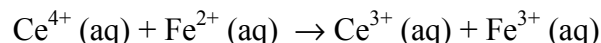


1. The rate for the oxidation of iron(II) by cerium(IV)



is measured at several different initial concentrations of the two reactants:

$[\text{Ce}^{4+}] (\text{mol L}^{-1})$	$[\text{Fe}^{2+}] (\text{mol L}^{-1})$	Rate ($\text{mol L}^{-1} \text{s}^{-1}$)
1.1×10^{-5}	1.8×10^{-5}	2.0×10^{-7}
1.1×10^{-5}	2.8×10^{-5}	3.1×10^{-7}
3.4×10^{-5}	2.8×10^{-5}	9.5×10^{-7}

(a) Write the rate expression for this reaction.

In general, $v = k[\text{Ce}^{4+}]^m[\text{Fe}^{2+}]^n$

From experiments 1 and 2,

$\text{Rate}_2/\text{Rate}_1 = (3.1 \times 10^{-7})/(2.0 \times 10^{-7}) = (k \times (1.1 \times 10^{-5})^m \times (2.8 \times 10^{-5})^n) / (k \times (1.1 \times 10^{-5})^m \times (1.8 \times 10^{-5})^n)$ or $1.55 = (1.55)^n$. Therefore, $n=1$.

From experiments 2 and 3,

$\text{Rate}_3/\text{Rate}_2 = (9.5 \times 10^{-7})/(3.1 \times 10^{-7}) = (k \times (3.4 \times 10^{-5})^m \times (2.8 \times 10^{-5})^n) / (k \times (1.1 \times 10^{-5})^m \times (2.8 \times 10^{-5})^n)$ or $3.1 = (3.1)^m$. Therefore, $m=1$.

The rate law for this reaction is $v = k[\text{Ce}^{4+}][\text{Fe}^{2+}]$.

(b) Calculate the rate constant k , and give its units.

To find the rate constant k , we will use $k = v/[\text{Ce}^{4+}][\text{Fe}^{2+}]$, and any experiment, for example, experiment 1:

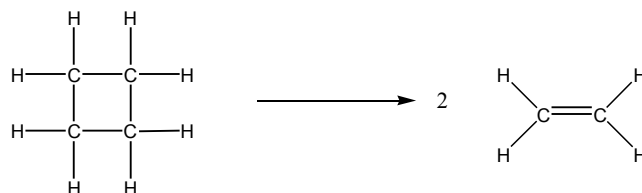
$$k = (2.0 \times 10^{-7}) / ((1.1 \times 10^{-5}) \times (1.8 \times 10^{-5})) = 1000 \text{ (1/M}\cdot\text{s)}.$$

(c) Predict the initial reaction rate for a solution in which $[\text{Ce}^{4+}]$ is $2.6 \times 10^{-5} \text{ M}$ and $[\text{Fe}^{2+}]$ is $1.3 \times 10^{-5} \text{ M}$.

$$v = k[\text{Ce}^{4+}][\text{Fe}^{2+}] = 1000 \times (2.6 \times 10^{-5}) \times (1.3 \times 10^{-5}) = 3.38 \times 10^{-7} \text{ (M/s)}.$$

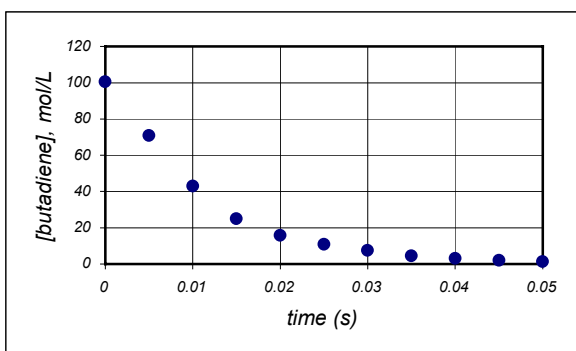
Your names _____

2. Cyclobutane decomposes to ethylene at elevated temperatures according to the reaction

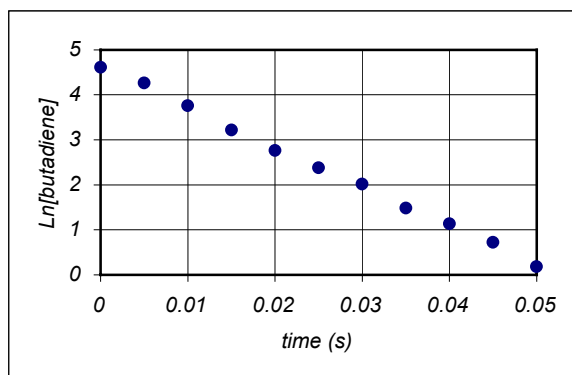
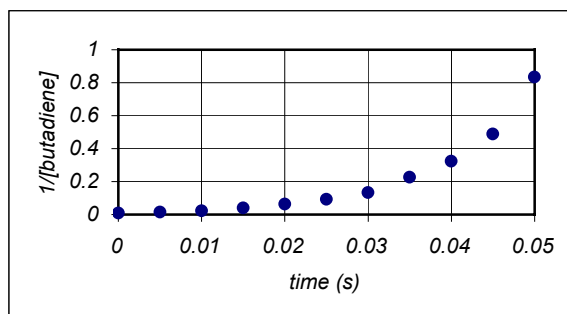


The decomposition was followed at 1273 K as a function of time, and the following data were obtained:

a)



b)



c)

a) From the graphs, determine whether the reaction follows first or second order kinetics. Justify your answer.

The reaction is first order, since the graph $\text{Ln}[\text{butadiene}]$ vs. time is linear. The first order kinetics gives rise to an integrated rate law of the form: $[\text{butadiene}] = [\text{butadiene}]_0 \times \text{Exp}[-kx]$, and its linear form: $\text{Ln}[\text{butadiene}] = \text{Ln}[\text{butadiene}]_0 - kx$

b) Using the appropriate plot (specify which one), determine the rate constant of this reaction. Give the units of the rate constant.

From plot c, one can determine the rate constant for the reaction: $k = -\text{slope} \sim 87 \text{ s}^{-1}$

Since the reaction obeys first order kinetics, the units of the rate constant are s^{-1}

Your names _____

c) Upon decreasing the temperature to 1223 K, the rate of the reaction drops by a factor of 10 (compared to the first measurement at 1273 K – see your answer to b). Calculate the activation energy of this reaction.

At 1273K, $k=87 \text{ s}^{-1}$; at 1223K, $k=0.87 \text{ s}^{-1}$. Using the Arrhenius equation, $k(T) = A \times \text{Exp}(-E_a/RT)$, we find the activation energy in the following way:

$$k_1(1273 \text{ K}) = A \times \text{Exp}(-E_a/(R \times 1273))$$

$$k_2(1223 \text{ K}) = A \times \text{Exp}(-E_a/(R \times 1223))$$

$$k_1/k_2 = \text{Exp}(E_a \times ((-1/(8.31 \times 1273)) + (1/(8.31 \times 1223))))$$

$$\text{Ln}(k_1/k_2) = E_a \times ((-1/(8.31 \times 1273)) + (1/(8.31 \times 1223)))$$

$$E_a = \text{Ln}(k_1/k_2) / ((-1/(8.31 \times 1273)) + (1/(8.31 \times 1223))) = 595801 \text{ J} = 595.8 \text{ kJ}$$