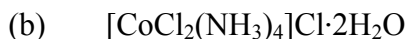
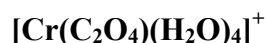
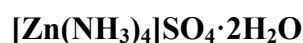
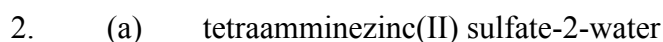




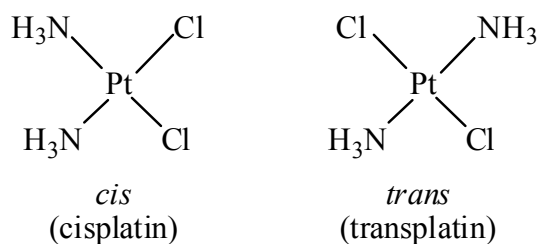
Potassium hexafluoroplatinate(IV)



Tetramminedichloridocobalt(III) chloride – 2 – water.

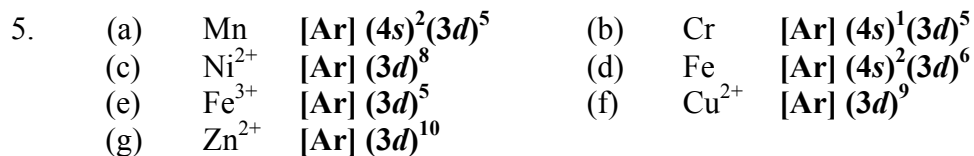


3. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ can exist as two geometric isomers:



4. **Coordination isomers have a ligand and a counter ion exchanged. $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{SO}_4$ has a Cl^- ion as a ligand and SO_4^{2-} as a counter ion.**

(c) **$[\text{Cr}(\text{H}_2\text{O})_5\text{SO}_4]\text{Cl}$ is a coordination isomer: it has a SO_4^{2-} ion as a ligand and Cl^- as a counter ion. (Note that SO_4^{2-} coordinates to a metal using oxygen atoms rather than the sulfur.)**



6. (a) **Between experiments (2) and (4), $[\text{Fe}^{2+}]$ and $[\text{O}_2]$ are unchanged. $[\text{H}^+]$ is doubled and this leads the rate to double. The reaction is first-order with respect to $[\text{H}^+]$.**

Between experiments (3) and (4), $[\text{Fe}^{2+}]$ and $[\text{H}^+]$ are unchanged. $[\text{O}_2]$ is doubled and this doubles the rate: the reaction is first-order with respect to $[\text{O}_2]$.

Between experiments (1) and (3), $[\text{O}_2]$ is unchanged. $[\text{Fe}^{2+}]$ and $[\text{H}^+]$ are both doubled and this leads to the rate increasing by a factor of 16. As the

reaction is first-order with respect to $[H^+]$, the rate would double because of the doubling in $[H^+]$. The doubling in $[Fe^{2+}]$ therefore increases the rate by a factor of 8: the reaction is third-order ($2^3 = 8$) with respect to $[Fe^{2+}]$.

Overall,

$$\text{rate} = k[Fe^{2+}]^3[O_2][H^+]$$

- (b) Using the first experiment, $[Fe^{2+}] = [O_2] = 1 \times 10^{-3} \text{ M}$ and $[H^+] = 0.1 \text{ M}$. The rate is $5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. Using the rate equation from (a):

$$\begin{aligned} \text{rate} &= k[Fe^{2+}]^3[O_2][H^+] \\ &= k \times (1 \times 10^{-3} \text{ M})^3 \times (1 \times 10^{-3} \text{ M}) \times (0.1 \text{ M}) = 5 \times 10^{-4} \text{ M s}^{-1} \end{aligned}$$

Hence, $k = 5 \times 10^9 \text{ M}^{-4} \text{ s}^{-1}$. The same value is obtained using the data from the other experiments.

The units of k are obtained by matching the units on the right and left-hand side of the rate equation.

The rate is the change in concentration with time and has units of " M s^{-1} ".

On the left-hand side of the rate law, $[Fe^{2+}]^3[O_2][H^+]$ has units of

$$\text{M}^3 \times \text{M} \times \text{M} = \text{M}^5.$$

To match, k must have units of " $\text{M}^{-4} \text{ s}^{-1}$ ":

$$\text{M s}^{-1} = (\text{M}^{-4} \text{ s}^{-1}) \times \text{M}^5$$

- (c) From the chemical equation, 4 mol of Fe^{3+} are made for every 1 mol of O_2 that is lost: rate of formation of $Fe^{3+} = 4 \times$ rate of loss of O_2 .

In experiment (3), the rate of loss of O_2 is $8 \times 10^{-3} \text{ M s}^{-1}$ so the rate of formation of $Fe^{3+} = 4 \times (8 \times 10^{-3}) = 3 \times 10^{-2} \text{ M s}^{-1}$.

- (d) When $[Fe^{2+}] = [O_2] = 4 \times 10^{-3} \text{ M}$ and $[H^+] = 0.1 \text{ M}$, the rate law gives:

$$\begin{aligned} \text{rate} &= k[Fe^{2+}]^3[O_2][H^+] \\ &= (5 \times 10^9 \text{ M}^{-4} \text{ s}^{-1}) \times (4 \times 10^{-3} \text{ M})^3 \times (4 \times 10^{-3} \text{ M}) \times (0.1 \text{ M}) \\ &= 0.128 \text{ M s}^{-1} \end{aligned}$$

As 4 mol of Fe^{2+} are consumed for every 1 mol of O_2 , the rate of loss of Fe^{2+} is $(4 \times 0.128) \text{ M s}^{-1} = 0.5 \text{ M s}^{-1}$.

7. (a) As $t_{1/2} = \frac{\ln 2}{k}$, $k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{6.00 \times 10^4 \text{ s}^{-1}} = 1.16 \times 10^{-5} \text{ s}^{-1}$

- (b) For a first-order reaction,

$$\ln \frac{[A]}{[A]_0} = -kt$$

After 1 hour = (60 × 60) s = 3600 s, the fraction that remain will be:

$$\frac{[A]}{[A]_0} = e^{-(1.16 \times 10^{-5} \times 3600)} = 0.959$$

The percentage that will have reacted is 4.1%.

8. The Arrhenius equation relates the rate constant with the temperature:

$$k = A e^{-E_a/RT}$$

If the rate constant is known at two temperatures, this can be rewritten as:

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

At 30 °C, T = (273 + 30) = 303 K and k is $5.1 \times 10^6 \text{ s}^{-1}$. At 50 °C, T = (273 + 50) = 323 K and k is $1.9 \times 10^7 \text{ s}^{-1}$:

$$\ln \left(\frac{1.9 \times 10^7 \text{ s}^{-1}}{5.1 \times 10^6 \text{ s}^{-1}} \right) = \frac{E_a}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})} \left(\frac{1}{(303 \text{ K})} - \frac{1}{(323 \text{ K})} \right)$$

Hence $E_a = 54000 \text{ J mol}^{-1} = 54 \text{ kJ mol}^{-1}$

This is a fairly typical activation energy and presumably corresponds, in the present case, to the partial breaking of the weak N-N bond in N₂O₄. An activation energy of this approximate size is quite common and leads to the ‘rule of thumb’ that the rate is doubled by increasing the temperature by 10 °C. In this example, the temperature increases from 30 °C to 50 °C and the rate quadruples.

At either temperature, $k = A e^{-E_a/RT}$ so using $k = 5.1 \times 10^6 \text{ s}^{-1}$ at T = 303 K:

$$5.1 \times 10^6 \text{ s}^{-1} = A \times e^{-(54000)/(8.314 \times 303)} \text{ so } A = 8.6 \times 10^{15} \text{ s}^{-1}.$$