Chapter 13 Exercises

Here are 12 questions for you lovingly selected from the pages of Tro, plus some supplementary method of initial rates problems because there seemed a shortage of real examples in Tro...

Additional "Method of Initial Rates" Exercises

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

2 ICl + H$_2$ →   I$_2$ + 2 HCl

[ICl] /mol.L^{-1}	[H$_2$] / mol.L^{-1}	Initial Rate/ mol.L^{-1}s^{-1}
0.10	0.01	0.002
0.20	0.01	0.004
0.10	0.04	0.008

Compare expt 1 & 2: [H$_2$] constant, double [ICl], double rate: therefore first order in [ICl]

Compare expt 1 & 3: [ICl] constant, quadruple [H$_2$], quadruple rate: therefore first order in [H$_2$]

Rate = k[H$_2$]^1[ICl]^1

Overall order = 1 + 1 = 2

To evaluate k choose any one experiment (selected expt #1 here):

Rate = 0.002 mol.L^{-1}.s^{-1} = k(0.10 mol.L^{-1})^1(0.01 mol.L^{-1})^1

So k = 0.002 mol.L^{-1}.s^{-1}/(0.10 mol.L^{-1})(0.01 mol.L^{-1}) = **2 mol^{-1}.L.s^{-1}**

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

$C_3H_6O + Br_2 \rightarrow C_3H_5OBr + HBr$

$[C_3H_6O]$ / mol.L^{-1}	$[Br_2]$ / mol.L^{-1}	Initial Rate/ mol.L^{-1}s^{-1}
0.10	0.10	1.64×10^{-5}
0.20	0.10	1.64×10^{-5}
0.10	0.20	3.29×10^{-5}

Compare expt 1 & 2: $[Br_2]$ constant, double $[C_3H_6O]$, no change in rate. Therefore zero order in $[C_3H_6O]$

Compare expt 1 & 3: $[C_3H_6O]$ constant, double $[Br_2]$, double rate: therefore first order in $[Br_2]$
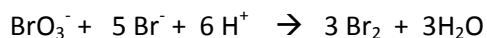
Rate = $k[C_3H_6O]^0[Br_2]^1$ = $k[Br_2]^1$

Overall order = 0 + 1 = 1

To evaluate k choose any one experiment (selected expt #1 here):

Rate = 1.64×10^{-5} mol.L^{-1}.s^{-1} = $k(0.10$ mol.L$^{-1})$

So k = 1.64×10^{-5} mol.L^{-1}.s^{-1}/(0.10 mol.L^{-1}) = **1.6×10^{-4} s^{-1}**

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

$BrO_3^- + 5\ Br^- + 6\ H^+ \rightarrow 3\ Br_2 + 3H_2O$

$[BrO_3^-]$ / mol.L^{-1}	$[Br_2]$ / mol.L^{-1}	$[H^+]$	Initial Rate/ mol.L^{-1}s^{-1}
0.10	0.10	0.10	8.0×10^{-4}
0.20	0.10	0.10	1.6×10^{-3}
0.20	0.20	0.10	$3{,}2 \times 10^{-3}$
0.10	0.10	0.20	3.2×10^{-3}

This is a more complex problem with 3 reagents, but we use the same methodology, i.e. keep all variables constant apart from one:

Compare expt 1 and expt 2: double $[BrO_3^-]$ double rate. First order in $[BrO_3^-]$

Compare expt 2 and expt 3: double $[Br_2]$ double rates. First order in $[Br_2]$

Compare expt 1 and expt 4: double $[H^+]$, quadruple rate. Second order in $[H^+]$

Rate = $k[BrO_3^-][Br_2][H^+]^2$

Overall order = 1+1+2 = 4.
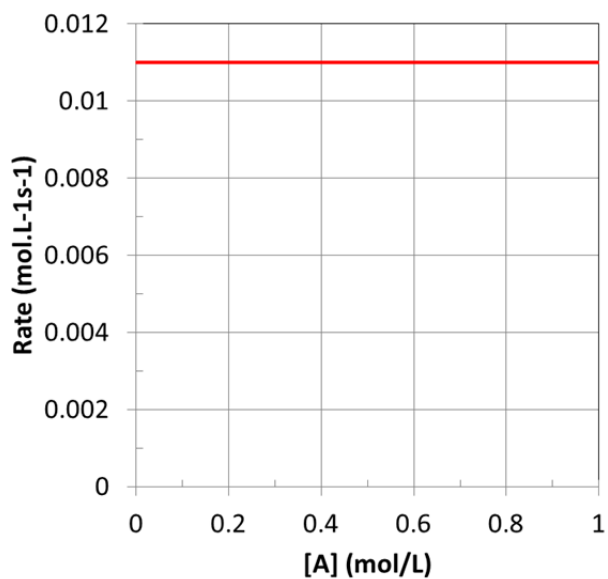
Now select an expt to solve for k. Here we use expt 1:

8.0×10^{-4} mol.L^{-1}s^{-1} = k(0.10 mol.L^{-1})(0.10 mol.L^{-1})(0.10 mol.L^{-1})^2

k = 8.0 mol^{-3}.L^3.s^{-1}

Rates of Chemical Reactions

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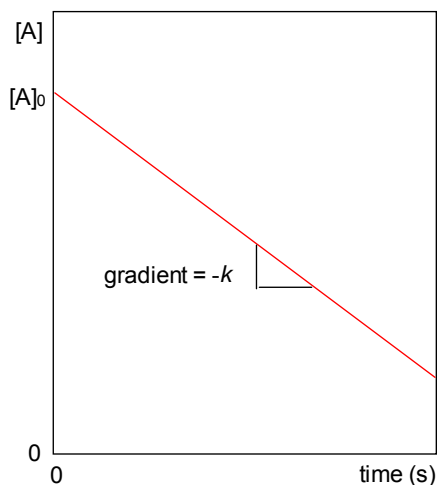

a.   What is the order of the reaction?

Zero order – the rate of the reaction is independent of concentration.

b.   Make a rough sketch of how a plot of [A] *vs* time would appear

The rate of the reaction is independent of [A] and the integrated rate law (which shows how [A] changes with time) is just $[A]_t = [A]_0 - kt$, i.e. it decreases linearly to zero.

c.   Write a rate law for the reaction including the value of k.

Rate $= k[A]^0 = k = $ **0.11 s^{-1}**

Because it is zero order the rate equation is independent of the concentration.

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.

a. Write a rate law for the reaction

Rate = $k[A]^0[B]^{1/2}[C]^2 = k[B]^{1/2}[C]^2$

b. What is the overall order of the reaction?

Overall order = 0.5 + 2 = 2.5

c. By what factor does the reaction rate change if [A] is doubled? (and the concentration of other reactants are held constant)

Increases by $2^0 = 1$ i.e. no change

d. By what factor does the reaction rate change if [B] is doubled? (and the concentration of other reactants are held constant)

Increases by $2^{0.5} = 1.414$
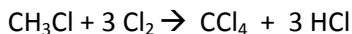
e. By what factor does the reaction rate change if [C] is doubled? (and the concentration of other reactants are held constant)

Increases by $2^2 = 4$ (i.e. quadrupled)

f. By what factor does the reaction rate change if the concentrations of all reactants are doubled?

Increases by $2^0 \times 2^{1/2} \times 2^2 = 2^{2.5} = 5.657$

Q44 The data below were collected for the reaction:

$CH_3Cl + 3\ Cl_2 \rightarrow CCl_4 + 3\ HCl$

[CH₃Cl]	[Cl₂]	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?

Expt 1 and Expt 2: $[Cl_2]$ constant, double CH_3Cl, double rate: first order in $[CH_3Cl]$

Now things get tricky as there are no data where $[CH_3Cl]$ is constant, so we have to compare experiments where two parameters are changed at once. Not normally advisable but we now know the reaction is first order in $[CH_3Cl]$. Lets compare expt 3 and expt 1:

Expt 3: $0.115 = k[CH_3Cl]^1[Cl_2]^x = k(0.200)^1(0.200)^x$ (Eq. 1)

Expt 1: $0.014 = k[CH_3Cl]^1[Cl_2]^x = k(0.050)^1(0.050)^x$ (Eq. 2)

We have two equations and two unknowns (x and k). Divide Eq. 1 by Eq. 2 to remove k:

$$\frac{0.115}{0.014} = \frac{(0.200)(0.200)^x}{(0.050)(0.050)^x}$$

$8.214 = 4(0.200)^x/(0.050)^x = 4(0.200/0.050)^x = 4(4)^x$

Rearranging:

$4^x = 8.214/4 = 2.0537$

Take logs of both sides:

$\log(4)^x = \log(2.0537)$ *or* $x\log(4) = \log(2.0537)$ [reminder $\log(a)^x = x\log(a)$]

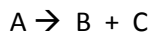$x = \log(2.0537)/\log(4) = 0.52 \sim 5.0$

So rate $= k[CH_3Cl][Cl_2]^{0.5}$

Now take any one expt and solve for k. Here I use expt 3:

$0.115 = k(0.200)^1(0.200)^{0.5} = k(0.200)^{1.5}$

$k = 0.115/(0.200)^{1.5} = 0.0894$

[Unitsof k?: rate $= mol.L^{-1}s^{-1}$ so k has units of $mol.L^{-1}s^{-1}/(mol.L^{-1})^{1.5}$ i.e. $mol^{-0.5}L^{0.5}s^{-1}$]

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

A → B + C

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

a) What is the value of the rate constant, k, for this reaction at this temperature

Since it is first order kinetics (see below) then the slope of the graph = -k. Hence k = 0.0045 s^{-1}. Note that the units of k also indicate first order.

b) Write the rate law for the reaction

Actually I answered this first! A linear plot of ln[A] *vs* t indicates first order kinetics, i.e. rate = k[A]

c) What is the half life?

For a first order reaction $kt_{1/2}$ = ln(2) so $t_{1/2}$ = ln(2)/0.0045 = 154s (**150s** to 2 sf)

d) What is the lifetime for this reaction?

We did not discuss lifetime (τ) specifically in class. In class we showed that for most reactions, the rate depends upon concentration and as the reaction proceeds the concentration decreases and so the reaction slows down. For many reactions it takes an infinite amount of time for the reaction to go to completion. Instead we use arbitrary values to give us a feel for how long we need to wait for things to occur. In class we focused on 'half life' which is the time taken for half the material to react. This is a conceptually easy value to work with.

The lifetime is a slightly odd measurement as it is the time for the reactant concentration to drop to 1/*e* of the starting concentration! [Maybe you can see why I elected not to discuss it! ;-)] For a first order reaction it turns out that τ = 1/*k*.

In the current case *k* = 0.0045s^{-1} so τ = 220s (2 sf)

e) If the initial concentration of A is 0.250 mol.L^{-1} what is the concentration of A after 225 s?

To determine concentration after a period of time t we use the integrated rate law:

$\ln[A]_t = \ln[A]_0 - kt$ = ln(0.250) – (0.0045)(225)

= -1.3863 – 1.0125 = -2.3988

$[A]_t = e^{-2.3988}$ = **0.091** mol.L^{-1}

Quick check: After one half life (154s) the concentration should be 0.125 mol.L^{-1}

After two half lives (308s) the concentration should be 0.0625 mol.L^{-1}

The value after 225s falls between the limits we expect.

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.

Preliminary notes:

Endothemic: Products should be higher in energy than starting materials

Activation energy twice the enthalpy.

Energy

Transition State

Ea

Products

ΔH_{rxn}

Reactants

Reaction coordinate
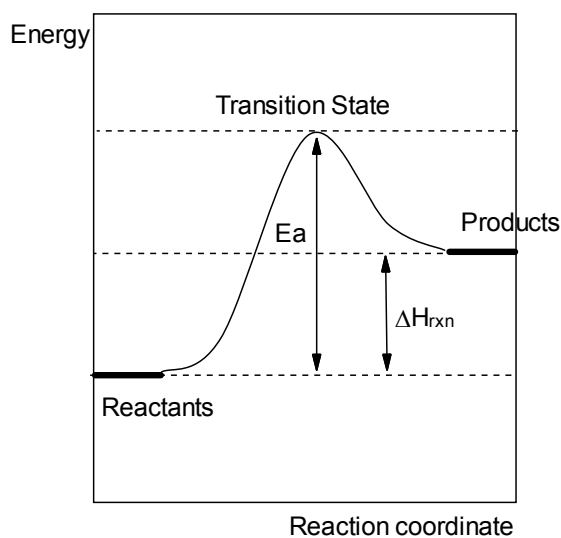
Q60 The rate constant of a reaction at 32 °C is 0.055 s^{-1}. If the frequency factor is 1.2 x 10^{13} s^{-1} , what is the activation energy for the reaction?

Kinetics questions: we should be working in Kelvin: 32 °C = 273 + 32 = 305 K

$$k = Ae^{-Ea/RT}$$

$$0.055 = (1.2 \times 10^{13})e^{-Ea/RT}$$

$$e^{-Ea/RT} = 0.055/(1.2 \times 10^{13}) = 4.583 \times 10^{-15}$$

Take natural logs of both sides:

$$-Ea/RT = \ln(4.583 \times 10^{15})$$

$$Ea = -RT\ln(4.583 \times 10^{15})$$

$$= -8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 305 \text{ K} \times (-33.016) = +83722 \text{ Jmol}^{-1} = \underline{84 \text{ kJmol}^{-1}} \text{ (2 sf since 32 °C)}$$

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 x 10^4 K. Calculate the activation energy for this reaction.

$k = Ae^{-Ea/RT}$

Taking logs of both sides: $\ln(k) = \ln(A) - E_a/RT$

So ln(k) *vs* 1/T is expected to be linear with gradient(slope) equal to $-Ea/R$

Hence $-Ea/R = -1.01 \times 10^4$ K

$Ea = 8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 1.01 \times 10^4 \text{ K} = 83971.4 \text{ Jmol}^{-1} = \underline{83.9 \text{ kJmol}^{-1}}$.

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

a) Determine the activation barrier for this reaction

This is a problem relating rate constants at two temperatures, so we should use the two point Arrhenius equation:

$$ln\left[\frac{k_2}{k_1}\right] = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Remember also we need to measure T in Kelvin: $27\,^\circ C = 273 + 27 = 300$ K $77\,^\circ C = 350$ K

$ln(0.228/0.000122) = (-E_a/8.314)\{(1/350) - (1/300)\}$

$7.5331 = \underline{-E_a\ (0.00286 - 0.00333)} = \underline{E_a\ (0.000476)}$
$\ 8.314 \quad 8.314$

$E_a = 7.5331$ x $(8.314/0.000476) = 131576$ $Jmol^{-1} = \underline{\textbf{130}}$ $kJmol^{-1}$ (2 sf)

b) What is the value of the rate constant at $17\,^\circ C$?

Now that we know Ea we can evaluate the rate constant at different temperatures:

Rewriting $ln(k_2/k_1)$ as $ln(k_2) - ln(k_1)$:

$ln(k_2) - ln(k_1) = -(Ea/R)\{(1/T_2) - (1/T_1)\}$

let us use $T_1 = 350$ K and $k_1 = 0.228$ and solve for k_2 when $T_2 = 17\,^\circ C = 290$ K.

$ln(k_2) - ln(0.228) = -(131576/8.314)\{(1/290) - (1/350)\}$

$ln(k_2) +1.4784 = -15826\{0.00345 - 0.00286\}$

$ln(k_2) = -9.3373 - 1.4784 = -10.8157$

$k_2 = e^{-10.8157} = \underline{\textbf{0.000020}}$ s^{-1} (to 2 sf since temp quoted to 2sf)

Check: does this seem right? The rate of the reaction increases with increasing temperature, so the value of k at $17\,^\circ C$ should be a little less than that at $27\,^\circ C$ (0.000122 s^{-1}). This answer therefore seems reasonable.

Q70 If a temperature increases from 20.0 °C to 35.0 °C triples the rate constant for a reaction what is the value of the activation barrier for the reaction?

This is a problem relating rate constants at two temperatures, so we should use the two point Arrhenius equation:

$$In\left[\frac{k_2}{k_1}\right] = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Let T_2 = 35.0 °C (308.15 K) and T_1 = 20.0 °C (293.15 K)

We are not given absolute rates this time but relative rates, i.e. the rate constant at 35 °C is three times as large as at 20 °C such that k_2/k_1 = 3.

$$In(3) = \frac{-Ea\{(1/308.15) - (1/293.15)\}}{R} = \frac{-E_a\{0.003245 - 0.003411\}}{R} = \frac{0.000166E_a}{R}$$

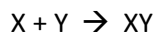Rearranging:

$$E_a = \frac{RIn(3)}{0.000166} = 55023 \text{ Jmol}^{-1} = \textbf{55 } kJmol^{-1}$$

Check: This seems a sensible number! It is in the 50 – 300 kJ/mol^{-1} region which I typical for bond breaking in the rate-determining step.

Reaction Mechanisms

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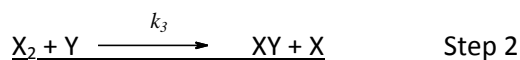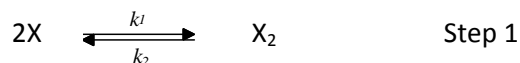
X + Y → XY

    a) Does the reaction occur in a single step in which X and Y collide?

If it was a single step reaction then it would be an elementary process and the rate equation would be: rate = $k[X]^1[Y]^1$

Since the experimentally observed rate equation is: rate = $k[X]^2[Y]^1$ then it cannot be a single step reaction.

    b) Use the steady-state approximation to determine the rate law predicted by the following mechanism. Is this mechanism valid? Under what conditions?

$$2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X_2 \qquad\qquad \text{Step 1}$$

$$X_2 + Y \xrightarrow{k_3} XY + X \qquad\qquad \text{Step 2}$$

X + Y   →   XY   **Check!:** Reaction sums to overall equation – yes.

Two options: either Step 1 is RDS or Step 2 is RDS.

If Step 1 is RDS then the rate law is: rate = $k_1[X]^2$.

This does not match the experimentally determined rate law so cannot be rate determining.

If Step 2 is RDS then the rate law is: rate = $k_3[X_2][Y]$

However X_2 is an intermediate (not a starting material or product) so we can't measure it directly, so we need to write it in terms of things we can measure. So we apply the Steady State Approximation.

Rate of formation of $X_2 = k_1[X]^2$

Rate of loss of $X_2 = k_2[X_2] + k_3[X_2][Y]$

Under steady state: $k_1[X]^2 = k_2[X_2] + k_3[X_2][Y]$

Rearranging: $[X_2] = \dfrac{k_1[X]^2}{k_2 + k_3[Y]}$

Now substitute into the rate equation: rate = $k_3[X_2][Y] = \dfrac{k_3k_1[X]^2[Y]}{k_2 + k_3[Y]}$

Now we make an mathematical approximation. Since step 2 is the rate determining (slow) step we can assume k_3 is very small in relation to k_2. Hence $k_2 + k_3[Y] \sim k_2$
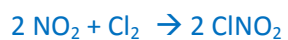
Now substitute into the rate equation: rate $= \dfrac{k_3k_1[X]^2[Y]}{k_2 + k_3[Y]} \sim \dfrac{k_3k_1[X]^2[Y]}{k_2} = k_{eff}[X]^2[Y]$

This is in agreement with the observed rate law suggesting the mechanism is plausible provided the second step is rate determining.

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

$$NO_2(g) + Cl_2(g) \xrightarrow{k_1} ClNO_2(g) + Cl(g) \qquad Slow$$

$$NO_2(g) + Cl(g) \xrightarrow{k_2} ClNO_2(g) \qquad Fast$$
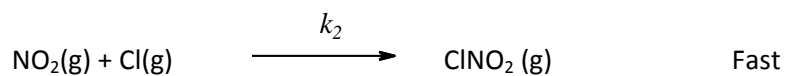
a) What is the overall reaction?

2 NO_2 + Cl_2 → 2 $ClNO_2$

b) Identify the intermediates in the mechanism

Cl atoms

c) What is the predicted rate law?

This may apparently seem more complex than normal as we have two steps which lead to loss of NO_2 and two which lead to formation of product. However the rate of reaction is controlled by the first,slow, rate-determining step:

Rate = $k_1[NO_2][Cl_2]$

Conceptually the Cl generated in step 1 will immediately react with NO_2 so we just need to concern ourselves with the first rate determining step.

Catalysis

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

This is a rates of reaction question so remember to use Kelvin! 25 $^{\circ}$C = 273 + 25 = 298 K

Let us write equations for the rate constants under catalysed and non-catalysed conditions:

Catalysed: k_{cat} = A e$^{-Ea(cat)/RT}$ = A e$^{-55000/(8.314 \times 298)}$ = A e$^{-22.2}$

Uncatalysed: k_{uncat} = A $e^{-Ea(uncat)/RT}$ = A $e^{-125000/(8.314 \times 298)}$ = A $e^{-50.4}$

Ratio of catalysed to uncatalysed reaction rates is:

$$\frac{k_{cat}}{k_{uncat}} = \frac{Ae^{-22.2}}{Ae^{-50.4}}$$

We are told the values of A are the same for both processes (so A/A = 1):

$$\frac{k_{cat}}{k_{uncat}} = \frac{e^{-22.2}}{e^{-50.4}} = \mathbf{1.8 \times 10^{12}}$$