

# Novel Demonstration of Heterogeneous Redox Catalysis using a Rotating Pencil Lead

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**Abstract** Heat-treated, pencil lead, in powder or rod form, is used as a heterogeneous redox catalyst for the oxidation of chloride to chlorine by Ce(IV) ions in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 2 M NaCl solution. When the lead is used in ground up powder form, the resulting decay of the Ce(IV) is first order over 3 half-lives and gives a chlorine yield of 79%. When a rotating 2 mm diameter, heat-treated form of the pencil lead is used in the same test system, the kinetics of Ce(IV) yields a series of different first order rate constants,  $k_1$ , as a function of rod rotation speed,  $\omega$ . A plot of  $k_1$  versus  $\omega^{0.7}$  yields a good straight line, which accords with the hydrodynamics of the system and the assumption that the rate of Ce(IV) reduction, by chloride, depends upon the rate of mass transport of the Ce(IV) ions to the surface of the pencil lead rod. The gradient of the plot allows a value for the diffusion coefficient for Ce(IV) ions in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 2 M NaCl solution to be calculated, namely:  $(2.7 \pm 0.1) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  which compares favourably with those reported previously.

**Keywords** Electrochemistry, Kinetics, Redox Catalysis, Pencil lead, Ceric ions, UV-Vis spectroscopy

## 1. Introduction

Most physical chemistry textbooks [1-3] discuss the behaviour of single redox couples, such as Ox<sub>1</sub>/Red<sub>1</sub>,



in terms of their redox potential defined by the Nernst equation; i.e.

$$E = E_1^0 + (RT/n_1 F) \ln([\text{Ox}_1]/[\text{Red}_1]) \quad (2)$$

where:  $E_1^0$ ,  $n_1$  and  $[\text{Ox}_1]/[\text{Red}_1]$  are the standard redox potential, number of electrons transferred and concentrations of the redox couple, Ox<sub>1</sub>/Red<sub>1</sub>, respectively,  $R$  is the gas constant,  $T$  is the thermodynamic temperature and  $F$  the Faraday constant. If two redox couples are present, i.e. Ox<sub>1</sub>/Red<sub>1</sub> and Ox<sub>2</sub>/Red<sub>2</sub>, as in a potentiometric titration, they are usually considered to be at equilibrium, i.e.



so that:

$$\begin{aligned} E &= E_1^0 + (RT/n_1 F) \ln([\text{Ox}_1]/[\text{Red}_1]) \\ &= E_2^0 + (RT/n_2 F) \ln([\text{Ox}_2]/[\text{Red}_2]) \end{aligned} \quad (4)$$

Such Nernstian reactions are associated with electrochemically reversible redox couples [4, 5], usually

involving the transfer of only one electron, a typical example of which is the classic potentiometric titration of an Fe(II) solution by a standard solution of Ce(IV) ions in acidic solution [6, 7].

A system in which two or more redox couples are present together, but not in equilibrium, is called a polyelectrode [5] and there are many examples of industrial and everyday processes involving polyelectrodes, such as the extraction of minerals from ores, electrodeless plating, the photographic process and corrosion. These redox reactions usually involve more than one electron being transferred and/or at least one of the couples being electrochemically irreversible, such as the reduction of O<sub>2</sub>. As a consequence, in such systems it is often found that in order for reaction (3) to proceed at a measurable rate a heterogeneous redox catalyst, often a metal or conductive metal oxide, must be present to mediate electron transfer between the two couples [5, 8]. Some typical examples illustrating the range of polyelectrodes and heterogeneous redox catalysts are given in Table 1 below [8-20].

The Ce(IV)/H<sub>2</sub>O and Ru(bpy)<sub>3</sub><sup>3+</sup>/H<sub>2</sub>O polyelectrodes [13-17] are routinely used [21, 22] to test new water oxidation catalysts by many of the research groups working on the development of inexpensive, stable artificial photosynthetic systems, usually for water splitting [23-25].

The very last entry in Table 1, refers to previous work carried out by this group investigating the efficacy of different types of powdered carbon, such as carbon blacks [18], graphite, diamond and C<sub>60</sub> [19], as a redox catalyst for the oxidation of chloride to chlorine by Ce(IV) ions in

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acidic (usually: 0.5 M H<sub>2</sub>SO<sub>4</sub> plus 2 M NaCl) solution, i.e.



In all cases the carbons yielded good first order kinetics for the decay of Ce(IV) to Ce(III), and an associated first order rate constant,  $k_1$  (units: s<sup>-1</sup>), along with high (90%), near stoichiometric yields of Cl<sub>2</sub> [18-20].

### 1.1. Theoretical Concepts

Redox catalysis is routinely interpreted using an electrochemical model [5, 20, 26-28] in which the redox catalyst acts as an electrode, or micro-electrodes if particles are used, that conduct electrons between the two redox couples. In this model the observed kinetics of the overall redox reaction are due to the combination of the current-voltage curves of the two contributing couples on the redox catalyst. For example, in the case of the redox reaction (5), the Ce(IV)/Ce(III) couple is known to be electrochemically reversible; i.e. it exhibits a high exchange current density,  $i_o = \text{ca. } 50 \text{ mA cm}^{-2}$ , [29] when used with most conducting materials, whereas Cl<sub>2</sub>/Cl<sup>-</sup> is, in comparison, irreversible;  $i_o = \text{ca. } 0.25 \text{ mA cm}^{-2}$  (on graphite) [30]. In addition, their standard redox potentials, i.e.  $E_{\text{Ce}}^\circ$  and  $E_{\text{Cl}}^\circ$ , are 1.72 and 1.36 V, respectively, and so the two current-voltage curves are well separated [20]. As a consequence, the very different current,  $i$  (units: A) voltage curves associated with these two couples at the start of the reaction can be represented by those illustrated in Figure 1.

The current-voltage curve for the oxidation of Cl<sup>-</sup> to Cl<sub>2</sub> is typical for an electrochemically irreversible reaction, where the reactant, [Cl<sup>-</sup>] is very large ([NaCl] = 2 M in this work) so that the electrochemical reaction is always controlled by electrochemical-driven, surface reaction kinetics, rather than mass-transport, and thus is described by a Tafel equation; i.e.

$$I = i_o A \exp(\ln(10)\{E - E_{\text{Cl}}^\circ\}/b) \quad (6)$$

where  $A$  is the electrode area,  $E$  is the applied potential and  $b$  is the Tafel slope, which is typically ca. 40-120 mV per decade on graphite [31]. The current-voltage curve for the reduction of Ce(IV) is that for a reversible reaction which, in the presence of a very limited amount of Ce(IV), as in this work ( $3.5 \times 10^{-3} \text{ M}$ ), and in the absence of any Ce(III), at

the start of the reaction, is described by:

$$I = -I_L / (1 + \exp(F\{E - E_{\text{Cl}}^\circ\}/RT)) \quad (7)$$

where  $I_L$  is the cathodic current limited by mass transport, i.e. the limiting current and  $F$  is Faraday's constant. The shape of the current-voltage curve for the Ce(IV)/Ce(III) couple illustrated in Figure 1 is that for a reversible reaction, in which the surface electrochemical kinetics are so fast that the overall reaction rate depends only on the rate of transport of the Ce(IV) to the electrode, which in turn depends upon the concentration gradient between the surface of the electrode and the bulk solution. Thus, as the potential on the electrode is made more negative, i.e. reducing, the surface concentration of [Ce(IV)] is lowered until it becomes effectively zero, at which point the concentration gradient will have reached a maximum, so that the now limiting current,  $I_L$ , cannot be increased further with any further decrease in potential. As a result a plateau is created in the current-voltage curve, as illustrated in Figure 1. It can be shown [4] that the limiting current is defined by the following expression:

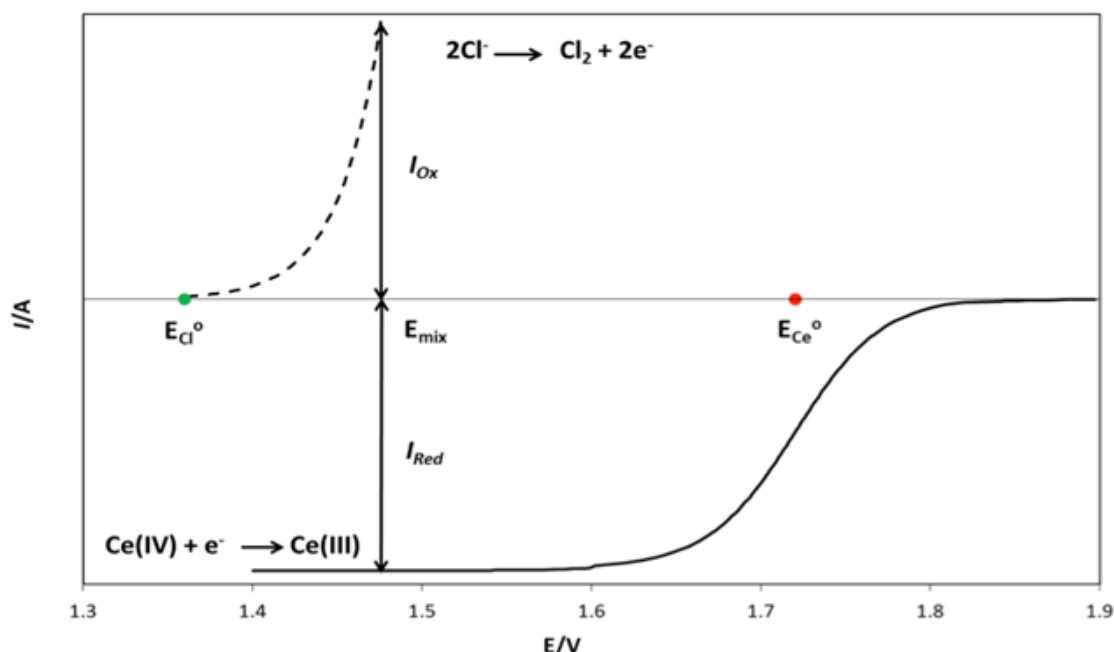
$$I_L = -FAk_m[\text{Ce(IV)}] \quad (8)$$

where  $k_m$  is the mass transfer coefficient, which in turns depends upon the diffusion coefficient ( $D$ ) for Ce(IV), and [Ce(IV)] is the bulk concentration of Ce(IV).

Figure 1 helps illustrate what happens in reaction (5), when mediated by carbon microelectrode redox catalyst particles. Thus, at the beginning, and indeed throughout the reaction, the carbon microelectrode particles adopt a mixed potential,  $E_{\text{mix}}$ , such that the current flowing through the redox catalyst due to the reduction of Ce(IV),  $I_{\text{Red}}$ , is matched by that for the oxidation of chloride to chlorine,  $I_{\text{Ox}}$ . The significant separation of the two standard redox potentials for reaction (5) suggests that  $I_{\text{Red}}$  will always lay in the plateau region of the current vs. voltage curve for the Ce(IV)/Ce(III) couple, so that the matched oxidation and reduction currents, and therefore the overall reaction rate, will depend upon the rate of diffusion of the Ce(IV) ions to the carbon microelectrode particles; this electrochemical model of reaction (5) is consistent with the observation of first order kinetics for the decay of Ce(IV) in reaction (5) noted above [18-20].

**Table 1.** Polyelectrodes and heterogeneous redox catalysts

Redox reaction	Redox catalyst	Ref.
$2\text{Fe(CN)}_6^{3-} + 3\text{I}^- \rightleftharpoons 2\text{Fe(CN)}_6^{4-} + 3\text{I}_3^-$	Pt foil	8
$2\text{Ce(IV)} + \text{H}_2 \rightleftharpoons 2\text{Ce(III)} + 2\text{H}^+$	Pt (black)	9
$(\text{CO}_2\text{H})_2 + 1/2\text{O}_2 \rightleftharpoons 2\text{CO}_2 + \text{H}_2\text{O}$	Pt sponge	10
$\text{C}_2\text{H}_5\text{I} + \text{Ag}^+ + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + \text{AgI} + \text{H}^+$	C (charcoal)	11
$\text{C}_2\text{H}_5\text{I} + \text{Ag}^+ + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + \text{AgI} + \text{H}^+$	AgI	11
$\text{Fe(CN)}_6^{3-} + \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{Fe(CN)}_6^{4-} + 1/2\text{S}_4\text{O}_6^{2-}$	Au (colloid)	12
$4\text{Ce(IV)} + 2\text{H}_2\text{O} \rightleftharpoons 4\text{Ce(III)} + 4\text{H}^+ + \text{O}_2$	RuO <sub>2</sub> , MnNi <sub>2</sub> O <sub>4</sub>	13,14
$4\text{Ru(bpy)}_3^{3+} + 2\text{H}_2\text{O} \rightleftharpoons 4\text{Ru(bpy)}_3^{2+} + 4\text{H}^+ + \text{O}_2$	RuO <sub>2</sub> , MnO <sub>2</sub>	15-17
$2\text{Ce(IV)} + 2\text{Cl}^- \rightleftharpoons 2\text{Ce(III)} + \text{Cl}_2$	Carbon (powder)	18-20



**Figure 1.** Initial current – voltage curves for the reversible reduction of Ce(IV) to Ce(III) and the irreversible oxidation of Cl<sup>-</sup> to Cl<sub>2</sub>; the standard redox potentials of the two couples,  $E_{\text{Ce}}^{\circ}$  and  $E_{\text{Cl}}^{\circ}$  are depicted, along with the mixed potential,  $E_{\text{mix}}$ , that the redox catalyst particles will be poised at initially, so that the redox current flowing through the particles,  $I_{\text{mix}}$ , is the same for the anodic,  $I_{\text{Ox}}$ , and cathodic,  $I_{\text{Red}}$ , processes

To date, reaction (5) has only been probed using dispersions of powdered forms of carbon as the redox catalyst [18-20], and yet it should be possible to glean more electrochemical information using a carbon rod with well-defined mass transport characteristics as both a macro heterogeneous redox catalyst and a wire-less indicator electrode. In particular, the diffusion-controlled nature of reaction (5) can be tested by rotating the rod, since this would then act as a wire-less, forced convection electrode. The hydrodynamics of a solid rotating cylinder, which are essentially the same as those for a rotating rod electrode, provided the cylinder area is much greater than that of its distal end, have been solved [28]. For a diffusion-controlled electrochemical reaction the current  $i$  (units: A) due to the reduction of species X with concentration  $[X]$  (units: mol cm<sup>-3</sup>), is related to the rotation speed,  $\omega$  (units: rpm), via the following expression:

$$I = -0.010 \times n.F.A.[X].D^{0.644} \omega^{0.7} d^{0.4} \nu^{-0.344} \quad (9)$$

where  $A$  is the electrode area (units: cm<sup>2</sup>) ( $= \pi h d$ , where  $h$  is the length of the exposed rod electrode of diameter,  $d$  (units: cm)),  $D$  is the diffusion coefficient for X (units: cm<sup>2</sup> s<sup>-1</sup>),  $\omega$  = rotation speed (units: rpm and  $\nu$  = kinematic viscosity (units: cm<sup>2</sup> s<sup>-1</sup>).

In the case of reaction (5), the kinetics can be monitored via the disappearance of the [Ce(IV)] so as to yield a value for  $k_1$  for each selected rotation speed,  $\omega$ . Under these conditions,

$$\text{Rate (units: mol cm}^{-3} \text{ s}^{-1}) = k_1 [\text{Ce(IV)}] = I/(FV) \quad (10)$$

where  $V$  = reaction solution volume (units: cm<sup>3</sup>). Thus, assuming  $n = 1$ , since the rate-determining step is the reduction of Ce(IV) to Ce(III), it follows that:

$$k_1 \text{ (units: s}^{-1}) = 0.0315 \times h.D^{0.644} \omega^{0.7} d^{1.4} \nu^{-0.343}/V \quad (11)$$

In the previous section, it was noted that heterogeneous redox catalysis is at present routinely used to identify new electrocatalysts for water oxidation [21-23] and also has widespread relevance to a number of different other industrial and everyday processes [5]. Thus, it is surprising to note that heterogeneous redox catalysis attracts little, if any, mention in most physical chemistry and electrochemical text books [1-3]. In the past education journals have championed the use of everyday, inexpensive items to help demonstrate a wide variety of chemical processes, and pencil lead, which comprises mainly a mixture of clay and graphite [32], has been used many times as an electrode to demonstrate different aspects of electrochemistry, such as: as an ion-selective electrode to detect nitrate [33] and perchlorate [34] and as an anode to determine the vitamin C content in commercial orange juice [35]. Building on that, this paper describes the use of pencil lead, in powder or wireless rotating rod form, as a heterogeneous redox catalyst for the oxidation of chloride to chlorine by Ce(IV) ions in acidic solution, in a novel demonstration of heterogeneous redox catalysis which helps illustrate its underlying simple electrochemical basis.

## 2. Experimental

The 0.1 M Ce(IV) sulphate solution in 0.5 M H<sub>2</sub>SO<sub>4</sub> (Sigma Aldrich) was either used as received (in the ground pencil lead experiment) or used to make up the 3.5x10<sup>-3</sup> M Ce(IV) sulfate in 0.5 M H<sub>2</sub>SO<sub>4</sub>, plus 2 M NaCl, which was employed in the rotating pencil lead experiments. The 2 mm

diameter KOH-I-NOOR 2H grade graphite pencil lead had the following weight % composition:  $w(\text{graphite}) = 0.60$ ;  $w(\text{clay}) = 0.34$  was purchased from Amazon and heated at 450°C for 30 min, prior to use, in order to burn off the wax (ca. 6 wt%) that is used as a coating. In the absence of this step the yield of  $\text{Cl}_2$  *via* reaction (5) is only 8%, but increases to 79% after heat conditioning. Presumably oxidisable adventitious impurities, in the clay or remnants of the wax, are responsible for the less than 100% yield of  $\text{Cl}_2$ , since the pencil lead is only ca. 60% graphite; *cf.* earlier results mentioned above [18-20].

In order to confirm the efficacy of the graphite in the pencil lead as a redox catalyst for reaction (5), one of the pencil leads was ground up in a pestle and mortar, heated to 450°C for 30 min before being used to create a suspension ( $60 \mu\text{g cm}^{-3}$ ) of the redox catalyst in a solution, comprising 0.5 M [M]  $\text{H}_2\text{SO}_4$  and 2 M NaCl,  $2.5 \text{ cm}^3$  and  $0.4 \text{ mg cm}^{-3}$  fumed silica (COK 84), which were placed in a 1 cm quartz cuvette, with a crown stirrer flea [36] and placed in a Cary 50 UV/Vis spectrophotometer, fitted with a magnetic stirrer. The fumed silica is an inert antifloculant, without which the carbon particles would tend to aggregate and become less effective as a redox catalyst [37]. The cell's contents were stirred continuously and the reaction was initiated *via* the injection of 90  $\mu\text{L}$  of the acid 0.1 M Ce(IV) sulphate solution to the stirred catalyst dispersion. The instrument was set to monitor the absorption spectrum of the spectrophotometric cell and its contents at 1.5 min intervals, or to monitor the decay of the absorbance due to the Ce(IV) at 430 nm.

In the wireless rotating pencil lead experiments, the heat-treated pencil lead was rotated using a 15 V DC electric motor (Rank Brothers Ltd., Cambridge, UK), the metal shaft of which was connected to a plastic sleeve which held the 2 mm pencil lead. The exposed cylinder to distal end area ratio was 61:1, suggesting that only ca. 2% of the observed kinetics were due to the rotating distal end, so that eqn (11) will be approximately true.

In a typical experiment, a 1 cm empty quartz cuvette was placed in the sample chamber of the Cary 50 UV/Vis spectrophotometer, which was set to monitor the absorbance of the contents of the spectrophotometric cell at 430 nm as a function of time. The 2 mm pencil lead was then placed in the centre of the empty 1 cm quartz cuvette, so that 3.1 cm of the rod's length would be exposed to the reaction solution and it was then rotated at the desired rotation speed (400-1200 rpm). The reaction was initiated by injecting  $3.5 \text{ cm}^3$  of the reaction solution, namely: acid  $3.5 \times 10^{-3} \text{ M}$  Ce(IV) sulfate, plus 2 M NaCl, aqueous solution, into the cuvette and the decay of the Ce(IV) was monitored spectrophotometrically as a function of time for 10 min.

This short monitoring time was chosen so that the whole experiment could be completed in 1.5-2 h; i.e. within an afternoon. All reactions were performed in a fume hood, so as to avoid operator exposure to the small amount of  $\text{Cl}_2$  generated ( $< 0.04 \text{ cm}^3$  per run). All reactions were studied under ambient conditions at room temperature, 22°C.

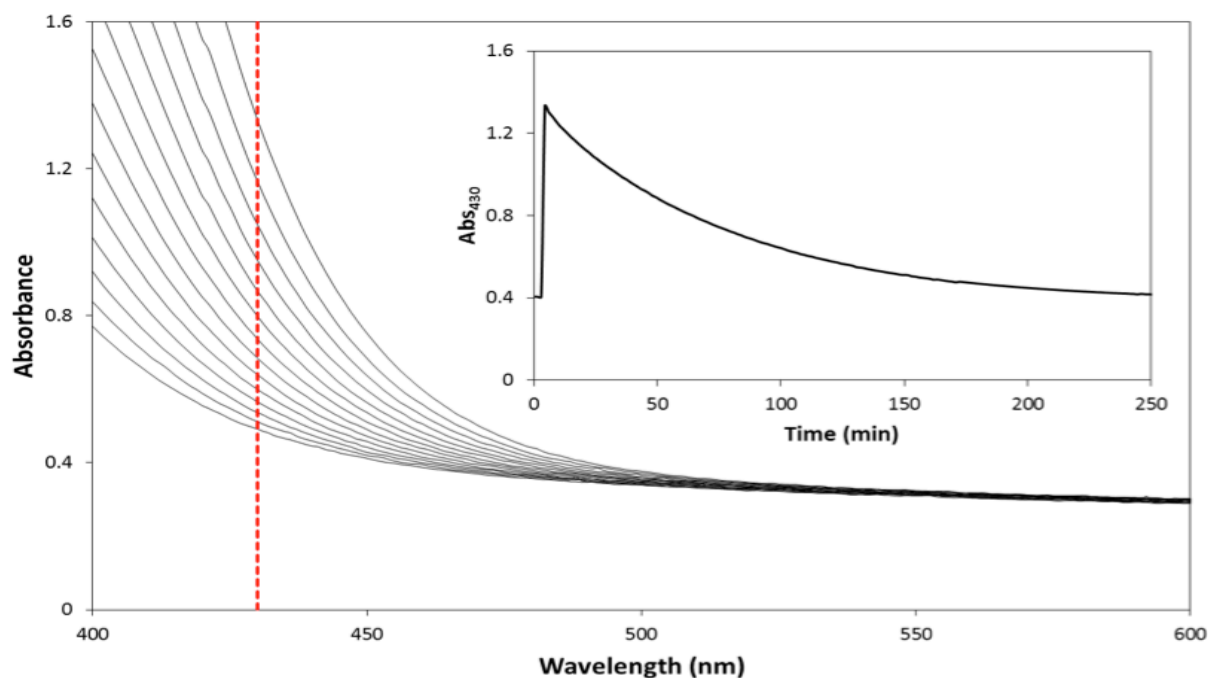
## 2.1. Hazards

Sulfuric acid and Ce(IV) sulfate are both corrosive. Avoid inhalation and skin and eye contact. If either is splashed into the eyes, rinse cautiously with water for several minutes. Remove contact lenses, if present, and easy to effect, and continue rinsing. Chlorine is an oxidising gas, which has acute toxicity if inhaled and may cause skin and eye irritation. Avoid inhalation and skin and eye contact. Carry out all experiments in a fume hood, wearing eye protection and gloves at all times.

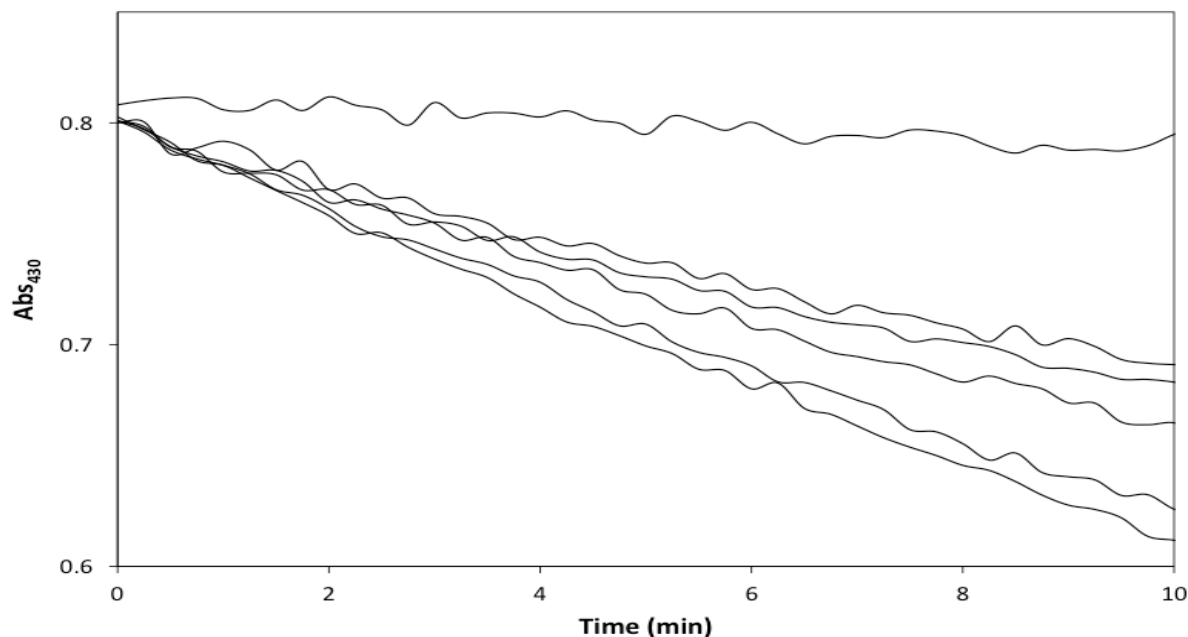
## 3. Results

Reaction (5) was studied initially using a dispersion of a ground up form of the heat-treated pencil lead and the results of this work are illustrated in Figure 2, which shows the change in the UV/Vis absorption spectrum of the  $3.5 \times 10^{-3} \text{ M}$  Ce(IV) sulfate solution, in 0.5 M  $\text{H}_2\text{SO}_4$  plus 2 M NaCl and  $60 \mu\text{g cm}^{-3}$  pencil lead, as a function of time. Ce(IV) sulfate is yellow coloured with an absorbance maximum at 320 nm and molar absorptivity,  $\epsilon(320)$  [20] of  $5580 \text{ M}^{-1}\text{cm}^{-1}$  in 0.5 M  $\text{H}_2\text{SO}_4$ . Thus, in this work, in order to monitor the decay kinetics of the Ce(IV) *via* its absorbance it was necessary to monitor its absorbance decay at a higher wavelength, where it does not absorb so strongly, which in this case was 430 nm (see Figure 2), since  $\epsilon(430) = 235 \text{ M}^{-1}\text{cm}^{-1}$  in a solution comprising 0.5 M  $\text{H}_2\text{SO}_4$  plus 2 M NaCl. A typical absorbance (at 430 nm) vs decay time profile, recorded using the above reaction conditions, is illustrated in the insert diagram in Figure 2. A first order analysis of the latter revealed an excellent straight line, with  $r^2 = 0.999$ , over 3 half-lives and a value for  $k_1 = 0.020 \text{ min}^{-1}$  (i.e.  $3.3 \times 10^{-4} \text{ s}^{-1}$ ).

In a subsequent study of reaction (5), the initial decay of the Ce(IV), due to the redox catalytic activity of the rotated heat-treated pencil lead was also monitored spectrophotometrically at 430 nm, and as a function of rod rotation speed, in rpm, and the results of this work are illustrated in Figure 3. As noted earlier, in the rotating rod experiments, each run was monitored over the first 10 min, so that the whole experiment could be completed in 1.5-2 h; i.e. within an afternoon and so corresponds to the top part of the decay curve in Figure 2.



**Figure 2.** Change in UV/Vis spectrum of a Ce(IV) in an initial  $3.5 \times 10^{-3}$  M Ce(IV) sulfate solution in 0.5 M  $\text{H}_2\text{SO}_4$  plus 2 M NaCl, and  $0.4 \text{ mg cm}^{-3}$  fumed silica (COK 84) containing  $60 \text{ } \mu\text{g cm}^{-3}$  of ground-up heat-treated pencil lead ( $450^\circ\text{C}$  for 30 min) as a function of time, with spectra recorded every 1.5 min. The vertical red line indicates the monitoring wavelength, 430 nm, used to record the decay profile for reaction (5) under the above conditions, a typical example of which is illustrated in the insert diagram. A first order analysis of the latter reveals a very good straight line over 3 half-lives ( $r^2 = 0.999$ ) with a gradient  $(-k_t) = 0.020 \text{ min}^{-1}$



**Figure 3.** Absorbance at 430 nm due to Ce(IV) in a  $3.5 \times 10^{-3}$  M Ce(IV) sulfate solution in 0.5 M  $\text{H}_2\text{SO}_4$  plus 2 M NaCl as a function of time as a function, for a 2 mm heat-treated 2H pencil lead spun at (from top to bottom): 0, 400, 600, 800 1000 and 1200 rpm, respectively

## 4. Discussion

The high yield (79%) of chlorine produced when using the heat-treated pencil lead, in powder or rod form, to mediate reaction (5) indicates that this is the major reaction

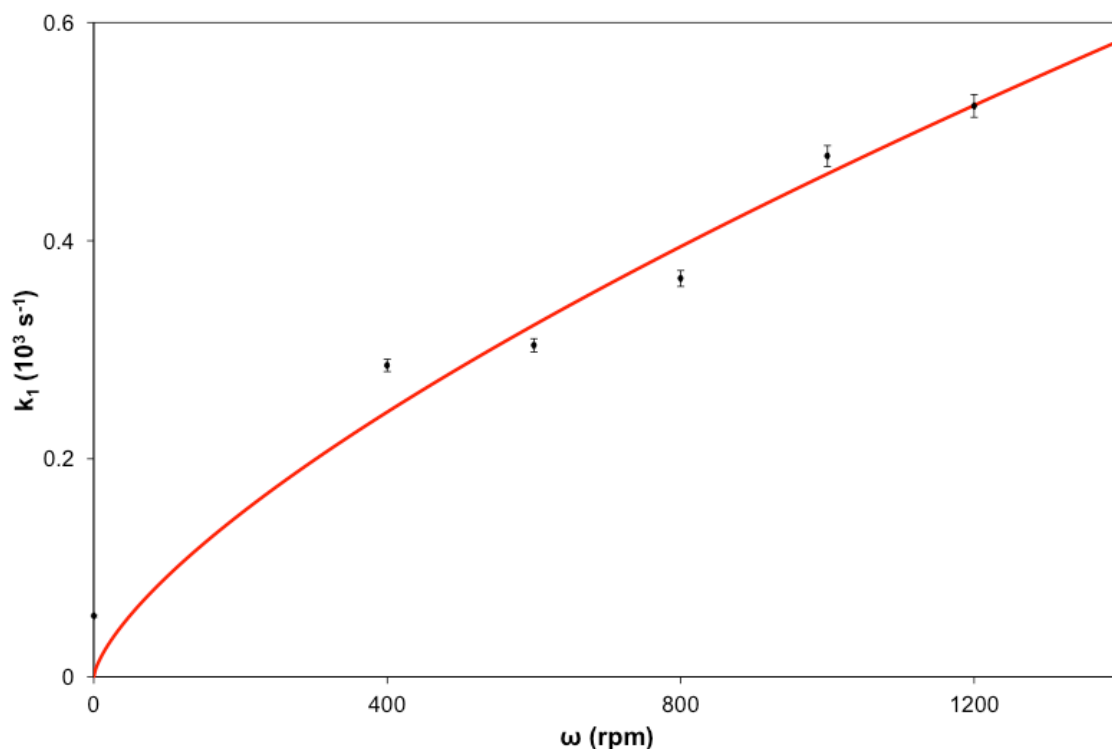
responsible for the reduction of Ce(IV). As noted earlier, the reduced yield with pencil lead graphite, compared to pure graphite, is probably because of adventitious impurities in the clay or remnants of the wax since the pencil lead is only ca. 60% graphite; cf. earlier results. The

excellent first-order kinetics for reaction (5), observed using a dispersion of the ground-up, heat-treated, powder form of the pencil lead, as illustrated in Figure 2, suggests that Ce(III) does not interfere with the reaction and that the kinetics are most probably controlled by the rate of diffusion of the Ce(IV) ions to the graphite particles, in accordance with the electrochemical model of redox catalysis based on the likely current voltage curves for the two redox couples, illustrated in Figure 1. It is assumed that these same conditions hold when the heat-treated pencil lead is used as a rotating wire-less electrode.

In the rotating pencil lead experiment, each of the decay curves, illustrated in Figure 3, gave a good fit to first order kinetics [ $r^2 > 0.996$ ] and a different value for  $k_1$  for each rotation speed,  $\omega$ . This data was then used; to create the data plot shown in Figure 4. A subsequent plot of  $(k_1/\text{s}^{-1})$  versus  $(\omega/\text{rpm})^{0.7}$ , derived from eqn(11), yielded a good straight line of best fit [ $r^2 = 0.996$ ] with a gradient,  $m = (3.67 \pm 0.18) \times 10^{-6}$ , which then enabled the data for the solid line in Figure 4 to be generated using eqn (11), given  $m = 0.0315(h/\text{cm})(D/\text{cm}^2\text{s}^{-1})^{0.644}(d/\text{cm})^{1.4}(\nu/\text{cm}^2\text{s}^{-1})^{0.343}/(V/\text{cm}^3)$ . The value of  $m = (3.67 \pm 0.18) \times 10^{-6}$  was also used to calculate the following value for the diffusion coefficient for Ce(IV) in the 0.5 M  $\text{H}_2\text{SO}_4$ :  $D = (2.7 \pm 0.1) \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ , given:  $h = 3.1 \text{ cm}$ ,  $d = 0.2 \text{ cm}$ ,  $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$  and  $V = 3.5 \text{ cm}^3$ ; this value compares well with those reported for Ce(IV) on Pt electrodes; i.e.  $(3.4\text{-}5) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  [38, 39].

## 5. Conclusions

A heat-treated rotating pencil lead can be used as a heterogeneous redox catalyst for the oxidation of chloride to chlorine by Ce(IV) ions in an aqueous solution comprising 0.5 M  $\text{H}_2\text{SO}_4$  and 2 M NaCl. When used in ground-up powder form, the decay of the Ce(IV) is first order over 3 half-lives and the yield of chlorine is high, 79%. When used as a rotating 2 mm heat-treated pencil lead the first order rate constant,  $k_1$ , for Ce(IV) reduction is found to depend directly upon  $\omega^{0.7}$ , where  $\omega$  is the rod rotation speed. This latter finding is as expected based on the modelled hydrodynamics of the system and the assumption that the rate of Ce(IV) reduction depends upon the rate of diffusion of the Ce(IV) ions to the surface of the spinning pencil lead rod. The gradient of the  $k_1$  vs  $\omega^{0.7}$  plot allows a value for the diffusion coefficient for Ce(IV) ions in 0.5 M  $\text{H}_2\text{SO}_4$  plus 2 M NaCl solution to be calculated, namely:  $(2.7 \pm 0.1) \times 10^{-6} \text{ cm}^2/\text{s}$  which compares favourably with those reported previously by others [38, 39]. This simple set of experiments provides an introduction to, and novel illustration of, heterogeneous redox catalysis, which is a process that is common in industry, but usually not mentioned in undergraduate textbooks.



**Figure 4.** Plot of the first order rate constant,  $k_1$ , derived from the data in figure 3, as a function of pencil lead rotation speed. The solid red line is the line of best fit, calculated using eqn (11) and  $m = 0.0315(h/\text{cm})(D/\text{cm}^2\text{s}^{-1})^{0.644}(d/\text{cm})^{1.4}(\nu/\text{cm}^2\text{s}^{-1})^{0.343}/(V/\text{cm}^3) = (3.67 \pm 0.18) \times 10^{-6}$

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