CHEM1902/4 Answers to Problem Sheet 11

1. (a) $K_2[PtF_6]$

Potassium hexafluoridoplatinate(IV)

(b) $[CoCl_2(NH_3)_4]Cl{\cdot}2H_2O$

Tetramminedichloridocobalt(III) chloride – 2 – water.

2. (a) tetraamminezinc(II) sulfate-2-water

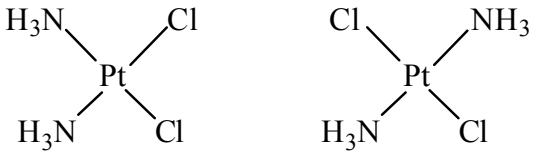
$[Zn(NH_3)_4]SO_4{\cdot}2H_2O$

(b) tetraaquaoxalatochromium(III) ion

$[Cr(C_2O_4)(H_2O)_4]^+$

3. (a) Mn **[Ar] $(4s)^2(3d)^5$** (b) Cr **[Ar] $(4s)^1(3d)^5$**
(c) Ni^{2+} **[Ar] $(3d)^8$** (d) Fe **[Ar] $(4s)^2(3d)^6$**
(e) Fe^{3+} **[Ar] $(3d)^5$** (f) Cu^{2+} **[Ar] $(3d)^9$**
(f) Zn^{2+} **[Ar] $(3d)^{10}$**

4. **$[PtCl_2(NH_3)_2]$ can exist as two geometric isomers:**



cis (cisplatin) *trans* (transplatin)

5. **Coordination isomers have a ligand and a counter ion exchanged.**
$[CrCl(OH_2)_5]SO_4$ has a Cl^- ion as a ligand and SO_4^{2-} as a counter ion.

(c) **$[Cr(OH_2)_5SO_4]Cl$ 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.)**

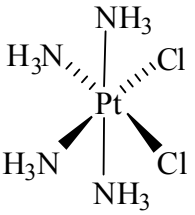
6. (a) **Ag^+ will react with uncoordinated Cl^- to form AgCl(s). As it reacts with two Cl^- ions per formula unit, there must be $2Cl^-$ counter ions. The remaining $2Cl^-$ ions and the $4NH_3$ molecules are coordinated to the metal.**

The oxidation number of the metal is +IV. The complex ion is thus $[PtCl_2(NH_3)_4]^{2+}$.

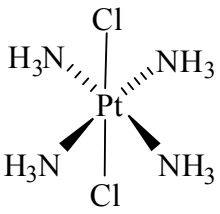
The coordination compound is $[PtCl_2(NH_3)_4]Cl_2$.

The name of this compound is tetraamminedichloridoplatinum(IV) chloride.

(b) **With $2Cl^-$ and $4NH_3$ ligands, two isomers are possible:**



cis-



trans-

(c) **Geometric (*cis* and *trans*) isomerism is possible (as above).**

(d) **Platinum is in group 10 so Pt(IV) has (10 – 4) = 6 *d*-electrons: $5d^6$.**

7. (a) **Between experiments (2) and (4), $[Fe^{2+}]$ and $[O_2]$ are unchanged. $[H^+]$ is doubled and this leads the rate to double. The reaction is first-order with respect to $[H^+]$.**

Between experiments (3) and (4), $[Fe^{2+}]$ and $[H^+]$ are unchanged. $[O_2]$ is doubled and this doubles the rate: the reaction is first-order with respect to $[O_2]$.

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

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

Hence, $k = 5 \times 10^9$ M^{-4} 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

$$M^3 \times M \times M = M^5.$$

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

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

(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 × rate of loss of O_2.

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

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

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

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

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

(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%.

9. 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 $5.1 \times 10^6\ s^{-1}$. At 50 °C, T = (273 + 50) = 323 K and k is $1.9 \times 10^7\ s^{-1}$:

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

Hence $E_a = 54000$ J $mol^{-1} = 54$ 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 N_2O_4. 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 $k = 5.1 \times 10^6\ s^{-1}$ at $T = 303$ K:

$5.1 \times 10^6\ s^{-1} = A \times e^{-(54000/(8.314\times303))}$ so $A = 8.6 \times 10^{15}\ s^{-1}$.