 x + x^2

0.58 x^2 + 0.000232 +0.0232 x = 0.0006 - 0.05 x + x^2

0.42x^2 -0.0732 x + 0.000368 = 0

$$
\begin{aligned}
x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\
&= \frac{-(-0.0732) \pm \sqrt{(-0.0732)^2 - 4 \times 0.42 \times (0.000368)}}{2 \times 0.42} \\
&= \frac{0.0732 \pm \sqrt{0.00536 - 0.00061824}}{0.84} \\
&= \frac{0.0732 \pm 0.0688}{0.84} \\
x &= 0.169 \\
&or \\
x &= 0.00523
\end{aligned}
$$

Second value is the correct value. Hence, concentrations are

[BrCl] =0.04-(2 x 0.00523)=0.05046 mol dm^{-3}

[Cl_2]= 0.02- 0.00523= 0.01477 moldm^{-3}

[Br_2]= 0.03 – 0.00523 = 0.02477 mol dm^{-3}