**Kinetics of electrocatalytic reduction of CO2 with manganese catalysts with bulky bipyridine ligands**

**Directions**: In the journal article Sampson, D.L.; Nguygen, D., Grice, K.A.; Moore, C.E.; Rheingold, A.L.; Kubiak, C.P. Manganese Catalysts with Bulky Bipyridine Ligands for the Electrocatalytic Reduction of Carbon Dioxide: Eliminating Dimerization and Altering Catalysis. *J. Am. Chem. Soc.* **2014**, *136*, 5460-5471, the authors studied the kinetics of the electrocatalytic reduction of carbon dioxide. Carefully read pages 5464-5465 with a focus on the *Electrocatalysis* portion of the **Results and Discussion** section to help answer the following questions.

**Questions:**

1. Identify, in general, the experimental conditions required for the pseudo-first-order kinetics assumption to be valid. Consult the article and specify the pseudo-first-order conditions applied in this study.

2. Identify each of the terms in the equation below. Describe how this compares to the *more familiar* molarity *versus* time in rate law.

 $i\_{cat} = n\_{cat}FA\left[cat\right]^{x}\left(Dk\_{cat}\left[Q\right]^{y}\right)^{1/2}$ (**eq 1**)

3. For a reaction in which a species **A** is consumed, sketch plots in which [**A**], ln[**A**], or 1/[**A**] *versus* time are linear. Classify each as zero-, first-, or second-order in species **A**.

4. Using the data below and **eq 1**, generate an appropriate plot (using available graphical analysis software). Analyze each plot to determine the reaction order (*x* or *y*) in catalyst, CO2, and acid (H2O).

|  |  |
| --- | --- |
| ***i*cat (μA)** | **[CO2] mol L–1** |
| 27.9 | 0.01 |
| 66.2 | 0.03625 |
| 96.2 | 0.05063 |
| 190.7 | 0.16 |
| 255 | 0.2704 |

|  |  |
| --- | --- |
| ***i*cat (mA)** | **[H2O] mol L–1** |
| 0.051 | 0.615 |
| 0.14 | 1.048 |
| 0.17 | 1.183 |
| 0.22 | 1.378 |
| 0.29 | 1.612 |
| 0.34 | 1.870 |
| 0.38 | 2.049 |
| 0.41 | 2.258 |
| 0.43 | 2.387 |

|  |  |
| --- | --- |
| ***J*cat (mA cm–2)** | **[cat] mol L–1** |
| 0.98 | 0.22 |
| 1.5 | 0.42 |
| 2.2 | 0.61 |
| 2.7 | 0.88 |
| 3.6 | 1.2 |
| 5.2 | 1.8 |

5.Describe what is meant by saturation kinetics.

6. Re-write the integrated-rate law (**eq 1**) with the order of **catalyst**, **CO2**, and **acid**.

7. Given the following conditions, calculate the rate constant (*k*cat). Be sure to give value with the *appropriate* units.

 *n*cat = 2

 *F* = 96845 C mol–1

 *A* = 7.4 cm2

 [cat] = 5 × 10–7 mol L–1

 [CO2] = 0.27 mol L–1

[H2O] = 3.5 mol L–1

 *D* = 1.1 × 10–5 cm2 s–1

*icat* = 0.00035 C/s