

# Kinetics and Mechanistic Approach into Electron-transfer of Permanganate Oxidation of Silver (I) in Aqueous Perchlorate Solutions

Refat M. Hassan <sup>\*1</sup>, Ishaq A. Zaafarany <sup>2</sup>, Fahd A. Tirkistani<sup>2</sup>, Ahmed Fawzy<sup>1,2</sup>, Hideo D. Takagi <sup>3</sup>

<sup>1</sup>Chemistry Department, Faculty of Science, Assiut University, Assiut, 71516 Egypt.

<sup>2</sup>Chemistry Department, Faculty of Applied Sciences, Umm Al-Qura University, Makkah Al-Mukarramah 13401, Saudi Arabia.

<sup>3</sup>Inorganic Chemistry Division, Research Center for Materials Science, Nagoya University, Furo-Cho Chikusa, Nagoya 464-01, Japan.

<sup>\*1</sup> rmhassan2002@yahoo.com; <sup>2</sup>ishaq\_zaafarany@yahoo.com; <sup>2</sup>drfahd999@gmail.com; <sup>1,2</sup>afsaad13@yahoo.com;

<sup>3</sup> h.d.takagi@nagoya-u.jp

## Abstract

The kinetics and mechanism of oxidation of silver (I) by permanganate ion in aqueous perchlorate solutions at a constant ionic strength of 1.0 mol dm<sup>-3</sup> have been studied spectrophotometrically. The reaction time curves of the pseudo first-order plots were found to be of sigmoidal shape throughout the entire course of reaction. The initial rates were found to be relatively fast in the early stages, followed by a more slow reaction over longer time periods. The experimental results indicated a first-order dependence in [MnO<sub>4</sub><sup>-</sup>] and fractional first-order kinetics with respect to [Ag<sup>+</sup>] for both stages. The results showed that the oxidation reaction was acid-catalyzed in which the reaction rates were increased with increasing the [H<sup>+</sup>]. Kinetic and spectrophotometric evidences for formation of 1:1 binuclear intermediate complex have been revealed in both two-stages. The activation parameters have been evaluated and a tentative reaction mechanism consistent with the kinetic results was discussed.

## Keywords

Oxidation; Kinetics; Mechanisms; Silver (I); Permanganate Ion

## 1. Introduction

The high tendency of Ag<sup>+</sup> to photolysis as well as the high oxidation potential value of Ag<sup>I</sup>/Ag<sup>II</sup> couple (-1.98 V) may be accounted for the comparatively less number of studies on its oxidation by other inorganic oxidants [1].

Permanganate is used as oxidizing agent for removing of organic molecules and heavy metals from nuclear waste as well as in organic synthesis and analytical chemistry.<sup>1</sup> However, the kinetics and mechanism of oxidation of most metal ions by acidic permanganate have been investigated earlier [2-6], the kinetics of reaction between Ag<sup>+</sup> and permanganate has not yet studied. This may be attributed to the estimated values of the relevant redox potentials of Mn<sup>VII</sup>/Mn<sup>VI</sup> (0.56V) or Mn<sup>VII</sup>/Mn<sup>II</sup> (1.51 V)[10] along with that of Ag<sup>I</sup>/Ag<sup>II</sup> (-1.98 V)[8,9] which indicates that the oxidation of silver(I) by permanganate ion is unfavorable from the thermodynamic points of view. But, preliminary experiments indicated the disappearance of the pink color of permanganate ion (Mn<sup>VII</sup>) on mixing with silver (I).

In view of the above aspects, the oxidation of silver(I) as mono-equivalent by this oxidant seems to be of great significant with the aims of shedding more light on the nature of electron-transfer process and the transition states in the rate-determining step as well as to gain some knowledge on the aqueous chemistry of silver(I) in acidic solutions. In addition, it is of interesting to extend our investigations on the kinetics of oxidation of inorganic metal cations by permanganate ion [10, 11] as a part of a series of investigations on kinetic studies performed in our laboratory.

## II. Experimental

### 1. Materials

Silver nitrite, silver nitrate and potassium permanganate reagents used were Analar (BDH). All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amount of the reagent in doubly distilled conductivity water. The temperature was controlled within  $\pm 0.05$  °C.

Preparation and standardization of  $\text{AgNO}_2$  [7],  $\text{AgNO}_3$  [7]  $\text{KMnO}_4$  [10, 11] stock solutions and the procedure of the kinetic runs were the same as described elsewhere.

### 2. Kinetic Measurements

Preliminary experiments showed that the oxidation kinetics is of considerable complexity. All kinetic runs were performed under pseudo-first-order conditions where  $[\text{Ag}^+]$  was present in a large excess over that of permanganate concentration at constant ionic strength of  $1.0 \text{ mol dm}^{-3}$  (maintained with  $\text{NaClO}_4$ ). The course of reaction was followed by monitoring the decrease in absorbance of permanganate ion at its absorption maximum, 525 nm, as a function of time. It was verified that there is no interference from all other reagents at this wavelength. The absorbance measurements were made in a thermostated cell compartment at the desired temperature within  $\pm 0.05$  °C on a Shimadzu UV-2101/3101 PC automatic scanning double beam spectrophotometer fitted with a wavelength program controller using cells of pathlength 1 cm. The spectral changes during the progress of the oxidation reaction are shown in Fig. 1.

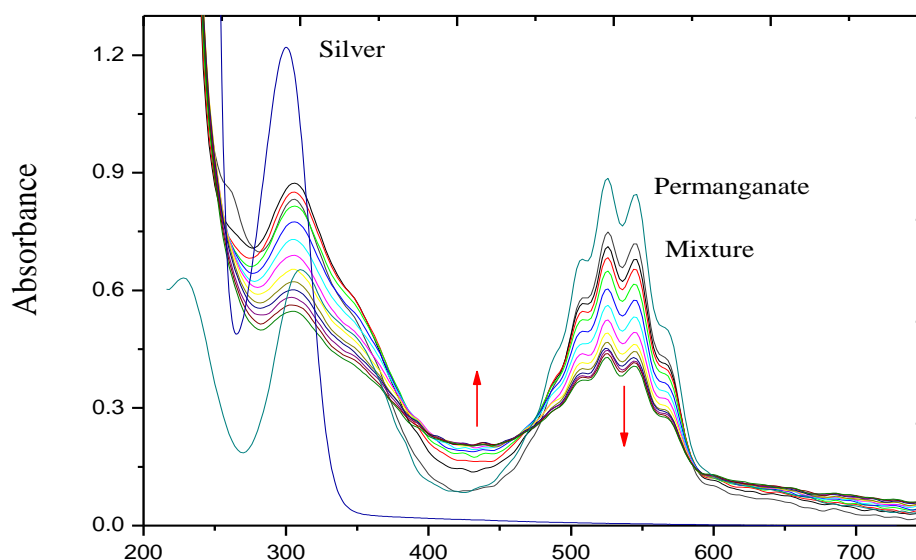


FIG. 1 SPECTRAL CHANGES (200-800) IN THE OXIDATION OF  $\text{Ag}^+$  BY  $\text{MnO}_4^-$  ION AT  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ ,  $[\text{Ag}^+] = 0.15$ ,  $[\text{H}^+] = 1.0$  AND  $I = 2.0 \text{ Mol dm}^{-3}$  AT  $40^\circ \text{C}$ .

Some experimental runs were performed using silver nitrate ( $\text{AgNO}_3$ ) as a reducing agent to conform the kinetic results obtained from silver nitrite reagent.

## III. Results

### 1. Reaction-Time Curves

The reaction time curves were found to be of sigmoidal shape throughout the entire course of reaction. The initial rates were relatively fast in the early stage (autoacceleration period), followed by a more decrease in the reaction rates (induction period) over longer time period. This behavior obeys the rate-law expression –

$$(A_\infty - A_t) = B_0 e^{-k_f t} + P_0 e^{-k_s t}$$

where  $k_f$  and  $k_s$  are the observed pseudo first-order rate constants for the fast and slow reactions.  $A_t$  and  $A_\infty$  are the absorbance at time  $t$  and infinity, while  $B_0$  and  $P_0$  represent the absorbance change for the fast and slow reacting

species, respectively. The analyses of the data were performed as described elsewhere [12-16]. The values of the rate constants  $k_f$  and  $k_s$  calculated by the least-squares method are summarized in Table 1.

TABLE 1 VALUES OF PSEUDO-FIRST-ORDER RATE CONSTANTS ( $k_f$  AND  $k_s$ ) IN THE OXIDATION OF  $\text{Ag}^+$  BY  $\text{MnO}_4^-$  ION AT  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ ,  $[\text{Ag}^+] = 0.30$ , AND  $I = 2.0 \text{ mol dm}^{-3}$  AT VARIOUS  $[\text{H}^+]$  AND DIFFERENT TEMPERATURES.

| $[\text{H}^+], \text{mol dm}^{-3}$ | Temp, °C | 40 °C                     |                           | 45 °C                     |                           |
|------------------------------------|----------|---------------------------|---------------------------|---------------------------|---------------------------|
|                                    |          | $10^4 k_f, \text{s}^{-1}$ | $10^5 k_s, \text{s}^{-1}$ | $10^4 k_f, \text{s}^{-1}$ | $10^5 k_s, \text{s}^{-1}$ |
| 1.0                                |          | 5.52                      | 5.75                      | 6.65                      | 6.88                      |
| 2.0                                |          | 7.00                      | 7.47                      | 8.59                      | 8.95                      |

## 2. Stoichiometry

Reaction mixtures containing different concentrations of the reactants at  $[\text{H}^+] = 1.0$  and  $I = 1.0 \text{ mol dm}^{-3}$  were equilibrated in dark bottles away from light. The unreacted permanganate was estimated periodically until it reached a constant value, i.e. completion of the reaction. Estimation of unreacted oxidant revealed that 1 mole of permanganate ion consumed  $5 \pm 0.1$  mol of silver (I). This result suggested the following stoichiometric eqn. (1).



The formation of  $\text{Ag}^{2+}$  was confirmed by bipyridyl test [17, 18].

## 3. Dependence of Reaction Rate on $[\text{MnO}_4^-]$ and $[\text{Ag}^+]$

The order with respect to permanganate ion was determined by studying the reaction at different initial concentrations of permanganate ion and constants of all other reagents. The  $[\text{MnO}_4^-]$  was varied in the range of  $(2-6) \times 10^{-4}$ ,  $[\text{Ag}^+] = 0.3$ ,  $[\text{H}^+] = 1.0$  and  $I = 2.0 \text{ mol dm}^{-3}$  at  $35^\circ\text{C}$ . The pseudo-first-order rate constants were calculated from the linear portions of the corresponding plots. The independence of such rate constants on the permanganate concentration may confirm that the reaction is first-order with respect to the permanganate ion concentration in both two stages. The average values of  $k_f$  and  $k_s$  were found to be  $3.82 \times 10^{-4}$  and  $4.12 \times 10^{-5} \text{ s}^{-1}$ , respectively.

The order with respect to silver (I) was deduced from the kinetic measurements at several  $[\text{Ag}^+]_0$  and fixed permanganate concentration. The non-constancy obtained for the second-order rate constants derived from dividing the rate constant by  $[\text{Ag}^+]_0$  indicates that the reaction is fractional first-order in silver(I) concentration in both autoacceleration and induction periods. When the values of  $1/k_f$  or  $1/k_s$  were plotted against  $1/[\text{Ag}^+]$ , straight lines with positive intercept on  $1/k_f$  or  $1/k_s$  axis were obtained as shown in Fig. 2. The dependence of the rate constants on the silver (I) concentration was found to follow Michaelis-Menten kinetics [19] for formation of 1:1 intermediate complex between the substrate and the oxidant throughout the two stages.

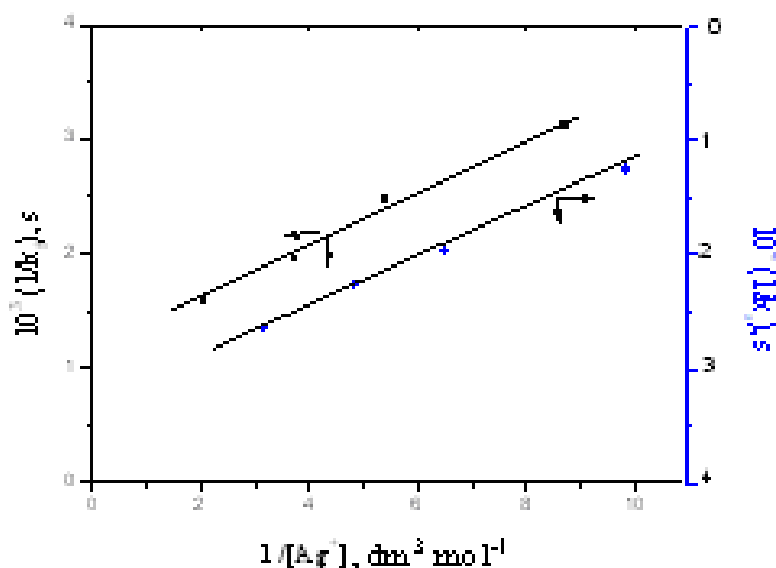


FIG.2 TYPICAL RECIPROCAL PLOTS OF  $1/k_f$  AND  $1/k_s$  VS.  $1/[\text{Ag}^+]$  IN THE OXIDATION OF  $\text{Ag}^+$  BY  $\text{MnO}_4^-$  ION AT  $[\text{MnO}_4^-] = 4 \times 10^{-4}$ ,  $[\text{H}^+] = 1.0$  AND  $I = 2.0 \text{ Mol dm}^{-3}$  AT  $40^\circ\text{C}$

At higher concentrations of  $\text{Ag}^+$ , the reaction rates were found to decrease with increasing  $[\text{Ag}^+]$ . This result may be explained by the formation of some complexes at higher  $[\text{Ag}^+] > 0.35 \text{ mol dm}^{-3}$  which resists the oxidation process. Therefore, the kinetic measurements of the present work were carried out at  $[\text{Ag}^+] < 0.35 \text{ mol dm}^{-3}$  in order to avoid such complexity.

#### 4. Dependence of Reaction Rate on $[\text{H}^+]$

The dependence of the reaction rate on  $[\text{H}^+]$  was examined in  $\text{HClO}_4 - \text{NaClO}_4$  solutions of different  $[\text{H}^+]$  and constant ionic strength and temperature in order to shed some light on the reaction kinetics and to elucidate a suitable reaction mechanism. An increase in acid concentration was found to accelerate the reaction rate in both two stages of oxidation. When the observed first-order rate constants were plotted against  $[\text{H}^+]$ , curved lines passing through the origin were obtained as shown in Fig. 3. The values of the rate constants were calculated by the method of least-squares and are summarized in Table 1.

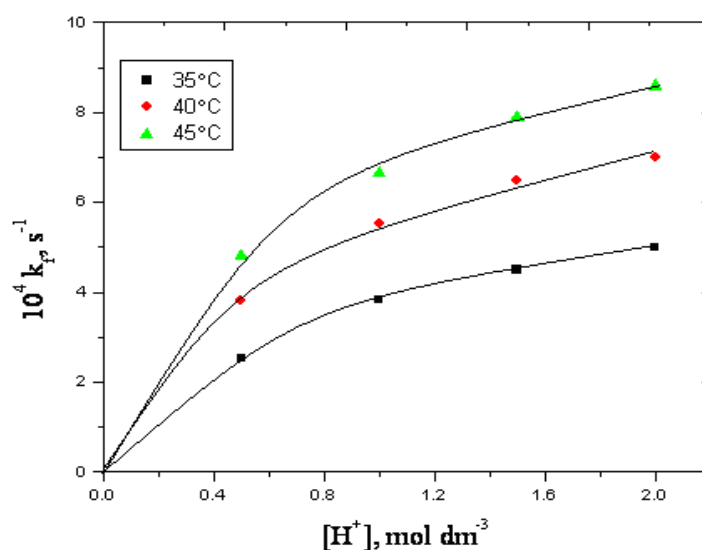


FIG. 3 PLOTS OF  $k_f$  VS.  $[\text{H}^+]$  IN THE OXIDATION OF  $\text{Ag}^+$  BY  $\text{MnO}_4^-$  ION AT  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ ,  $I = 2.0$ ,  $[\text{Ag}^+] = 0.3 \text{ mol dm}^{-3}$  AT VARIOUS  $[\text{H}^+]$  AND DIFFERENT TEMPERATURES.

#### 5. Dependence of Reaction Rate on Ionic Strength

In order to investigate the effect of ionic strength on the reaction rate, kinetic runs were performed at constant  $[\text{H}^+] = 0.8 \text{ mol dm}^{-3}$  as the  $\text{NaClO}_4$  concentration was increased to  $2.0 \text{ mol dm}^{-3}$ . The values of the observed rate constants were found to increase with increasing the ionic strength. A plot  $\ln k_f$  against  $I^{0.5}$  according to Bronsted-Debye-Hückel<sup>20</sup> was found to be linear with a positive slope. At  $[\text{MnO}_4^-] = 4 \times 10^{-4}$ ,  $[\text{Ag}^+] = 0.3$  and  $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$  at  $35^\circ\text{C}$ , the observed first-order rate constants,  $k_f$ , were found to be  $3.82 \times 10^{-4}$ ,  $4.58 \times 10^{-4}$  and  $5.27 \times 10^{-4} \text{ s}^{-1}$  at ionic strengths of 2.0, 2.5 and  $3.0 \text{ mol dm}^{-3}$ , respectively. However, the present measurements, of necessity lie far outside the Bronsted-Debye-Hückel region, covering a range over which the activity coefficients of many electrolytes are known to be fairly dependent on ionic strength [21]. The ionic strength dependence is qualitatively as expected when considering the charges involved [22].

#### 6. Dependence of Reaction Rate on Added Salts

It is well known [23,24] that acidified permanganate is reduced by addition of  $\text{Mn}^{2+}$  to give  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  which are removed by fluoride or pyrophosphate ions through complex formation.

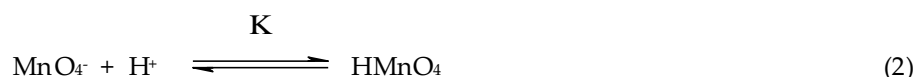
If  $\text{MnO}_4^-$  ions were primarily responsible for oxidation, a reduction in the initial rate should be observed in the presence of  $\text{Mn}^{2+}$  ions, whereas an acceleration of the reaction rate should be noticed if  $\text{Mn}^{3+}$  or  $\text{Mn}^{4+}$  was the reactive species. Unfortunately, addition of  $\text{F}^-$  or  $\text{Mn}^{2+}$  ions could not be tested owing to the precipitation of their respective complexes of  $\text{AgF}$  and  $\text{AgCl}$  ( or  $\text{Ag}_2\text{SO}_4$  ), respectively.

## IV. Discussion

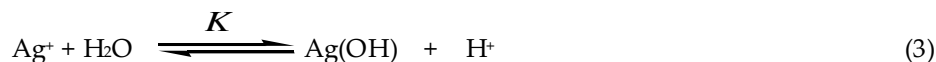
Although the redox potentials of  $\text{Mn}^{\text{VII}}/\text{Mn}^{\text{II}}$  (1.51 V) and  $\text{Ag}^{\text{I}}/\text{Ag}^{\text{II}}$  (- 1.98 V) couples indicates the difficulty of

oxidation of Ag(I) by permanganate ion, the pink color of permanganate ion was rapidly disappeared on addition of silver nitrite solution but very slow in case of silver nitrate addition. This result may be interpreted by suggestion that silver (I) is existed as  $\text{AgO}^-$  [9] which alters the  $E^\circ$  value of  $\text{Ag}^I/\text{Ag}^{II}$  couple to (-0.33 V) [3] and, hence, the oxidation reaction becomes more favorable from the thermodynamic points of view. On the other hand, the nitrogen in nitrate ion is already in its maximum oxidation state (V) and, hence, could not be reduced by permanganate ion; while the nitrogen is in trivalent state (III) in nitrite ion and, hence, can be oxidized by permanganate ion to give its corresponding nitrate form of higher oxidation state

It is well-known that permanganate ion has a high affinity for protonation in aqueous solutions in accordance to the following equilibrium

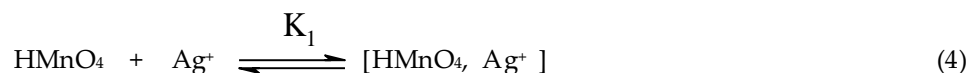


where  $K$  is the protonation constant of  $\text{MnO}_4^-$  which equals to  $2.99 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$  at  $25^\circ \text{C}$  [26,27]. The fractional first-order dependence observed with respect to  $[\text{H}^+]$  suggests that, at least one reaction-path should involve hydrogen ions in the rate-determining step. Again, silver (I) ion may tend to hydrolyze in aqueous solution to form an aqueous  $\text{Ag}(\text{OH})$

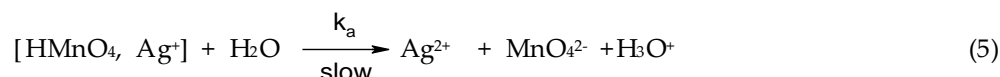


with  $K = 9.3 \times 10^{-13} \text{ mol dm}^{-3}$  at  $25^\circ \text{C}$ .<sup>25</sup> Under our experimental conditions of the hydrogen ion concentration, the unhydrolyzed  $\text{Ag}^+$  species are suggested to be the reactive species.

In view of the above arguments and our experimental observations, two mechanisms may be suggested for the initial rapid part. The first one involves a rapid reaction between the protonated permanganate and silver (I) to form an intermediate complex,



followed by electron-transfer process in the rate determining step forming  $\text{Ag}^{2+}$  and manganate (VI) as initial oxidation products,



This mechanism was based on the observed fractional first-order dependency in  $[\text{H}^+]$  and the Michaelis-Menten kinetics for formation of 1:1 intermediate complex. The formation of manganate (VI) as an initial reduced form of permanganate was confirmed by the increase of absorbance at a wavelength of 606 during the progress of reaction at lower temperatures (Fig. 4).

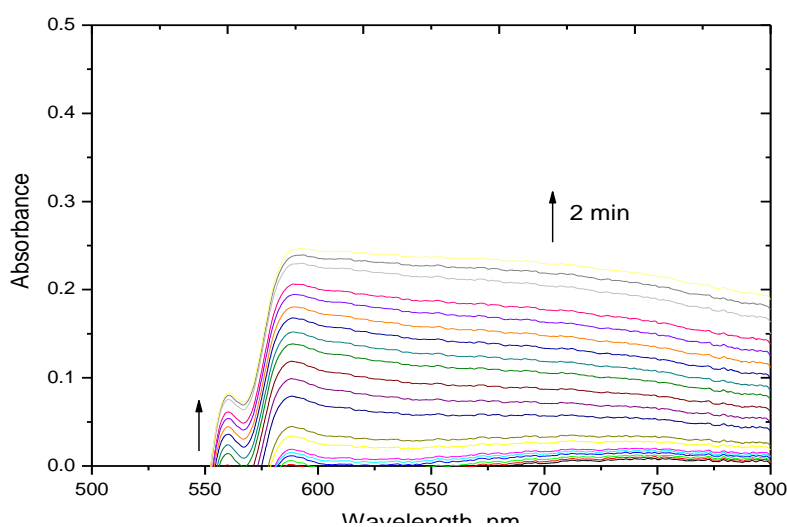


FIG. 4 SPECTRAL CHANGES (550-800 NM) IN THE OXIDATION OF  $\text{Ag}^+$  BY  $\text{MnO}_4^-$  ION AT  $[\text{MnO}_4^-] = 4 \times 10^{-4}$ ,  $[\text{Ag}^+] = 0.3$ ,  $[\text{H}^+] = 1.0$  AND  $I = 2.0 \text{ MoI dm}^{-3}$  AT  $25^\circ \text{C}$  (REFERENCE CELL =  $[\text{MnO}_4^-]$  AND  $[\text{H}^+]$  OF THE SAME REACTION MIXTURE CONCENTRATION).

The change of the rate constant with the change in the silver (I) and hydrogen ion concentrations may be expressed by the following rate-law equation

$$Rate = \frac{(k_a K_1 [H^+]) [Ag^+] [MnO_4^-]_T}{1 + K[H^+] + K K_1 [H^+] [Ag^+]}$$
 (6)

where  $[MnO_4^-]_T$  represents the analytical total concentration of permanganate ion.

Under pseudo first -order conditions of the presence of excess  $[Ag^+]$  over that of permanganate concentration and considering that  $1 + K K_1 [H^+] [Ag^+] \gg K[H^+]$ , the following relationship is obtained.

$$\frac{1}{k_f} = \frac{1}{k_a [H^+] [Ag^+]} + \frac{1}{k_a}$$
 (7)

where  $k_a = k_a K K_1$ . According to Eq. (7), plots of  $1/k_f$  against either of  $1/[Ag^+]$  (Fig. 2) or  $1/[H^+]$  (Fig. 5) gave good straight lines from whose slopes and intercepts, the values of  $k_a$  and  $k_a$  can be evaluated. These values were calculated from these two plots (Figs. 2 and 5) by the method of least-squares and were found to be in good agreement with each other confirming the validity of the suggested mechanism. By using the reported values of  $K$  for permanganate [26,27], the formation constant  $K_1$  can be evaluated. The value of  $K$  was found to be the order of  $10^3 \text{ dm}^3 \text{ mol}^{-1}$  at  $40^\circ\text{C}$ .

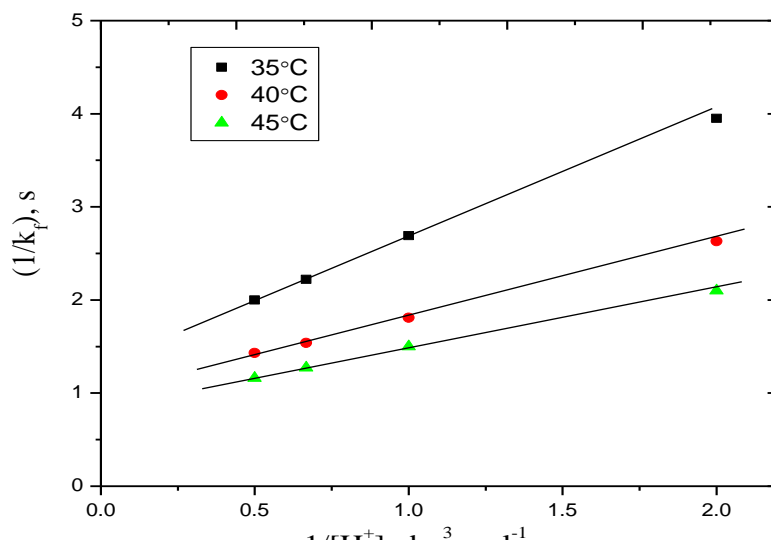
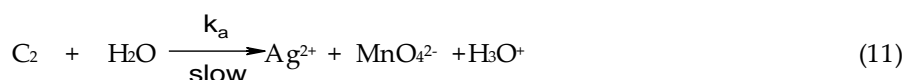


FIG. 5 RECIPROCAL PLOTS OF  $1/k_f$  VS.  $1/[H^+]$  IN THE OXIDATION OF  $Ag^+$  BY  $MnO_4^-$  ION AT  $[MnO_4^-]=4.0 \times 10^{-4}$ ,  $I=2.0$ ,  $[Ag^+]=0.3 \text{ Mol dm}^{-3}$  AT VARIOUS  $[H^+]$  AND DIFFERENT TEMPERATURES.

The second mechanism involves two competitive reactions between the unprotonated and protonated permanganate with silver(I) through formation of the intermediate complexes ( $C_1$ ) and ( $C_2$ ) prior to the rate-determining steps,



followed by the decomposition of these intermediates in the rate -determining steps in order to give rise to the initial oxidation products



where  $K_1$  and  $K_2$  are the protonation constants of the formed complexes  $C_1$ , and  $C_2$ , respectively.

In a similar manner to that followed in the former mechanism, the change of the rate constant with the change in the hydrogen ion and silver(I) ion concentrations may be expressed by the following rate-law equation,

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = \frac{(k_b K_2 + k_a K K_1 [H^+]) [\text{Ag}^+] [\text{MnO}_4^-]_T}{1 + K[H^+] + K_2[\text{Ag}^+] + K K_1 [H^+] [\text{Ag}^+]}$$
 (12)

Since plots of  $k_s$  vs.  $[H^+]$  gave curved lines passing through the origin (Fig. 3), the first term of Eqn.(12) corresponding to reaction(8) can be neglected. Considering that  $(1 + K K_1 [H^+] [\text{Ag}^+]) \gg (K [H^+] + K_2 [\text{Ag}^+])$  and rearrangement, a rate-law expression similar to Eqn. (7) can be deduced.

The activation parameters of  $k_a$  and  $k_a'$  were calculated from the temperature-dependence of the rate constants using the Arrhenius and Eyring equations by the method of least-squares and are summarized in Table 2. The formation of the intermediate complex was confirmed not only by the obedience of the results to the Michaelis-Menten kinetics but also by the increase of the absorbance over that of initial permanganate ion observed in the visible region and the distinct shift of the peak to a more longer wavelength in the visible region specially at lower of temperatures and reactants concentration. Again, the appearance of two isobestic points at 475 and 375 nm (Fig.1) may support the formation of the intermediate. The failure of spectrophotometric detection of any formed intermediate may be attributed to the lower absorptivity of the intermediates under our experimental conditions.

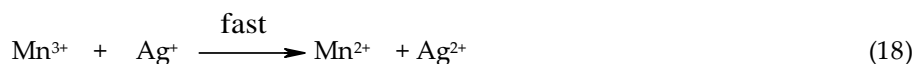
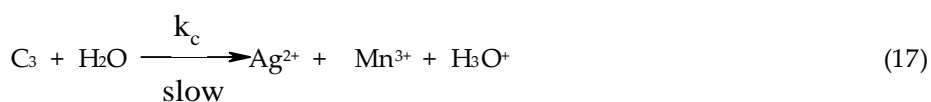
TABLE 2 ACTIVATION PARAMETERS IN THE OXIDATION OF  $\text{Ag}^+$  BY  $\text{MnO}_4^-$  FOR THE INITIAL RAPID PART AT  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ ,  $[\text{Ag}^+] = 0.30$  AND  $I = 1.0$   $\text{mol dm}^3$ .

| Parameters<br>Constants | $\Delta H^\ddagger$<br>$\text{kJmol}^{-1}$ | $\Delta S^\ddagger$<br>$\text{Jmol}^{-1}\text{K}^{-1}$ | $\Delta G^\ddagger$<br>$\text{kJmol}^{-1}$ | $E^\ddagger$<br>$\text{kJmol}^{-1}$ | A<br>$\text{mol}^{-1} \text{s}^{-1}$ |
|-------------------------|--|--|--|-------------------------------------|--------------------------------------|
| $k_a$                   | 35.06                                      | -191.12  | 92.02                                      | 37.62                               | $1.18 \times 10^3$                   |
| $k_a'$                  | 57.73                                      | -107.10  | 89.29                                      | 60.34                               | $4.40 \times 10^7$                   |

The slow second stage (induction period) may be explained by the reaction between  $\text{Mn}^{4+}$  and or/  $\text{Mn}^{3+}$  formed as intermediates with new species of  $\text{Ag}^+$  ion



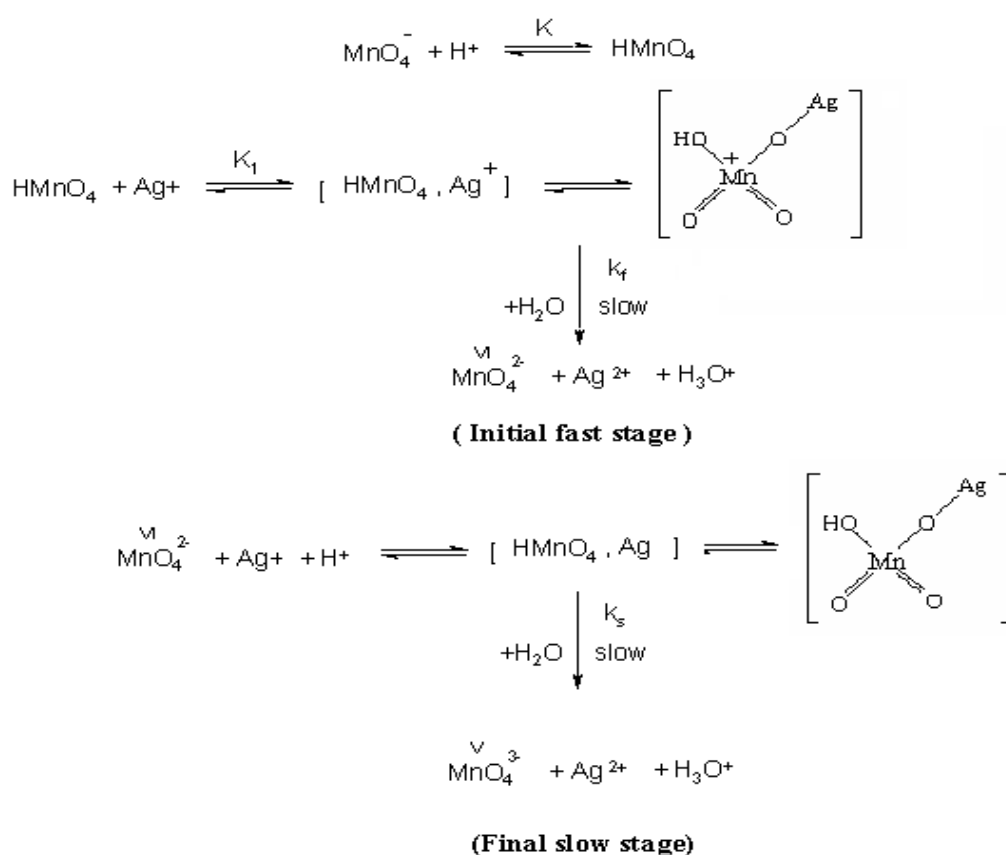
The continuous increase of absorbance at wavelengths 470 nm may indicate the formation of soluble  $\text{Mn}^{\text{IV}}$  rather than  $\text{Mn}^{\text{III}}$  (Fig. 1). The rate constants of the slow stage were found to increase with increasing the hydrogen ion concentration. A fractional first-order dependence in  $[H^+]$  ( $(k_s = [H^+]^n)$ ) was observed. Again, the dependence of the rate constants on  $[\text{Ag}^+]$  was also found to obey Michaelis-Menten kinetics for the formation of 1:1 intermediate complex (Fig. 2). Unfortunately, the kinetics of this induction period could not be studied in more details owing to the extreme slow reaction. Indeed, a plausible reaction mechanism may be suggested for this period. It involves a fast complexation between manganese (IV) and silver (I) to form an intermediate complex ( $C_3$ ) prior to the electron-transfer process, followed by the decomposition of the complex in the rate determining step to give rise to the final products



A question of basic interest in connection with multi-valent oxidants in redox systems such as in the present case is whether electron transfer proceeds through successive one electron changes in a sequence or by a simultaneous two electron transfer in a single step. It is difficult to decide the nature of electron-transfer owing to the difficulty for performing any tests to examine the catalytic effects. But the presence of silver (I) ion as a one-valent reductant may support the one-electron-transfer mechanism.

Furthermore, the thermodynamic parameters observed for a series of common reactions may be considered as good evidence to support the reaction mechanism [4,5,28]. It has been reported that  $\Delta S^\ddagger$  values for a group of outer-sphere reactions involving permanganate ion as an oxidant tend to be more positive than  $\Delta S^\ddagger$  for a set of inner-sphere reactions of negative entropy of activations [28-34]. The observed values of  $\Delta S^\ddagger$  were in the range of inner-sphere reactions (Table 2). In view of these interpretations and the experimental observations, the oxidation of  $\text{Ag}^+$  by  $\text{MnO}_4^-$  is suggested to proceed by successive one-electron transfer of inner-sphere nature.

The formation and decomposition of the intermediate complexes in the former mechanism may be suggested by Scheme (I).



SCHEME I. A SUGGESTED MECHANISM FOR OXIDATION IN THE OXIDATION OF  $\text{Ag}^+$  BY  $\text{MnO}_4^-$  ION.

## V. Conclusion

The oxidation of silver (I) as one-valent by permanganate ion seems to be of great importance in order to shed some light on the nature of electron-transfer process and the reaction mechanistic in such redox reactions. The present oxidation was thought to be of great importance to gain some information on the aqueous chemistry of silver (I) in acidic solutions.

## REFERENCES

- [1] Deutch E, Sullivan JC, and Watkins, KO "Reactivity Pattern Governing Oxidation of Aquometal Ions by Neptunium (VII). Oxidation of Silver (I) and Cobalt (II) In Aqueous Perchloric Acid Media." *Inorganic Chemistry* 14(1975): 550-555.
- [2] Chang HS, Korshin GV, and Ferguson JF. "Examination of Reaction Mechanisms and Reaction Products for the Oxidation



- of EDTA by Permanganate at High pH Values." *Environmental Science & Technology* 40(2006): 5089-5094.
- [3] Thabaj KA, Kullarni SD, Chimata dar SA, and Nandibewoor ST. "Oxidative Transformation of Ciprofloxacin by Alkaline Permanganate - A kinetic and Mechanistic Study." *Polyhedron* 26(2007):4877-4885; Hiremath GA., Timmanagoudar PL, and Nandibewoor ST. "Kinetics of Oxidation of Thallium (I) by Permanganate in Aqueous Hydrochloric Acid Medium Using the Stopped-Flow Technique." *Transition Metal Chemistry* 21(1996): 560-564.
- [4] Rawoof MA and Sutter JR. "Kinetic Studies of Permanganate Oxidation Reactions II. Reaction with Ferricyanide Ion." *Journal of Physical Chemistry* 71(1967): 2767-2771.
- [5] Hicks KW and Sutter JR. "Kinetic Studies of Permanganate Oxidation Reactions III. With Trace (1, 10-Phenanthroline) Iron (II)." *Journal of Physical Chemistry* 75(1971):1107-1113.
- [6] Moore FM, and Hicks K W. "Mechanism of Permanganate Oxidation of Vanadium (IV)." *Inorganic Chemistry* 14(1975): 413-417.
- [7] Thomas L, and Hicks KW. "Kinetics of the Permanganate Ion-Potassium Octacyanomolybdate (IV) Reaction." *Inorganic Chemistry* 13(1974): 749-752.
- [8] Milazzo G, Carroll S, and Sharma VK. "Tables of Standard Electrode Potentials." New York, 1978.
- [9] Moore FM, M. Sc. Thesis, Eastern Michigan University, 1975.
- [10] Hassan RM, El-Gaiar SA, and Summan AM. "Kinetics of Oxidation of Selenium (IV) by Permanganate Ion in Perchlorate Solutions." *Collection of Czechoslovak Chemical Communications* 58(1993):538-546.
- [11] Hassan RM, Mousa MA, and El-Shatoury SA. "Kinetics of the Oxidation of Uranium (IV) by Permanganate Ion in Aqueous Perchlorate Media." *Journal of Chemical Society Dalton Transactions* (1988): 601-603.
- [12] Abdel-Hamid M, Khairou KS, and Hassan RM. "Kinetics and Mechanism of Permanganate Oxidation of Pectin in Acid Perchlorate Media." *European Polymer Journal* 39(2003): 381-387.
- [13] Hassan RM, Fawzy A, Ahmed GA, Zaafarany IA, Asghar BH, and Khairou, KS. "Acid-Catalyzed Oxidation of Some Sulfated Macromolecules. Kinetics and Mechanism of Permanganate Oxidation of Kappa-Carrageenan Polysaccharides in Acid Perchlorate Solutions." *Journal of Molecular Catalysis A* 309(2009): 95-102.
- [14] Hassan RM, Abdel-Kader DA, Ahmed SM, Fawzy A, Zaafarany IA, Asghar BH, and Takagi HD. "Acid-Catalyzed Oxidation of Carboxymethyl Cellulose. Kinetics and Mechanism of Permanganate Oxidation of Carboxymethyl Cellulose in Acid Perchlorate Solutions." *Catalysis Communications* 11(2009):184-190.
- [15] Hicks KW and Hurless M. "An Investigation of the Vanadium (V)-Octacyanomolybdate (VI) Reaction." *Inorganic Chimica Acta* 74(1983): 229-235.
- [16] Pole PD, Kathari, CP, and Nandibewoor ST. "Kinetics and Mechanism of Ruthenium (III)-Catalyzed Oxidation of Tellurium (IV) by Alkaline Diperoxydicarbonate(IV)." *Transition Metal Chemistry* 28(2003): 209-216.
- [17] Honig DS, and Kastin K. "The Nitrosilver(II) Stability Quotient in Aqueous Acid Solution." *Journal of Inorganic and Nuclear Chemistry* 32(1970):1599-1609.
- [18] Miller JD. "The Kinetics of Formation of A Silver (II) and A Silver (III) Complex by Peroxydisulphate Oxidation." *Journal of Chemical Society A* (1968):1778-1780.
- [19] Michaelis L, and Menten M.L. "Die Kinetik der Invertionwirkung." *Biochemische Zeitschrift* 49(1913): 333-369.
- [20] Basalo F, and Pearson RG. "Mechanisms of Inorganic Reactions, 2nd edn., Wiley, New York, 1967.
- [21] Wiberg KB and Stewart R. "The Mechanisms of Permanganate Oxidation. II. The Oxidation of Formate Ions." *Journal of American Chemical Society* 78(1956):12-18.
- [22] Laidler K. "Chemical Kinetics, McGraw-Hill, New York, 1976.
- [23] Waters WA. "Mechanisms of Oxidation by Compounds of Chromium and Manganese." *Quarterly Review Chemical Society* 12 (1958): 277-300.
- [24] Radhakrishnamurti PS and Rao MD. "Oxidation of Aliphatic Ketones, Substituted Acetophenones and Cyclic Ketones by

- Potassium Permanganate." *Indian Journal of Chemistry, Sec.52A* (1977): 524-527.
- [25] Baes CF, and Mesmer RE. "The Hydrolysis of Cations, Wiley, New York, 1976.
- [26] Bailey N, Carrington A, Lott T, and Symons MCRJ." Structure and Reactivity of the Oxyanions of Transition Metals. Part VIII. Acidities and Spectra of Protonated Oxyanions." *Journal of the Chemical Society* (1960): 290-297.
- [27] Carrington A, and Symons MCRJ. "Structure and Reactivity of the Oxyanions of Transition Metals." *Chemical Review* 63(1963): 443-460.
- [28] Sutin N. "Free Energies, Barriers and Reactivity Patterns in Electron Transfer Reactions." *Accounts of Chemical Research* 1(1958):225-231.
- [29] Hicks KW. "Kinetics of the Permanganate Ion-Potassium Octa Cyanotungstate (IV) Reaction." *Journal of Inorganic and Nuclear Chemistry* 38(1976):1381-1383.
- [30] Moore F, and Hicks KW. "Mechanism of Permanganate Oxidation of Vanadium (IV)." *Inorganic Chemistry* 14, (1975):413-416.
- [31] Freeman F. *Journal of American Chemical Society* 103(1981): 1154-1158.
- [32] Hassan RM. "Kinetics of Reaction of Uranium (IV) and Hexachloroiridate(IV) in Acid Perchlorate Solutions." *Journal of Chemical Society, Dalton Transactions* (1991): 3003-3008.
- [33] Hassan RM. "A Mechanistic Approach to The Kinetics of Oxidation of Uranium (IV) by Hexachloroplatinate(IV) in Aqueous Perchlorate Solutions. Evidence of the Formation of a Binuclear Intermediate Complex." *Journal of Physical Chemistry* 115(2011): 13338-13345.
- [34] Hassan RM, Zaaferany IA, Takagi HD, and Ikeda Y.: *New Journal of Chemistry*, 37 (2013) 2700-2708.