

# Aqueous Phase Reductive Detoxification of Cr (VI) By Sodium Dithionite: Kinetics, Thermodynamics and Stoichiometric Studies

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**Abstract:** In this study  $\text{Na}_2\text{S}_2\text{O}_4$  was assessed as an inorganic reductant of Cr (VI) in aqueous phase. The absorbance of Cr(VI) was monitored at 349 nm using a Milton Roy Spectronic 20D UV/Visible spectrophotometer at different temperatures (298 – 323 K) to study the effect of temperature on reduction while, the effect of pH was studied at pH 3, 5, 7, 9 and 12. The effect of concentration was also considered by varying the concentrations of  $\text{Na}_2\text{S}_2\text{O}_4$  (i.e. 0.02, 0.04, 0.05, 0.06 and 0.07 mM) over a pH of 5 and 9 at 298 K and 5 minutes with concentration of Cr(VI) set at 0.19 mM. The temperature effect showed that the reaction rate increased slightly with increase in temperature. It was found that there was a logarithmic increase in time required to reach a certain percentage reduction of the  $[\text{Cr(VI)}]_{\text{initial}}$  as the pH was increased. The kinetic results showed that the reaction was first – order with respect to Cr(VI) with the rate equation of  $-\frac{d[\text{Cr(VI)}]}{dt} = k[\text{Cr(VI)}]$ . The activation entropy obtained from plots of  $\ln(k_{\text{obs}}/T)$  vs.  $1/T$  was  $-197.53 \text{ J.K}^{-1}.\text{mol}^{-1}$  agreeing with the formation of a condensed compound. The activation enthalpy varied from  $(-5.82 \times 10^{-5} - 1.66 \times 10^{-4} \text{ kJmol}^{-1})$  and most cases it was negative showing that the reaction was rather exothermic. The activation energies obtained were 58.87, 60.84, 62.82, 63.80 and 65.78  $\text{kJmol}^{-1}$  for the respective Kelvin temperatures of 298, 308, 318, 323 and 333. This increase in activation energy with increasing temperature implied that bond breakage and product formation was more favourable at lower temperature. The stoichiometry therefore suggested that the Cr(VI) : Reductant millimolar ratio was 1 Cr(VI) : 0.45  $\text{Na}_2\text{S}_2\text{O}_4$ , this value was found to be in agreement with the theoretically obtained result. This implies that the stoichiometry does not depend on pH. The findings from the research show that  $\text{Na}_2\text{S}_2\text{O}_4$  could be used for the reductive detoxification of Cr(VI) in polluted areas.

**Keywords:** Aqueous phase, Reduction, Kinetics, thermodynamics, stoichiometry.

## 1. Introduction

Chromium (Cr) has extensive use in industrial applications such as metal finishing, leather tanning, pigment products, textiles, magnetic tapes, wood preservation and corrosion control agents in cooling waters, etc.[1, 2]. These anthropogenic activities necessitate the proliferation of Cr in the environment in different forms and speciation. In nature, chromium exists in numerous oxidation states between -2 to +6, but only Cr(III) and Cr(VI) are stable. It is interesting to note that these two forms of Cr exhibit very different toxicities and mobilities. Cr(VI) usually occurs as highly soluble and toxic chromate anions ( $\text{HCrO}_4^-$  or  $\text{Cr}_2\text{O}_7^{2-}$ ) and is a suspected carcinogen and mutagen [3]. Cr(VI) exposure in humans can induce allergies, irritations, eczema, ulceration, nasal and skin irritations, perforation of eardrum, respiratory track disorders and lung carcinoma. Moreover, Cr(VI) evidences the capability to accumulate in the placenta, damaging fetal development. Cr(VI) pollution in the environment alters the structure of soil microbial communities, reducing microbial growth and related enzymatic activities, with a consequent persistence of organic matter in soils and accumulation of Cr(VI).

In contrast, Cr(III) is relatively insoluble over pH 5 in aqueous systems and exhibits little or no toxicity than Cr(VI) [4, 5]. Thus, the discharge of Cr(VI) into surface water is regulated to below 0.05 mM by the U.S. EPA [5].

Methods for removing Cr(VI) ions from wastewaters include chemical reduction, electrochemical treatment, ion exchange

and evaporative recovery. The choice of a particular method depends on certain factors such as the rate at which such removal should occur, the effectiveness of such method adopted and the cost implication of such methods. Studies elsewhere [6,7,8] have proposed that Cr(VI) contaminated areas can be treated by detoxification using living cells. Fundamental draw backs associated with the use of living cells, such as cell death due to Cr(VI) toxicity, supply of nutrients, complex facilities and separation of the liquid treated have made this method unpoplar.

Besides commercial chemical reductants, various natural minerals or industrial wastes containing iron can be used to reduce toxic Cr(VI) to less toxic Cr(III). [9, 10] used siderite ( $\text{FeCO}_3$ ) and clino-pyrrhotite ( $\text{Fe}_{0.88}\text{S}$ ) as a reductant for Cr(VI) removal from aqueous solution, respectively.

The U.S. Environmental Protection Agency (EPA) has approved several chemical reductants for in situ treatment of Cr(VI) these include; sodium dithionite, ferrous sulphate, sodium metabisulphite, calcium polysulphides, nano – zero valent Iron [11]. This research work aimed at reducing Cr(VI) with sodium dithionite and evaluating some kinetics, thermodynamics and the stoichiometry of the reduction.

## 2. Materials and Methods

### 2.1 Preparation of Solutions

All solutions were prepared using distilled water. All glass wares and plastics were washed with distilled water, rinsed

with (1:1)  $\text{HNO}_3$  and finally with distilled water.  $\text{Cr(VI)}$  stock solution was prepared from commercially obtained  $\text{K}_2\text{Cr}_2\text{O}_7$  (BDH) by dissolving 2.828g of the salt in 1 litre of distilled water. A 0.04mM  $\text{Cr(VI)}$  solution was prepared measuring exactly 2mL of the stock solution in 1 L of distilled water.  $\text{Na}_2\text{S}_2\text{O}_5$  stock solution was prepared by dissolving 1.0g of the salt in a litre of distilled water. Interferences were avoided by adding diphenyl carbazide to  $\text{Cr(VI)}$  before adjusting the pH of the solution.

## 2.2 Experimental Procedures

The reduction of  $\text{Cr(VI)}$  by  $\text{Na}_2\text{S}_2\text{O}_4$  was conducted in accordance with the method described elsewhere [11, 12] with slight modifications. A 10 mL portion of 0.04 mM  $\text{Cr(VI)}$  was measured into a 250mL beaker. Next, a 20-mL aliquot of 0.12 M  $\text{Na}_2\text{S}_2\text{O}_4$  was added and the mixture shaken thoroughly. The pH of the solution was adjusted using 1.0 M  $\text{H}_2\text{SO}_4$  in the acidic regime and 1.0 M  $\text{NaOH}$  in the alkaline regime before they were made to come in contact. The UV/Visible spectrophotometer (Milton Roy Company U.S.A., Spectronic 20D) was set at 349 nm after a spectrum was ran and the absorbance of  $\text{Cr(VI)}$  was read at that wavelength. The absorbance of  $\text{Na}_2\text{S}_2\text{O}_4$  was found to be weak at this wavelength. The set up was done in triplicate at temperatures of 298, 308, 318, 323 and 333 K. In order to study the effect of reaction time on  $\text{Cr(VI)}$  reduction, separate set ups of the above mixture was made and each monitored for different time intervals of 0, 1, 2, 3, 4, 5 minutes to minimize interference due to withdrawal of samples. The reaction was done for the initial pH values of 3, 5, 7, 9 and 12.

The stoichiometric study was conducted using five concentrations of the reductant: 0.02, 0.03, 0.05, 0.06 and 0.07 M to assess the concentration – dependence of the reduction. The reaction was conducted under a moderately acidic pH of 5 and an alkaline pH of 9 at 298 K. The initial concentration of  $\text{Cr(VI)}$  was set at about 0.2 mM and the reaction time was 5 minutes. Equal volumes of 10mL each of the reductant and  $\text{Cr(VI)}$  was used for the mixture.

## 3. Results and Discussion

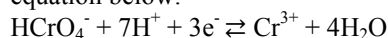
### 3.1 Effect of pH

Figures 1 - 5 presents the results of the reduction of  $\text{Cr(VI)}$  by  $\text{Na}_2\text{S}_2\text{O}_4$  at different temperature and pH conditions in aqueous phase. A first glance reveals that the reduction progresses with time. The rate of reduction was basically increasing with decrease in pH. The rate of reduction was also slightly affected by increase in temperature with most reaction reaching completion at 180 seconds when the initial temperature was increased to 308 K. The rate in acidic and neutral solutions was faster than in basic solution. This observation agreed with that of Bill [13] where an in situ kinetic reduction of  $\text{Cr(VI)}$  by ferrous iron in solid phase was studied. The findings of the present study are also found to be consistent with those of Wittbrodt and Palmer, [14].

The rate of reduction depends on the speciation of chromium in a given pH range as this is shown in the Pourbaix diagram (figure 6). In order to explain the increase in reaction rate

with decreasing pH, one needs to take into account the speciation of both  $\text{Cr(VI)}$  and the reductants under these conditions. The  $Eh$ -pH diagram shown (Fig. 6) provides a generalized depiction of the major aqueous chromium species and redox stabilities under conditions of chemical equilibrium. The dominant  $\text{Cr(VI)}$  species are  $\text{HCrO}_4^-$  at pH 1-6 and  $\text{CrO}_4^{2-}$  at pH > 6.  $\text{Cr(VI)}$  also forms other species, such as  $\text{HCr}_2\text{O}_7^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ . However, their formation requires  $\text{Cr(VI)}$  concentrations >  $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ . The increase in reaction rate with decreasing pH can therefore probably be attributed to  $\text{HCrO}_4^-$  which is reduced more easily than  $\text{CrO}_4^{2-}$  [15].

In acidic solution  $\text{Cr(VI)}$  demonstrates a very high positive redox potential ( $E^0$  within 1.33 and 1.38 V, Figure 1) [16, 17] which denotes that it is strongly oxidizing and unstable in the presence of electron donors. As the  $\text{HCrO}_4^-$  reduction is accompanied by the  $\text{H}^+$  consumption as shown in the equation below:



In more basic solution the reduction of  $\text{CrO}_4^{2-}$ , generates  $\text{OH}^-$  against a gradient as shown in the equation below [18]. The reduction potential of chromate to  $\text{Cr(III)}$  hydroxide is -0.13 V in basic medium.

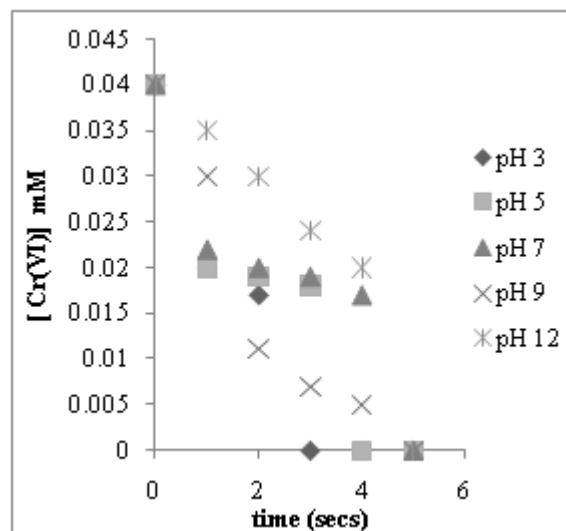
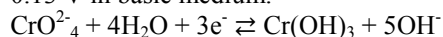


Figure 1: A plot of  $[\text{Cr(VI)}]$  against time at 298 K over different pH

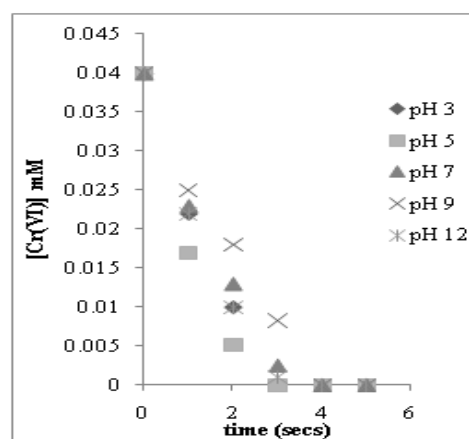


Figure 2: A Plot of  $[\text{Cr(VI)}]$  against time at 308 K over different pH

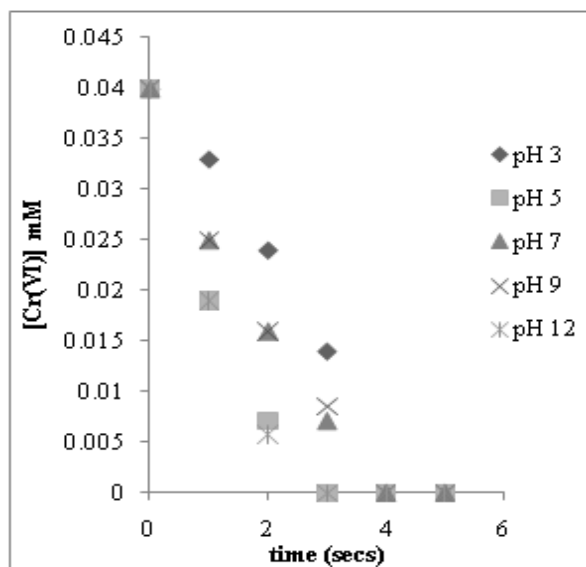


Figure 3: A plot of [Cr(VI)] against time at 318 K over different pH.

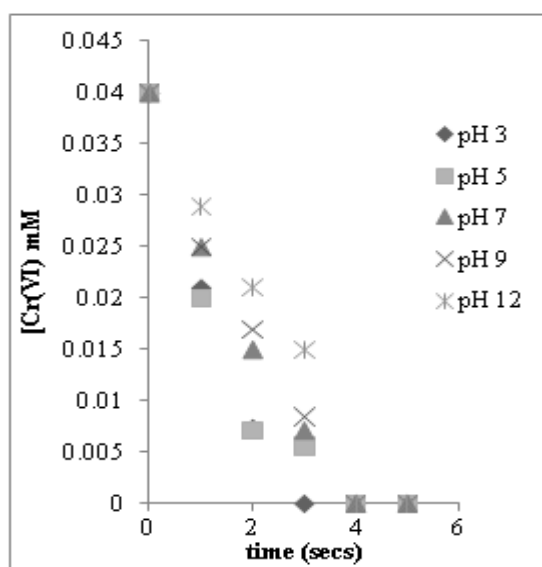


Figure 4: A plot of [Cr(VI)] against time at 323 K over different pH.

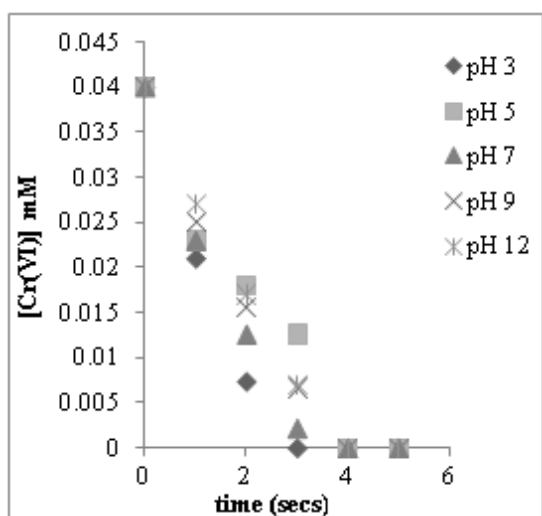


Figure 5: A plot of [Cr(VI)] against time at 333 K over different pH

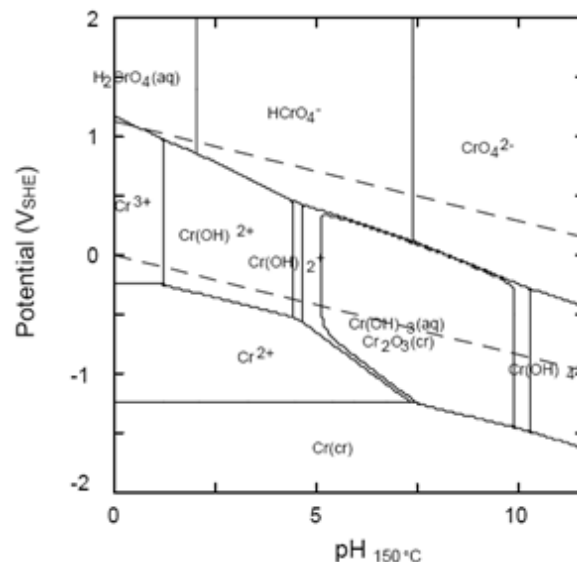


Figure 6: A simplified Pourbaix diagram for chromium species at 150 °C and  $[Cr(aq)] = 10^{-8} M$  (Source: [19, 20])

When a plot of the logarithm of time taken to attain 90% reduction against the pH, it was found that there was a linear logarithm relationship between pH and the time taken given by

$$\log(t_{0.9}) \propto \log\left(\frac{1}{[H^+]}\right) = pH \quad (1)$$

and the relationship showed that the Cr(VI) – Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> reaction system rate law has first – order dependence on [H<sup>+</sup>]. This observation was in agreement with findings obtained elsewhere [11, 19, 20, 21]).

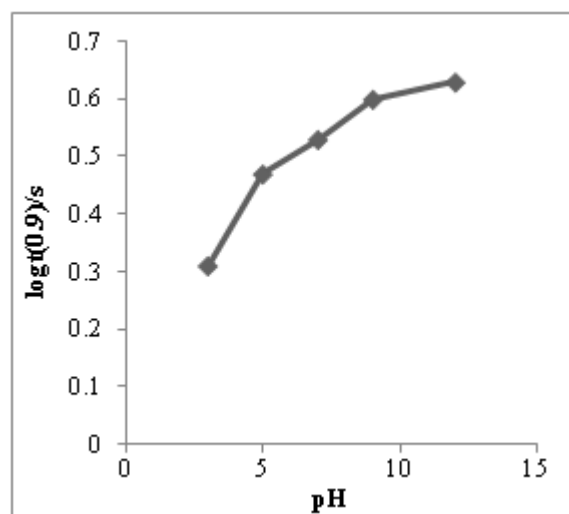


Figure 7: A plot of Time required to reach 90% reduction of the initial  $[Cr(VI)]$   $t_{0.9}$  at 298 K against pH.

### 3.2 Kinetic study

After monitoring the reactions at physiological temperature (298 K), the reactions were further considered at higher initial temperatures of 308, 318, 323 and 333 K. The reactions were observed to be faster as the temperature of the reaction was increased most of the reaction were completed at a temperature of about 308 K and at a time of 180 seconds. A plot of  $\ln[Cr(VI)]$  against time was made (figures 8 – 11) and it showed that the reaction had a first –

order dependence on Cr(VI). The observed rate constants  $k_{obs}$  was obtained from the slopes of the plots.

For each pH and reductant, another plot of  $\ln(k_{obs}/T)$  against  $1/T$  was made, this was in accordance with Elovitz and Fish, (1994). The graph was found to be linear with very nice regression coefficients of  $0.987 \geq r^2 \leq 0.960$ . The observed rate constant was found to be highest at a pH of 3 and this also increased as the temperature was increased. For example, the  $k_{obs}$  for the reduction of Cr(VI) by  $\text{Na}_2\text{S}_2\text{O}_4$  was found to  $1.94 \text{ s}^{-1}$  at 298 K and when the temperature was increased to 308 K, the  $k_{obs}$  also increased to  $2.01 \text{ s}^{-1}$ . And as the temperature was raised to 318, 323 and 333 K, the  $k_{obs}$ , there was a correspondent increase of 2.07, 2.11 and  $2.17 \text{ s}^{-1}$  respectively. When the pH was increased to 5, it was observed that the reaction became slower but the rate still increased as the temperature was increased. It was seen that the  $k_{obs}$  at 298 K was  $0.797 \text{ s}^{-1}$  and other temperatures such as 308, 318, 323 and 333 K had 0.824, 0.85, 0.86 and  $0.91 \text{ s}^{-1}$  respectively. This shows that the reaction is slower at a higher pH and faster at higher temperature. The higher  $k_{obs}$  values at lower pH can be attributed to the fact that there are so many protons at lower pH that deplete the electrons thereby causing reduction at a higher rate. Increased temperature increases the rate of interaction between reacting species; this is why the  $k_{obs}$  increased when the temperature was increased. The trend was also observed at hyper alkaline region regions of pH 9 and 12. At pH 9, the rate of reduction was significantly slow; this could be seen for the decrease in the  $k_{obs}$  values. At a temperature of 298 K, the value was found to be  $0.00813 \text{ s}^{-1}$  but rose to  $0.084 \text{ s}^{-1}$  when the temperature was increased to 308 K and for 318, 323 and 333 K, the observed rate constants became 0.0867, 0.088 and  $0.00908 \text{ s}^{-1}$  respectively. These slow rate observed at the high pH values can be attributed to the formation of other species as seen in figure 3 or the complete depletion of Cr(VI) in the solution. This observation agrees with the assertions of Beukes [19].

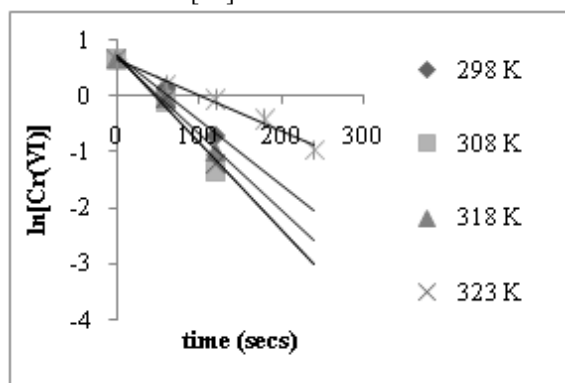


Figure 8: A plot of  $\ln[\text{Cr(VI)}]$  vs time at pH 5

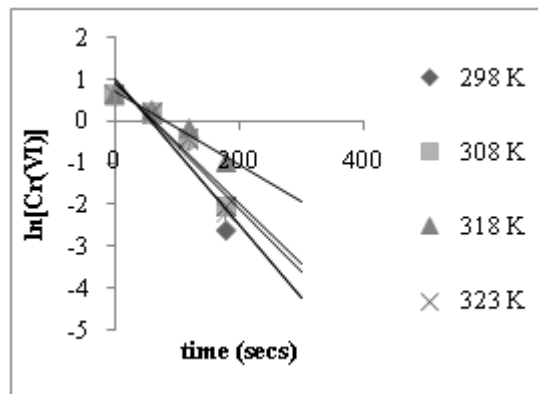


Figure 9: A plot of  $\ln[\text{Cr(VI)}]$  vs time at pH 7

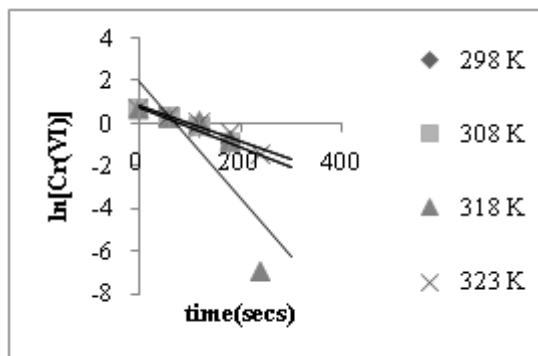


Figure 10: A plot of  $\ln[\text{Cr(VI)}]$  vs time at pH 9

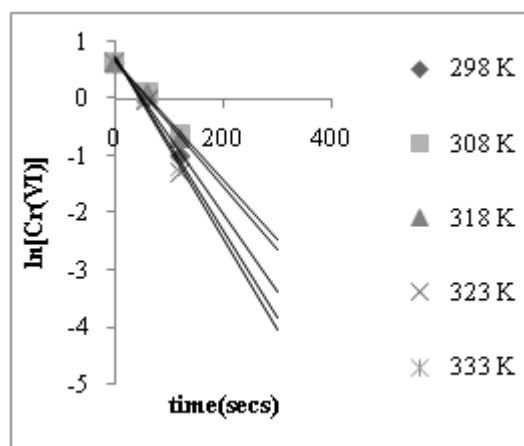


Figure 11: A plot of  $\ln[\text{Cr(VI)}]$  vs time at pH 12

The activation enthalpies and entropies ( $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ) was obtained from the slopes and intercepts of another plot of  $\ln(k_{obs}/T)$  against  $1/T$  (As presented in figure 8). This is in accordance with the Elovitz and Fish [15] equation

$$\ln\left(\frac{k_{obs}}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2)$$

where

$T$  is temperature in Kelvin,

$k_b$  is Boltzman's constant ( $1.38 \times 10^{-23} \text{ J/K}$ ),

$h$  is Planck's constant ( $6.63 \times 10^{-34} \text{ Js}$ ), and

$R$  is gas constant ( $8.314 \text{ J/K/mol}$ ).



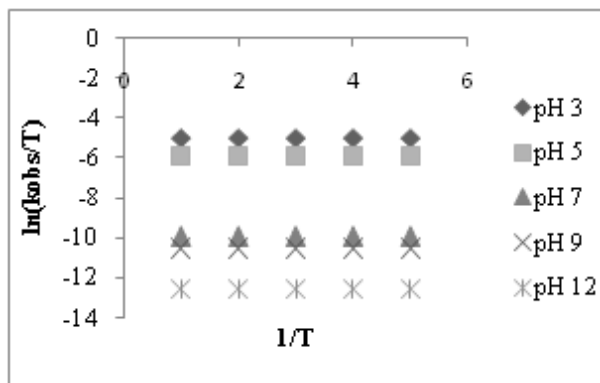


Figure 12: A plot of  $\ln(k_{\text{obs}}/T)$  against  $1/T$

The activation energies were therefore computed from the relationship:

$$E_a = \Delta H - T\Delta S \quad (3)$$

Because of the empirical manner in which the rate coefficients were derived, the activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  must be taken as composite values for all reactions prior to and including the rate-limiting step. The activation entropy ( $\Delta S^\ddagger$ ) is often used as an indicator of the configuration of the activated complex. A large negative number indicates that the reactant molecules are separated by short bonds, thus the decrease in entropy is large and the pre-exponential factor  $[(k_b T/h) \exp(\Delta S^\ddagger/R)]$  is small. The values of the activation energy obtained when compared with that of some organic compounds used in chromium reduction was relatively lower at 298 K. The values also revealed that  $\text{Na}_2\text{S}_2\text{O}_4$  activation energies that are almost the same at a given temperature and pH. For example, activation energy ( $E_a$ ) of 58.8645, 60.8395, 62.8153, 63.8029 and 65.7783  $\text{kJ mol}^{-1}$  was obtained at 298, 308, 318, 323 and 333 K at pH 3 to 12. The activation enthalpy ( $\Delta H^\ddagger$ ) of the reduction was found to vary with pH but remained constant with change in temperature. For example, it maintained a value of  $-5.82 \times 10^{-6} \text{ kJ mol}^{-1}$  at pH 3 but for pH 5, 7, 9 and 12, the values became  $1.66 \times 10^{-4}$ ,  $-3.3 \times 10^{-5}$ ,  $-8.31 \times 10^{-6}$  and  $3.3 \times 10^{-5} \text{ kJ mol}^{-1}$ , respectively, while the activation entropy ( $\Delta S$ ) was  $-197.5323 \text{ J K}^{-1} \text{ mol}^{-1}$  for all pH and temperature. The activation data was compared with the values obtained by Xu, [22] at 298 K (table 1) and it was clearly seen that the  $\Delta H^\ddagger$  obtained when  $\text{Na}_2\text{S}_2\text{O}_4$  was adopted as model reductant was lower than the ones obtained by Xu, [22]. This is the same when the  $\Delta S^\ddagger$  obtained was compared as it was  $-197.5323 \text{ J K}^{-1} \text{ mol}^{-1}$  against the higher values obtained for the organic reductants.

Table 1: Activation data for Cr(VI) reduction by organic compounds at 25 °C

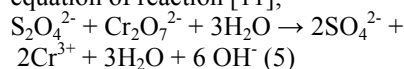
Reductant	$\Delta H^\ddagger (\text{KJ/mol})$	$-\Delta S^\ddagger (\text{J/K/mol})$	$E_a (\text{KJ/mol})$
Vitamin C	42.4	71.0	63.5
Ethanol	49.0	120.2	84.8
Isopropyl alcohol	53.2	107.7	85.3
Benzyl alcohol	26.6	180.8	80.5
Triphenylcarbinol	49.4	105.0	80.7
Benzhydrol	24.7	155.2	70.9

Source: Xu, [22].

## Stoichiometry

Cr(VI) reacts with  $\text{Na}_2\text{S}_2\text{O}_4$  producing Cr(III) [11], this reaction with  $\text{Na}_2\text{S}_2\text{O}_4$  generates a theoretical stoichiometric equation [11]:  $\text{K}_2\text{Cr}_2\text{O}_7 + 3\text{H}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{O}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + 3\text{H}_2\text{O}$  (4)

Table 2 below shows the amount (mM) of Cr(VI) consumed when the concentration of  $\text{Na}_2\text{S}_2\text{O}_4$  was varied. Here, it was observed that the 0.02mM of  $\text{Na}_2\text{S}_2\text{O}_4$  consumed exactly 0.044mM of Cr(VI) giving a stoichiometric mass balance Cr(VI)/  $\text{Na}_2\text{S}_2\text{O}_4$  ratio of 1:0.45. This ratio was maintained when the concentration of  $\text{Na}_2\text{S}_2\text{O}_4$  was varied from 0.02 to 0.07 mM and the result obtained from the experiment was in agreement with the theoretical ratio obtained elsewhere [11]. When the pH was adjusted to 9, the ratio was the same as presented in Table 2. The theoretical stoichiometry of the reaction obtained in alkaline solution had the following equation of reaction [11];



This therefore implies that the stoichiometry of the reduction reaction does not depend on pH.

Table 2: Showing the amount of Cr(VI) consumed as the concentration of  $\text{Na}_2\text{S}_2\text{O}_4$  is varied

$\text{Na}_2\text{S}_2\text{O}_4$	$^{(a)}\text{Cr(VI)}(\text{mM})$	$^{(b)}\text{Cr(VI)}(\text{mM})$
0.02	$0.146 \pm 0.01$	$0.044 \pm 0.01$
0.04	$0.120 \pm 0.02$	$0.072 \pm 0.02$
0.05	$0.099 \pm 0.00$	$0.092 \pm 0.00$
0.06	$0.076 \pm 0.01$	$0.115 \pm 0.01$
0.07	$0.054 \pm 0.04$	$0.138 \pm 0.04$

$^{(a)}$ residual Cr(VI)  $^{(b)}$  consumed Cr(VI) mean of triplicate determinations.

## 4. Conclusion

This study has demonstrated that whereas  $\text{Na}_2\text{S}_2\text{O}_4$  reduced Cr(VI) in aqueous phase, the reduction rate decreased with increasing pH and the activation entropy ( $\Delta S$ ) of the reduction was largely negative with a relatively small value of the activation enthalpy ( $\Delta H$ ). This gave rise to a Gibb's energy of activation that has a smaller value when compared with the activation energy obtained from the reduction of Cr(VI) by some organic compounds under similar experimental conditions. These observations are rather advantageous because, whereas organic compounds reduce Cr(VI) higher energy of activation,  $\text{Na}_2\text{S}_2\text{O}_4$  reduced Cr(VI) with a lower energy of activation meaning that  $\text{Na}_2\text{S}_2\text{O}_4$  is a better reductant which can be used for cleanup and will complete the process in shorter time. The reduction process further showed that the stoichiometry does not depend on pH.

Future prospects of the research will be to engage in the mechanistic studies of the reduction process to ascertain the nature of the products formed through Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM).

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