

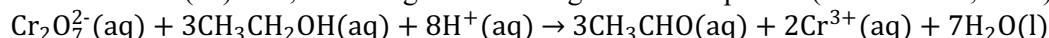
## Investigating the effect of ethanol concentration on the rate of production of chromium (III) ion by acidified potassium dichromate

### Scope

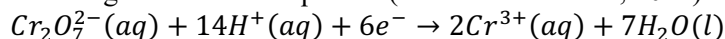
Drinking alcohol prior to driving is a well-known criminal offence severely penalized in many different countries due to the potential harm this action can bring to not only the occupants of the vehicle, but also others driving normally and pedestrians. According to statistics from the Centers for Disease Control and Prevention (2012), young drivers between the age of 16 to 20 are 17 times more likely to die in an accident when alcohol is involved. The danger mainly comes from increased blood alcohol content, which causes decreased attention and judgement ability, and it is important for law enforcements to be able to identify those who are drunk driving. One of many methods used to accomplish this is the use of chemical breath analyzers where a reaction solution changes colour through oxidizing the alcohol in the air breathed out by the test subject is introduced. It is important to know how a breath analyzer reacts differently to different concentrations of alcohol since different time taken for the colour change to take place or the different proportion of colour change could be an indication of different blood alcohol concentration.

### Background Information

The breathalyzer uses acidified potassium dichromate solution to detect the presence of alcohol, such as ethanol, in the air (Freudenrich, 2021). When ethanol is dissolved in the acidified potassium dichromate solution, the ethanol is oxidized, losing a hydrogen to form ethanal, while dichromate ions are reduced into chromium (III) ions, following the following chemical equation (Hassan et al., 2011):



In this reaction, the most visible change as the reaction occurs is the change in colour from the bright orange of the acidified potassium dichromate solution to a dark green of the mixture of chromium (III) ions. This is caused by the change in oxidation state of the chromium between the two types of ions, which is shown in the following electron half equation (CK-12 Foundation, 2021):



In dichromate ions, the oxidation state of chromium is +6, while the oxidation state of chromium (III) ions is +3. This difference in oxidation states makes the two types of chromium absorb lights of different wavelengths and therefore transmit different colours in a solution (Flowers et al., 2015). To monitor the reaction, the Beer-Lambert law would be used to determine the concentration of chromium (III) ion present in the reaction mixture. The law states (Helmenstine, 2020):

$$A = \epsilon bC$$

Where  $A$  represents the absorbance of the solution,  $\epsilon$  represents the extinction coefficient of the specific chemical species being monitored at a specific wavelength,  $b$  represents the path length the light travels through the solution, and  $C$  represents the concentration of the chemical species in the solution.

Through preliminary trials it was determined that the absorbance of a reacted reaction mixture has a peak at approximately 580 nm, where the absorbance of the initial unreacted acidified potassium dichromate is relatively low. Therefore, to determine the concentration of chromium (III) ion after the reaction began, the absorbance at 580 nm would be measured using a spectrophotometer with glass cuvette with constant path length. Since the absorbance at a given time would be the sum of absorbance of all chemical species in the solution, the absorbance in the reaction mixture at any given time would be sum of absorbance of dichromate ions and chromium (III) ions (Harvey, 2019):

$$\begin{aligned} A_{580} &= A_{580, \text{Cr}_2\text{O}_7^{2-}} + A_{580, \text{Cr}^{3+}} \\ &= \epsilon_{580, \text{Cr}_2\text{O}_7^{2-}} b [\text{Cr}_2\text{O}_7^{2-}(\text{aq})] + \epsilon_{580, \text{Cr}^{3+}} b [\text{Cr}^{3+}(\text{aq})] \end{aligned}$$

Substituting the product of extinction coefficient and path length for dichromate ion with the measurements of concentration and absorbance of unreacted dichromate ion solution, and the concentration of dichromate ions was substituted with the initial concentration of dichromate ion subtracted by the change in concentration, which is then substituted with the production of chromium (III) ions using mole ratio.

$$A_{580} = \left( \frac{A_{580, i}}{[\text{Cr}_2\text{O}_7^{2-}(\text{aq})]_i} \right) \left( [\text{Cr}_2\text{O}_7^{2-}(\text{aq})]_i - \frac{[\text{Cr}^{3+}(\text{aq})]}{2} \right) + \epsilon_{580, \text{Cr}^{3+}} b [\text{Cr}^{3+}(\text{aq})]$$

## Investigating the effect of ethanol concentration on the rate of production of chromium (III) ion by acidified potassium dichromate

$$[Cr^{3+}]_{30} = \frac{A_{580,i} - A_{580}}{\frac{A_{580,i}}{2[Cr_2O_7^{2-}(aq)]_i} - \epsilon_{580, Cr^{3+}} b}$$

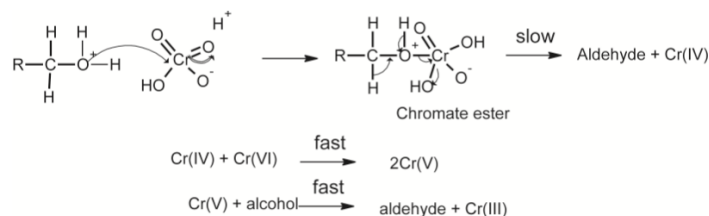
To determine the product of the extinction coefficient and the path length for chromium (III) ion at 580 nm, acidified potassium dichromate solution was reacted with concentrated 95% (v/v) ethanol for a duration of approximately 1.5 hours as an attempt to determine the final absorbance of a fully reacted reaction mixture, where the concentration of chromium (III) ion was determined through stoichiometry calculations, assuming that all the dichromate ions were reduced to chromium (III) ions:

$$\begin{aligned} A_{580,f} &= \epsilon_{580, Cr^{3+}} b [Cr^{3+}(aq)] \\ A_{580,f} &= \epsilon_{580, Cr^{3+}} b (2[Cr_2O_7^{2-}(aq)]_i) \\ \epsilon_{580, Cr^{3+}} b &= \frac{A_{580,f}}{2[Cr_2O_7^{2-}(aq)]_i} \end{aligned}$$

The focus of this investigation would be on the kinetics of this reaction, specifically how the concentration of ethanol affects the rate of production of chromium (III) ions. At the core of chemical kinetics is the collision theory, which states that for reaction to take place, particles must collide with sufficient kinetic energy to overcome the activation requirement in the correct collision geometry. For a reaction to occur at a higher rate, the frequency of successful collisions would have to be increased (Brown & Ford, 2014). The two major factors that could affect the frequency of successful collisions for the oxidation of ethanol would be the concentration of the reactants and the temperature of the solutions. When concentration of the reactants increases, more particles exist in the same volume, and the frequency of collisions between particles increases, which increases the probability of successful collisions and thus increase the rate of production of products. When temperature increases, the average kinetic energy of the reactant particles increases, and thus more particles would have enough energy to overcome the activation requirement, meaning that the frequency of successful collisions increases, which increases the rate of production of products (Brown & Ford, 2014). For this investigation, the temperature would be held approximately constant to ensure that the only factor that affects the rate of production of chromium (III) ions is the concentration of ethanol.

The relationship between concentration of individual reactants of a chemical reaction and the rate of simple reactions is determined by the molecularity of the reaction and is directly proportional to the product of the concentration of each of the reactants in this reaction with variable concentrations raised to the power of their individual coefficient in the balanced chemical equation (Brown & Ford, 2014).

In a complex reaction, such as the reaction investigated in this experiment, the rate of reaction would be limited by the slowest elementary step of the reaction mechanism, which is the rate determining step. In the oxidation of alcohols (including ethanol) by acidified potassium dichromate, the proposed mechanism is as following (Hassan et al., 2011):



**Figure 1:** Proposed reaction mechanism for the oxidation of various aliphatic alcohols by potassium dichromate (Hassan et al., 2011)

According to this proposed mechanism, the rate determining step would be the decomposition of the chromate ester into aldehyde and chromium (IV) ions. Since chromate ester is an intermediate in this reaction, its concentration would be determined by the faster steps which produce the chromate ester. In the previous elementary steps, both alcohol and chromate ion (which is produced from the preparation of acidified potassium dichromate solution ("Jones reagent," n.d.)) are involved once, while hydrogen ions are involved twice, both in the production of the protonated alcohol and the formation of the chromate

## Investigating the effect of ethanol concentration on the rate of production of chromium (III) ion by acidified potassium dichromate

ester. Therefore, the reaction rate would be first order with respect to both the alcohol and the dichromate ion, and second order with respect to the acid in the solution (Hassan et al., 2011).

From this, it can be determined that the rate law for the oxidation of ethanol by acidified potassium dichromate is:

$$r = k[H^+(aq)]^2[Cr_2O_7^{2-}(aq)][CH_3CH_2OH(aq)]$$

Since this investigation focuses on the rate of production of chromium (III) ions, using the mole ratio from the overall reaction, for every mole of reaction, two moles of chromium (III) ions are produced, therefore the rate of production of chromium (III) ion is:

$$r_{Cr^{3+}} = 2k[H^+(aq)]^2[Cr_2O_7^{2-}(aq)][CH_3CH_2OH(aq)]$$

To determine the rate of production of chromium (III) ion, the concentration of chromium (III) ion in the reaction mixture determined at set times after the start of the reaction would be graphed against time, and the initial gradient of the graph would be the initial rate of production of chromium (III) ions.

Through preliminary trials, it was recorded that using 5.00 mL of 0.0500 M acidified potassium dichromate in 10.0 mL reaction mixture would yield a relatively slow rate of reaction, which appears to have a strong linear correlation when plotting the concentration-time graph. Therefore, the gradient of a linear line of best fit would be used to determine the initial rate of production of chromium (III) ions in every trial. Also, the slow rate allows more time to transfer the sample of reaction mixture into the spectrophotometer.

The initial rate of production of chromium (III) ion would be graphed against the initial molar concentration of ethanol in the reaction mixture to determine the effect of various ethanol concentrations in the reaction mixture on the rate of production of chromium (III) ion. Also, the gradient of the rate-concentration graph would be used to be compared with a literature value.

Since the experiment uses % (v/v) concentration for all ethanol, to determine the initial molar concentration of ethanol in the 10.0 mL reaction mixture from the 5.00 mL ethanol solution, the following calculation would be done, using ethanol density of  $789.3 \frac{g}{L}$  and ethanol molar mass of  $46.07 \frac{g}{mol}$  (National Center for Biotechnology Information, 2021):

$$\begin{aligned} [CH_3CH_2OH(aq)] &= \frac{n_{CH_3CH_2OH}}{V_{ReactionMixture}} \\ &= \frac{V_{CH_3CH_2OH} \rho_{CH_3CH_2OH}}{V_{ReactionMixture} MM_{CH_3CH_2OH}} \\ &= \frac{C_{CH_3CH_2OH, \% (v/v), 5.00 mL} V_{initialSolution} \left(789.3 \frac{g}{L}\right)}{V_{ReactionMixture} \left(46.07 \frac{g}{mol}\right)} \end{aligned}$$

One literature article for the rate of reaction of the oxidation of alcohol by acidified potassium dichromate states that  $R = k_2[Alcohol][Dichromate]$  using 4 M sulfuric acid, where  $k_2$  for ethanol at 297K is  $5.781 M^{-1} min^{-1}$  (Hassan et al., 2011). Using  $r = k[H^+(aq)]^2[CH_3CH_2OH(aq)][Cr_2O_7^{2-}(aq)]$  and the rate constant literature value:

$$\begin{aligned} k[H^+(aq)]_{lit}^2 &= k_2 \\ k &= \frac{k_2}{[H^+(aq)]_{lit}^2} \end{aligned}$$

Substituting  $k$  into the rate law equation for the rate of production of chromium (III) ions:

$$r_{Cr^{3+}} = \frac{2k_2}{[H^+(aq)]_{lit}^2} [H^+(aq)]^2 [Cr_2O_7^{2-}(aq)] [CH_3CH_2OH(aq)]$$

Using the initial concentrations in the reaction mixture used in this experiment,  $[H^+(aq)] = 0.25 M$  and  $[Cr_2O_7^{2-}(aq)] = 0.0250 M$ :

$$\begin{aligned} r_{Cr^{3+}} &= \frac{2 \left(5.781 M^{-1} min^{-1} \times \frac{1 min}{60 s}\right)}{(4 M)^2} (0.25 M)^2 (0.0250 M) \times [CH_3CH_2OH(aq)] \\ r_{Cr^{3+}} &= (1.9 \times 10^{-5} s^{-1}) \times [CH_3CH_2OH(aq)] \end{aligned}$$

## Investigating the effect of ethanol concentration on the rate of production of chromium (III) ion by acidified potassium dichromate

Therefore, it is expected that the rate of production of chromium (III) ion has a direct linear correlation with a gradient of  $1.9 \times 10^{-5} \text{ s}^{-1}$  when graphed against the initial molar concentration of ethanol in the reaction mixture.

### Research Question

How does the concentration of ethanol (5.0% (v/v), 10.0% (v/v), 15.0% (v/v), 20.0% (v/v), 25.0% (v/v)) affect the initial rate of production of chromium (III) ion after 5.00 mL of ethanol is added to a fixed volume of acidified potassium dichromate solution with fixed concentration under constant temperature, as measured by the absorbance of the solution mixture at 580.000 nm every 30.00 s after the reactants are mixed, for a total of 180.00 s using a spectrophotometer with fixed path length?

### Variables

**Independent variable:** The concentration of 5.00 mL ethanol (5.0% (v/v), 10.0% (v/v), 15.0% (v/v), 20.0% (v/v), 25.0% (v/v))

**Dependent variable:** The initial rate of production of chromium (III) ion after 5.00 mL of ethanol is mixed with a 5.00 mL solution of acidified potassium dichromate, as measured by the absorbance of the solution mixture at 580.000 nm every 30.00 s after reactants are mixed, for a total of 180.00 s using a spectrophotometer.

### Controlled variables:

- The volume of ethanol solution added to the acidified potassium dichromate solution (5.00 mL)
- The volume of acidified potassium dichromate solution (5.00 mL)
- Potassium dichromate concentration in the acidified potassium dichromate solution (0.0500 M)
- Sulfuric acid concentration in the acidified potassium dichromate solution (0.50 M)
- The path length of the glass cuvette used for the spectrophotometer (10.0 mm)
- Room temperature (measured on each day of experimentation)

### Materials

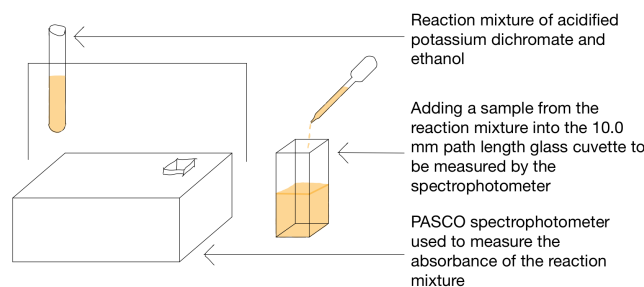
#### Equipment:

- PASCO spectrophotometer ( $\pm 0.001$ ,  $\pm 0.001 \text{ nm}$ ), 1
- Glass cuvettes (10.0 mm), 3
- Lens paper, 1
- Test tubes (19 mL), 4
- Test tube rack, 1
- Parafilm, 18
- Graduated pipette ( $10.00 \pm 0.06 \text{ mL}$ ), 4
- Beaker (200 mL), 3
- Beaker (50 mL), 2
- Volumetric flask ( $100.00 \pm 0.08 \text{ mL}$ ), 1
- Volumetric flask ( $50.00 \pm 0.05 \text{ mL}$ ), 1
- Electronic balance ( $\pm 0.01 \text{ g}$ ), 1
- Weather station ( $\pm 0.1 \text{ }^\circ\text{C}$ ), 1

#### Chemicals:

- $5.0 \pm 0.4\%$  (v/v) ethanol ( $15.0 \pm 0.2 \text{ mL}$ )
- $10.0 \pm 0.5\%$  (v/v) ethanol ( $15.0 \pm 0.2 \text{ mL}$ )
- $15.0 \pm 0.6\%$  (v/v) ethanol ( $15.0 \pm 0.2 \text{ mL}$ )
- $20.0 \pm 0.7\%$  (v/v) ethanol ( $15.0 \pm 0.2 \text{ mL}$ )
- $25.0 \pm 0.2\%$  (v/v) ethanol ( $15.0 \pm 0.2 \text{ mL}$ )
- 95% (v/v) ethanol ( $15.0 \pm 0.2 \text{ mL}$ )
- 0.0500 M potassium dichromate solution acidified with 0.50 M sulfuric acid ( $100.0 \pm 0.2 \text{ mL}$ )
- Deionized water

### Diagram



**Figure 2:** Collection of a sample from a 10.0 mL reaction mixture of 5.00 mL acidified potassium dichromate and 5.00 mL ethanol, after the reactants were mixed, to measure the absorbance using PASCO spectrophotometer

## **Investigating the effect of ethanol concentration on the rate of production of chromium (III) ion by acidified potassium dichromate**

### **Procedure**

1. The room temperature was recorded as measured by the weather station.
2. The spectrophotometer was calibrated using a sample from a blank mixture of 2.50 mL 1.0 M sulfuric acid and 5.00 mL ethanol solution of appropriate concentration (5.0% (v/v), 10.0% (v/v), 15.0% (v/v), 20.0% (v/v), 25.0% (v/v)) in a 10.0 mm glass cuvette.
3. The absorbance at 580.000 nm of a sample from a mixture of 0.0250 M potassium dichromate solution was recorded by the calibrated spectrophotometer using the 10.0 mm glass cuvette to determine the absorbance of unreacted potassium dichromate solution.
4. 5.00 mL of 0.0500 M potassium dichromate acidified with 0.50 M sulfuric acid solution was mixed with 5.00 mL of ethanol solution with appropriate concentration (5.0% (v/v), 10.0% (v/v), 15.0% (v/v), 20.0% (v/v), 25% (v/v)), and the absorbance of a sample from this reaction mixture at 580.000 nm was recorded every 30.00 s after the solutions were mixed for a total of 300.00 s by the calibrated spectrophotometer using the 10.0 mm glass cuvette.

### **Changes to the procedure:**

Originally, the acidified potassium dichromate solution was prepared separately for every trial. However, it was soon discovered that this was not the appropriate way to prepare acidified potassium dichromate solution, therefore in the experiment, 100.00 mL of acidified potassium dichromate with 0.0500 M potassium dichromate and 0.50 M sulfuric acid was prepared prior to all trials, and the blank solution used in the calibration of the spectrophotometer was changed to only ethanol of appropriate concentration, and the measurement of unreacted potassium dichromate solution used a sample from the 0.0250 M potassium dichromate 0.25 M sulfuric acid solution.

The number of measurements of absorbance at 580.000 nm for every trial was reduced from recording the value every 30.00 s for a total of 300.00 s to recording the value every 30.00 s for a total of 180.00 s to reduce the time required to complete every trial.

The absorbance at 580.000 nm of a sample from reaction mixture of 5.00 mL of 95% (v/v) ethanol mixed with 5.00 mL of acidified potassium dichromate solution was taken approximately 1.5 hours after the reaction began to be used to determine the concentration of chromium (III) ion in every absorbance measurement.

### **Safety, Environmental and Ethical Concerns**

In this experiment, the potassium dichromate solution used is toxic that may cause allergic reaction from direct contact, and long-term exposure may cause cancer (Fisher Scientific, 2018a). Sulfuric acid is a strong acid that is corrosive and can cause severe burn if in direct contact with skin and eyes (Fisher Scientific, 2018b). Ethanol is flammable, can cause severe eye irritation, and may be fatal if swallowed or enters airways (Fisher Scientific, 2021). A product of the reaction is ethanal, which is extremely flammable, may cause severe eye irritation, and may cause cancer (Fisher Scientific, 2020). To ensure safety, goggles were used to protect the eyes from direct contact of any solution that may cause eye irritation, any body part exposed to the solutions was immediately rinsed with running water, and hands were thoroughly washed after working with these solutions. All reactions were conducted away from open flames, and to prevent accidental inhalation of vaporized solutions, ventilation was used throughout the experiment.

All the reactants and products in this experiment may be harmful for the environment, especially the potassium dichromate, which is a heavy metal waste (Fisher Scientific, 2018a, 2018b, 2020, 2021). Therefore, any used and unused chemicals in this experiment were not to be disposed to the sink and was collected in a mixed heavy-metal waste container to be properly disposed.

To prevent waste of materials, the potassium dichromate solution and the sulfuric acid were prepared efficiently, and most of the solution were used with little to no waste.

## Investigating the effect of ethanol concentration on the rate of production of chromium (III) ion by acidified potassium dichromate

### Data Collection

**Table 1:** Absorbance at 580.000 nm measured by spectrophotometer using 10.0 mm glass cuvettes of  $10.0 \pm 0.1$  mL reaction mixtures of  $5.00 \pm 0.06$  mL 0.0500 M potassium dichromate solution acidified with 0.50 M sulfuric acid mixed with  $5.00 \pm 0.06$  mL ethanol with varying concentrations, measured every 30.00 s after the reactants were mixed for a total of 180.00 s, and the absorbance at 580.000 nm of  $0.0250 \pm 0.0005$  M potassium dichromate acidified by 0.25 M sulfuric acid, measured after calibration of spectrophotometer for every ethanol concentration, at room temperature between 21.3°C and 21.6°C.

Concentration of $5.00 \pm 0.06$ mL ethanol in $10.0 \pm 0.1$ mL reaction mixture, $C_{CH_3CH_2OH}$ / % (v/v)	Absorbance of $0.0250 \pm 0.0005$ M acidified potassium dichromate at 580.000 nm, $A_{580,i} / \pm 0.001$	Time when the absorbance was recorded, $t / \pm 0.01$ s	Absorbance of the reaction mixture at 580.000 nm at time $t$ , $A_{580,t} / \pm 0.001$			Qualitative Observations
			Trial 1	Trial 2	Trial 3	
$5.0 \pm 0.4$	0.005	30.00	0.012	0.009	0.009	Colour change in the solution is minimal, solutions turned from light orange to a slightly darker orange
		60.00	0.013	0.012	0.012	
		90.00	0.017	0.016	0.018	
		120.00	0.021	0.018	0.018	
		150.00	0.025	0.022	0.022	
		180.00	0.029	0.025	0.024	
$10.0 \pm 0.5$	0.023	30.00	0.048	0.035	0.019	Solution turned from light orange to a slightly darker orange
		60.00	0.047	0.042	0.026	
		90.00	0.049	0.050	0.032	
		120.00	0.051	0.055	0.038	
		150.00	0.056	0.062	0.042	
		180.00	0.060	0.068	0.049	
$15.0 \pm 0.6$	0.010	30.00	0.022	0.020	0.080	Solution turned from light orange to a darker shade of orange with a slight shade of green
		60.00	0.030	0.030	0.084	
		90.00	0.037	0.037	0.092	
		120.00	0.045	0.044	0.100	
		150.00	0.052	0.052	0.110	
		180.00	0.060	0.060	0.112	
$20.0 \pm 0.7$	0.020	30.00	0.023	0.014	0.068 <sup>1</sup>	Solution turned from light orange to a darker orange with dark green colour
		60.00	0.034	0.022	0.020	
		90.00	0.047	0.031	0.030	
		120.00	0.060	0.040	0.044	
		150.00	0.066	0.051	0.059	
		180.00	0.078	0.060	0.072	
$25.0 \pm 0.2$	0.054	30.00	0.058	0.064	0.131	Solution turned from light orange to dark yellow-green colour
		60.00	0.070	0.076	0.148	
		90.00	0.085	0.093	0.161	
		120.00	0.097	0.105	0.173	
		150.00	0.109	0.119	0.185	
		180.00	0.120	0.132	0.197	

<sup>1</sup> For this trial, the cuvette was inserted into the spectrophotometer after 30.00 s, which may have affected the measurement. Therefore, this value was not used in further sections.

## Investigating the effect of ethanol concentration on the rate of production of chromium (III) ion by acidified potassium dichromate

**Table 2:** Absorbance at 580.000 nm of  $10.0 \pm 0.1$  mL reaction mixtures of  $5.00 \pm 0.06$  mL 0.0500 M potassium dichromate solution acidified with 0.50 M sulfuric acid mixed with  $5.00 \pm 0.06$  mL 95% (v/v) ethanol, measured 1.5 h after the reaction started using spectrophotometer with 10.0 mm glass cuvette at 21.3°C.

Absorbance of the $10.0 \pm 0.1$ mL reaction mixtures of $5.00 \pm 0.06$ mL 0.0500 M potassium dichromate solution acidified with 0.50 M sulfuric acid mixed with $5.00 \pm 0.06$ mL 95% (v/v) ethanol at 580.000 nm approximately 1.5 hours after the reactants were mixed, $A_{580,f} / \pm 0.001$		
Trial 1	Trial 2	Trial 3
0.652	0.664	0.687

Qualitative observations: All solutions turned from light orange to dark blue with slight green in them.

### Data Processing

Calculation to determine the initial concentration of dichromate ions in a  $10.0 \pm 0.1$  mL reaction mixtures containing  $5.00 \pm 0.06$  mL 0.0500 M potassium dichromate solution acidified with 0.50 M sulfuric acid:

$$\begin{aligned}
 [Cr_2O_7^{2-}(aq)]_i &= \frac{[Cr_2O_7^{2-}(aq)]_{5.00\text{mL } K_2Cr_2O_7}}{V_{\text{ReactionMixture}}} \\
 &= \frac{(0.0500 \text{ M})(5.00 \pm 0.06 \text{ mL})}{(10.0 \pm 0.1 \text{ mL})} \\
 &= 0.0250 \text{ M} \pm 2\% \\
 &= 0.0250 \pm 0.0005 \text{ M}
 \end{aligned}$$

Sample calculation of the product of the extinction coefficient of chromium (III) ion and the path length, using absorbance measurement of trial one for the reaction from the  $10.0 \pm 0.1$  mL reaction mixtures of  $5.00 \pm 0.06$  mL 0.0500 M potassium dichromate solution acidified with 0.50 M sulfuric acid mixed with  $5.00 \pm 0.06$  mL 95% (v/v) ethanol:

$$\begin{aligned}
 \epsilon_{580, Cr^{3+}+b} &= \frac{A_{580,f}}{2[Cr_2O_7^{2-}(aq)]_i} \\
 &= \frac{(0.652 \pm 0.001)}{2(0.0250 \pm 0.0005 \text{ M})} \\
 &= 13.04 \text{ M}^{-1} \pm 2\% \\
 &= 13.0 \pm 0.3 \text{ M}^{-1}
 \end{aligned}$$

Sample calculation for determining the average of the product of the extinction coefficient of chromium (III) ion and the path length:

$$\begin{aligned}
 (\epsilon_{580, Cr^{3+}+b})_{ave} &= \frac{(\epsilon_{580, Cr^{3+}+b})_1 + (\epsilon_{580, Cr^{3+}+b})_2 + (\epsilon_{580, Cr^{3+}+b})_3}{3} \\
 &= \frac{13.0 \pm 0.3 \text{ M}^{-1} + 13.3 \pm 0.3 \text{ M}^{-1} + 13.7 \pm 0.3 \text{ M}^{-1}}{3} \\
 &= \frac{40.0 \pm 0.9 \text{ M}^{-1}}{3} \\
 &= 13.3 \pm 0.3 \text{ M}^{-1}
 \end{aligned}$$

Sample calculation for determining the concentration of chromium (III) ion for trial 1 of  $5.0 \pm 0.4\%$  (v/v) ethanol measured at  $30.00 \pm 0.01$  s:

$$\begin{aligned}
 [Cr^{3+}] &= \frac{A_{580,i} - A_{580}}{\frac{A_{580,i}}{2[Cr_2O_7^{2-}(aq)]_i} - \epsilon_{580, Cr^{3+}+b}} \\
 &= \frac{(0.005 \pm 0.001) - (0.012 \pm 0.001)}{\frac{(0.005 \pm 0.001)}{2(0.0250 \pm 0.0005 \text{ M})} - (13.3 \pm 0.3 \text{ M}^{-1})} \\
 &= 0.0005 \text{ M} \pm 31\% \\
 &= 0.0005 \pm 0.0002 \text{ M}
 \end{aligned}$$

## Investigating the effect of ethanol concentration on the rate of production of chromium (III) ion by acidified potassium dichromate

Sample calculation of the initial molar concentration of ethanol for  $5.00 \pm 0.06$  mL  $5.0 \pm 0.4\%$ (v/v) ethanol in  $10.0 \pm 0.1$  mL reaction mixture:

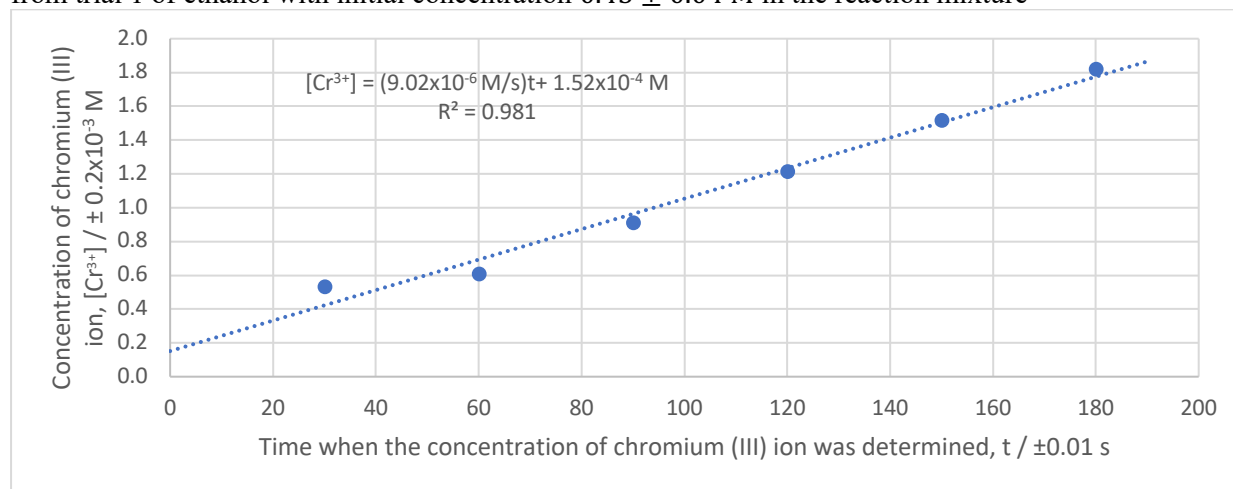
$$\begin{aligned}
 [CH_3CH_2OH(aq)] &= \frac{C_{CH_3CH_2OH, \%(v/v), 5.00 \text{ mL}} V_{\text{initialSolution}} \left(789.3 \frac{\text{g}}{\text{L}}\right)}{V_{\text{ReactionMixture}} \left(46.07 \frac{\text{g}}{\text{mol}}\right)} \\
 &= \frac{\left(5.0 \pm 0.4\%(v/v) \times \frac{1}{100\%}\right) (5.00 \pm 0.06 \text{ mL}) \left(789.3 \frac{\text{g}}{\text{L}}\right)}{(10.0 \pm 0.1 \text{ mL}) \left(46.07 \frac{\text{g}}{\text{mol}}\right)} \\
 &= 0.43 \frac{\text{mol}}{\text{L}} \pm 10\% \\
 &= 0.43 \pm 0.04 \frac{\text{mol}}{\text{L}}
 \end{aligned}$$

**Table 3:** Sample processing table for concentration of chromium (III) ion in the reaction mixture every 30.00 s after the reaction begun for a total of 180.00 s for trial 1 with initial molar concentration of ethanol in the reaction mixture of  $0.43 \pm 0.04$  M.

Time when the concentration of chromium (III) ion was determined, $t / \pm 0.01$ s	Concentration of chromium (III) ion at time $t$ $[Cr^{3+}(aq)] / 10^{-3} \text{ M}$
30.00	$0.5 \pm 0.2$
60.00	$0.6 \pm 0.2$
90.00	$0.9 \pm 0.2$
120.00	$1.2 \pm 0.2$
150.00	$1.5 \pm 0.2$
180.00	$1.8 \pm 0.2$

When determining the concentration of chromium (III) ions, there were some data points where the concentration was determined to be negative (concentration of chromium (III) ion at 30.00 s of trial 3 of initial ethanol concentration of  $0.86 \pm 0.06$  M, and at 30.00 s of trial 2 of initial ethanol concentration of  $1.7 \pm 0.1$  M), and there was one concentration of 0 at 60.00 s for trial 3 of initial ethanol concentration of  $1.7 \pm 0.1$  M ethanol which meant that the reaction did not occur for 60.00 s after the reactants were mixed. Since negative concentrations do not exist, and there should have at least been some reactions taking place, these values were not used in further calculations as they may be caused by errors from the measurement devices.

**Graph 1:** Sample processing to determine the initial rate of production of chromium (III) ion, using data from trial 1 of ethanol with initial concentration  $0.43 \pm 0.04$  M in the reaction mixture





## Investigating the effect of ethanol concentration on the rate of production of chromium (III) ion by acidified potassium dichromate

The rate of production of chromium (III) ion would be the gradient of the line of best fit, with the uncertainty of rate determined by the maximum and minimum gradient allowed by the uncertainties of the first and last data points:

$$\begin{aligned} r_{Cr^{3+}} &= 9.02 \times 10^{-6} \frac{M}{s} \pm \frac{r_{Cr^{3+},max} - r_{Cr^{3+},min}}{2} \\ &= 9.02 \times 10^{-6} \frac{M}{s} \pm \frac{1.11 \times 10^{-5} \frac{M}{s} - 6.21 \times 10^{-6} \frac{M}{s}}{2} \\ &= (9 \pm 2) \times 10^{-6} \frac{M}{s} \end{aligned}$$

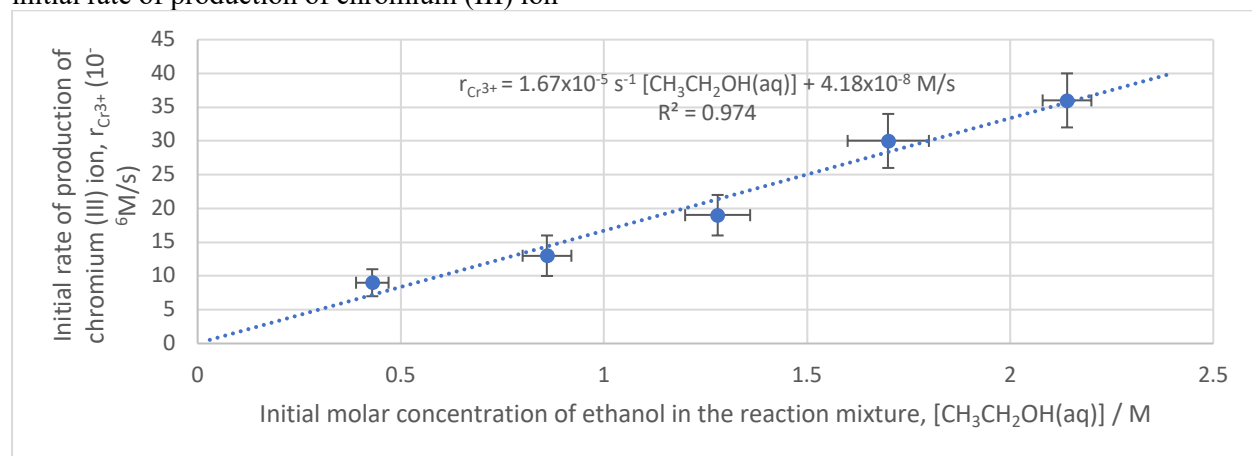
Sample calculation of determining the average rate of production of chromium (III) ion for all three trials for initial ethanol concentration of  $0.43 \pm 0.04$  M:

$$\begin{aligned} r_{Cr^{3+},ave} &= \frac{r_{Cr^{3+},1} + r_{Cr^{3+},2} + r_{Cr^{3+},3}}{3} \\ &= \frac{(9 \pm 2) \times 10^{-6} \frac{M}{s} + (8 \pm 2) \times 10^{-6} \frac{M}{s} + (8 \pm 2) \times 10^{-6} \frac{M}{s}}{3} \\ &= \frac{(26 \pm 6) \times 10^{-6} \frac{M}{s}}{3} \\ &= (9 \pm 2) \times 10^{-6} \frac{M}{s} \end{aligned}$$

**Table 4:** The average initial rate of production of chromium (III) ion for various initial ethanol concentrations

Initial molar concentration of ethanol in the reaction mixture, $[CH_3CH_2OH(aq)] / M$	Average initial rate of production of chromium (III) ion, $r_{Cr^{3+},ave} / 10^{-6} \frac{M}{s}$
$0.43 \pm 0.04$	$9 \pm 2$
$0.86 \pm 0.06$	$13 \pm 3$
$1.28 \pm 0.08$	$19 \pm 3$
$1.7 \pm 0.1$	$30 \pm 4$
$2.14 \pm 0.06$	$36 \pm 4$

**Graph 2:** Relationship between various initial concentrations of ethanol in the reaction mixture and the initial rate of production of chromium (III) ion



Since the rate of production of chromium (III) ion has a linear correlation with the initial molar concentration of ethanol in the reaction mixture, it can be determined from the graph that the overall reaction is first order with respect to ethanol.

## Investigating the effect of ethanol concentration on the rate of production of chromium (III) ion by acidified potassium dichromate

The gradient of the line of best fit for the rate concentration graph is  $1.67 \times 10^{-5} \text{ s}^{-1}$ , which was used to determine the percentage error of this experiment by comparing to an expected gradient of  $1.9 \times 10^{-5} \text{ s}^{-1}$ :

$$\begin{aligned}\%Error &= \left| \frac{\text{Gradient}_{\text{Experiment}} - \text{Gradient}_{\text{Expected}}}{\text{Gradient}_{\text{Expected}}} \right| \times 100\% \\ &= \left| \frac{1.67 \times 10^{-5} \text{ s}^{-1} - 1.9 \times 10^{-5} \text{ s}^{-1}}{1.9 \times 10^{-5} \text{ s}^{-1}} \right| \times 100\% \\ &= 10\%\end{aligned}$$

### Evaluation

#### **Conclusion**

Through this investigation, it was determined that the effect of ethanol concentration on the initial rate of production of chromium (III) ion is that as the concentration of ethanol increases, the initial rate of production of chromium (III) ions increases proportionally to the increase of ethanol concentration. This can be shown through the strong linear correlation between the initial rate of production of chromium (III) ion and the initial molar concentration of ethanol in the reaction mixture, which is visible through the linear trendline shown in **Graph 2**.

The trendline that was determined when graphing the initial rate of production of chromium (III) ions and the concentration of ethanol is:

$$r_{\text{Cr}^{3+}} = 1.67 \times 10^{-5} \text{ s}^{-1} [\text{CH}_3\text{CH}_2\text{OH}(\text{aq})] + 4.18 \times 10^{-8} \frac{\text{M}}{\text{s}}$$

This line of best fit has an  $R^2$  coefficient of 0.974, meaning that 97.4% of the variance in the data processed can be explained by this trendline, showing that this model is a good fit for the data. In addition, the linear line of best fit between the initial rate of production of chromium (III) ion and the concentration of ethanol is supported by the rate law determined, which was first order with respect to ethanol.

Furthermore, the percentage error when comparing the gradient of  $1.67 \times 10^{-5} \text{ s}^{-1}$  of this line and the expected gradient determined from the literature value was 10%, which was a reasonably low error showing that the result of this experiment agrees with the theory in both the trend and the values. The intercepts of this graph are relatively low and are very close to the origin, indicating that the direct correlation is not heavily affected by systematic errors.

#### **Sources of Systematic Errors**

The concentration of ethanol in the reaction may be lower than the concentration that was intended to be used. Throughout the experiment, a stock solution of 25% (v/v) ethanol was prepared at the beginning of every experiment day and left in a beaker. During this time, a portion of the ethanol could have evaporated due to exposure to open space and decreased the concentration. Therefore, the rate of production of chromium (III) ion through the oxidation of ethanol by acidified potassium dichromate could be decreased, and most significantly affecting the experimental trials with higher concentrations of ethanol as it would evaporate faster. As a result, the gradient of the line of best fit when the initial rate of production of chromium (III) ion was graphed against concentration of ethanol could be lower than expected, which could be a possible explanation of the 10% error. To reduce this error, ethanol solutions should be kept in a closed container prior to use, and the ethanol not in the container should be placed away from any heat source that would accelerate the evaporation.

The extinction coefficient determined for chromium (III) ion was lower than it should be. When determining the extinction coefficient for chromium (III) ion, reaction mixtures using concentrated 95% (v/v) ethanol were allowed to react for approximately 1.5 hours, and it was assumed that all the dichromate ions were reduced to chromium (III) ions. Since the allocated experiment time was only 2 hours per day and storing the reaction mixture overnight could have resulted in ethanol evaporating thus making the result unreliable, this was the maximum time available to allow the reaction to proceed. However, from the absorbance measured for the three trials, the absorbance was still increasing between the trials, meaning that the absorbance recorded was lower than what the absorbance would have been when the reaction is at completion, which would lead to a lower extinction coefficient being calculated,

## **Investigating the effect of ethanol concentration on the rate of production of chromium (III) ion by acidified potassium dichromate**

meaning that the concentration of chromium (III) ion determined using this would be higher, and thus the rate of production of chromium (III) ion calculated using this value would be faster than what it should have been. To solve this issue, a calibration curve using various known chromium (III) ion concentration should be made to determine the extinction coefficient of chromium (III) ion from its absorbance.

The concentration of reaction mixture, and the recorded absorbance of the reaction mixture were lower than it should have been. After every experimental trial, the glass cuvette was rinsed using deionized water to remove any remaining solutions present in the cuvette. However, after each rinse, even after the cuvette was wiped, some deionized water remained in the cuvette, and since there was not enough glass cuvette for a completely dried cuvette to be used after each trial, cuvettes with water in it were used. This could have potentially diluted the reaction mixture sample in the cuvette and caused the absorbance measurement to be lower than it should have been, which would decrease the rate of production of chromium (III) ions calculated from this. This error could be solved by obtaining more glass cuvettes to be used, while allowing the cuvettes that were rinsed to air-dry over time.

### **Extensions to Experiment**

One potential extension to this experiment would be to investigate the effect of the concentrations of other reactants in the oxidation of ethanol, such as varying the concentration of dichromate ion or varying the concentration of sulfuric acid. This would be useful to determine the most effective concentrations of reactants in a breath analyzer. In addition, another potential extension would be to measure the current generated by the redox reaction between ethanol and acidified potassium dichromate, since more modern breath analyzers do not rely on colour change of reactants and measure electrical currents to achieve a more accurate result.

## Investigating the effect of ethanol concentration on the rate of production of chromium (III) ion by acidified potassium dichromate

### References

- Brown, C., & Ford, M. (2014). *Pearson Baccalaureate Higher Level Chemistry* (2nd ed.). Pearson Education Limited.
- Centers for Disease Control and Prevention. (2012, October 2). *Teen drinking and driving*. Retrieved December 15, 2021, from <https://www.cdc.gov/vitalsigns/teendrinkinganddriving/index.html>
- CK-12 Foundation. (2020, June 22). *22.10 Balancing redox reactions: half-reaction method*. Retrieved December 15, 2021, from <https://flexbooks.ck12.org/cbook/ck-12-chemistry-flexbook-2.0/section/22.10/primary/lesson/balancing-redox-reactions>
- Fisher Scientific. (2018, January 17). *Potassium dichromate - safety data sheet*. Retrieved November 25, 2021, from <https://www.fishersci.com/store/msds?partNumber=SP1701&productDescription=POT+DICHROMATE+SOL+N%2F10+CR+1L&vendorId=VN00033897&countryCode=US&language=en>
- Fisher Scientific. (2018, July 6). *Sulfuric acid - safety data sheet*. Retrieved November 25, 2021, from <https://www.fishersci.com/msdsproxy%3FproductName%3DA300700LB%26productDescription%3DSULFURIC%2BAC%2BACS%2B700LB%26catNo%3DA300-700LB%26vendorId%3DVN00033897%26storeId%3D10652>
- Fisher Scientific. (2020, November 12). *Safety data sheet*. Retrieved November 25, 2021, from <https://www.fishersci.com/store/msds?partNumber=AC427171000&productDescription=ACETALDEHYDE%2C+ACROSEAL%28T+100ML&vendorId=VN00032119&countryCode=US&language=en>
- Fisher Scientific. (2021, November 5). *Ethanol - safety data sheet*. Retrieved November 25, 2021, from <https://www.fishersci.com/msdsproxy%3FproductName%3DA405P4%26productDescription%3DETHANOL%2BAHYD%2BHISTO%2B4L%26catNo%3DA405P-4%2B%26vendorId%3DVN00033897%26storeId%3D10652>
- Flowers, P., Robinson, W. R., Langley, R., & Theopold, K. (2015). *Chemistry*. Openstax. Retrieved November 26, 2021, from <https://openstax.org/books/chemistry/pages/1-introduction>
- Freudenrich, C. (2021, April 9). *How breathalyzers work*. HowStuffWorks. Retrieved December 15, 2021, from <https://electronics.howstuffworks.com/gadgets/automotive/breathalyzer.htm>
- Harvey, D. (2019, June 5). *10.2: Spectroscopy based on absorption*. Chemistry LibreTexts. Retrieved November 26, 2021, from [https://chem.libretexts.org/Courses/Northeastern\\_University/10%3A\\_Spectroscopic\\_Methods/10.2%3A\\_Spectroscopy\\_Based\\_on\\_Absorption](https://chem.libretexts.org/Courses/Northeastern_University/10%3A_Spectroscopic_Methods/10.2%3A_Spectroscopy_Based_on_Absorption)
- Hassan, M., Al-Hakimi, A. N., & Alahmadi, M. D. (2011). Kinetics of oxidation of aliphatic alcohols by potassium dichromate in aqueous and micellar media. *South African journal of chemistry*, 64(1), 237-240.
- Helmenstine, A. M. (2020, August 28). *Beer's law definition and equation*. ThoughtCo. Retrieved November 26, 2021, from <https://www.thoughtco.com/beers-law-definition-and-equation-608172>
- Jones reactant. (n.d.). Organic Chemistry Portal. Retrieved December 15, 2021, from <https://www.organic-chemistry.org/chemicals/oxidations/jones-reagent.shtm>
- National Center for Biotechnology Information (2021). PubChem Compound Summary for CID 702, Ethanol. Retrieved November 27, 2021, from <https://pubchem.ncbi.nlm.nih.gov/compound/Ethanol>