

## Chapter 13 Exercises

Here are 12 questions for you lovingly selected from the pages of Tro, plus some supplementary method of initial rates problems (S1 – S3) because there seemed a shortage of ‘real world’ examples in Tro...

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### Additional “Method of Initial Rates” Exercises

S.1 Determine the rate equation and rate constant  $k$  for the following reaction:



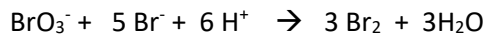
[ICl] / mol.L <sup>-1</sup>	[H <sub>2</sub> ] / mol.L <sup>-1</sup>	Initial Rate/ mol.L <sup>-1</sup> s <sup>-1</sup>
0.10	0.01	0.002
0.20	0.01	0.004
0.10	0.04	0.008

S2. Determine the rate equation and rate constant  $k$  for the following reaction:



[C <sub>3</sub> H <sub>6</sub> O] / mol.L <sup>-1</sup>	[Br <sub>2</sub> ] / mol.L <sup>-1</sup>	Initial Rate/ mol.L <sup>-1</sup> s <sup>-1</sup>
0.10	0.10	1.64 x 10 <sup>-5</sup>
0.20	0.10	1.64 X 10 <sup>-5</sup>
0.10	0.20	3.29 X 10 <sup>-5</sup>

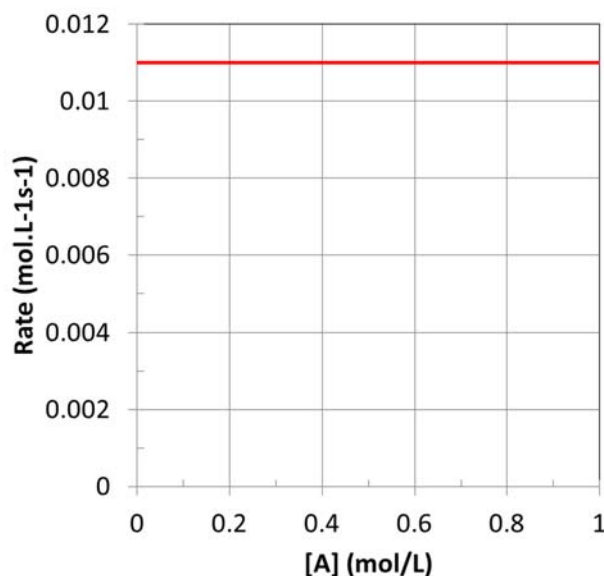
S3. Determine the rate equation and rate constant  $k$  for the following reaction:



[BrO <sub>3</sub> <sup>-</sup> ] / mol.L <sup>-1</sup>	[Br <sup>-</sup> ] / mol.L <sup>-1</sup>	[H <sup>+</sup> ]	Initial Rate/ mol.L <sup>-1</sup> s <sup>-1</sup>
0.10	0.10	0.10	8.0 x 10 <sup>-4</sup>
0.20	0.10	0.10	1.6 X 10 <sup>-3</sup>
0.20	0.20	0.10	3.2 X 10 <sup>-3</sup>
0.10	0.10	0.20	3.2 x 10 <sup>-3</sup>

### Rates of Chemical Reactions

Q36 The graph below shows a plot of the rate of a reaction versus concentration of the reactant.



- What is the order of the reaction?
- Make a rough sketch of how a plot of [A] vs time would appear
- Write a rate law for the reaction including the value of  $k$ .

Q40. A reaction in which **A**, **B** and **C** react to form products is zero-order in **A**, one half order in **B** and second order in **C**.

- Write a rate law for the reaction
- What is the overall order of the reaction?
- By what factor does the reaction rate change if [A] is doubled? (and the concentration of other reactants are held constant)
- By what factor does the reaction rate change if [B] is doubled? (and the concentration of other reactants are held constant)
- By what factor does the reaction rate change if [C] is doubled? (and the concentration of other reactants are held constant)
- By what factor does the reaction rate change if the concentrations of all reactants are doubled?

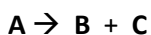
Q44 The data below were collected for the reaction:



[CH <sub>3</sub> Cl]	[Cl <sub>2</sub> ]	Initial rate
0.050	0.050	0.014
0.100	0.050	0.029
0.200	0.200	0.115

Write an expression for the rate law and calculate the value of the rate constant,  $k$ . What is the overall order of the reaction?

Q50 The following reaction was monitored as a function of time:



A plot of  $\ln[\text{A}]$  versus time yields a straight line with slope  $-0.0045 \text{ s}^{-1}$

- What is the value of the rate constant,  $k$ , for this reaction at this temperature
- Write the rate law for the reaction
- What is the half life?
- What is the lifetime for this reaction?
- If the initial concentration of **A** is  $0.250 \text{ mol.L}^{-1}$  what is the concentration of **A** after 225 s?

### Activation Energies for Chemical Reactions

Q58 A chemical reaction is endothermic and has an activation energy which is twice the value of the enthalpy of the reaction. Draw a diagram depicting the energy of the reaction as it progresses. Label the position of the reactants, and products and indicate both the enthalpy and activation energy for the reaction.

Q60 The rate constant of a reaction at  $32 \text{ }^\circ\text{C}$  is  $0.055 \text{ s}^{-1}$ . If the frequency factor is  $1.2 \times 10^{13} \text{ s}^{-1}$ , what is the activation energy for the reaction?

Q62 The rate constant  $k$  for a reaction was measured as a function of temperature. A plot of  $\ln(k)$  vs  $1/T$  (in K) is linear and has a slope of  $-1.01 \times 10^4 \text{ K}$ . Calculate the activation energy for this reaction.

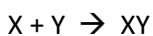
Q68. A reaction has a rate constant of  $0.000122 \text{ s}^{-1}$  at  $27^\circ\text{C}$  and  $0.228 \text{ s}^{-1}$  at  $77^\circ\text{C}$ .

- Determine the activation barrier for this reaction
- What is the value of the rate constant at  $17^\circ\text{C}$ ?

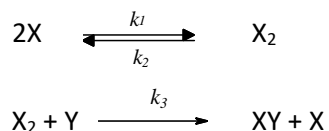
Q70 If a temperature increases from  $20.0^\circ\text{C}$  to  $35.0^\circ\text{C}$  triples the rate constant for a reaction what is the value of the activation barrier for the reaction?

### Reaction Mechanisms

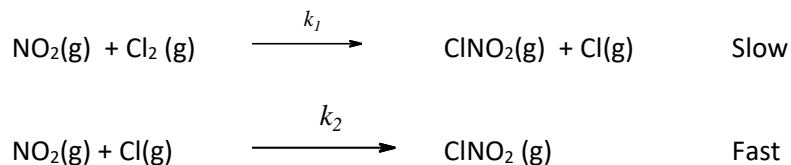
Q74 Consider the overall reaction which is experimentally observed to be second order in X and first order in Y.



- Does the reaction occur in a single step in which X and Y collide?
- Use the steady-state approximation to determine the rate law predicted by the following mechanism. Is this mechanism valid? Under what conditions?



Q76. Consider the two-step mechanism for a reaction:



- What is the overall reaction?
- Identify the intermediates in the mechanism
- What is the predicted rate law?

### Catalysis

- Q79 Suppose that a catalyst lowers the activation barrier of a reaction from  $125 \text{ kJmol}^{-1}$  to  $55 \text{ kJmol}^{-1}$ . By what factor would you expect the reaction rate to increase at  $25 \text{ }^\circ\text{C}$ ? [Assume that the frequency factors for the catalysed and uncatalysed reactions are the same].