

Sample Exam 1 solutions

1. (a) To find the reaction orders, look at the dependence of rate on concentrations. From rows 1 and 3, cutting the $[\text{OCl}^-]$ in half cuts the rate in half, so the reaction is **1st order in OCl^-** . Similarly, from rows 2 and 3, cutting the $[\text{I}^-]$ in half cuts the rate in half, so it's also **first order in I^-** . From rows 3, 4 and 5 it is clear that cutting hydroxide concentration in half doubles the rate, so it is **inverse first order in OH^-** .

(b) The overall reaction order will then be $1+1-1 = 1$

(c) The rate law is

$$\text{rate} = k [\text{OCl}^-][\text{I}^-]/[\text{OH}^-]$$

To find the rate constant k , plug in some data. From row 1, for example,

$$\text{rate} = 4.8 \times 10^{-4} \text{Ms}^{-1} = k [0.0040\text{M}] [0.0020\text{M}]/[1.00\text{M}]$$

$$k = 60\text{s}^{-1}$$

2. Note for 2003, 2004, 2005, etc. If you found this one difficult, don't worry too much....we have not looked at similar 'pressure' problems this year.

First define P = total pressure, P_0 = initial pressure of $\text{C}_2\text{H}_4\text{O}$, P_a = pressure of $\text{C}_2\text{H}_4\text{O}$, $P_b = P_c$ = pressure of CH_4 = pressure of CO , and x = number of moles of $\text{C}_2\text{H}_4\text{O}$ consumed at a given time in the reaction. You need to convert the total pressure to the pressure of A (P_a), and then do the usual plots of this pressure (which is proportional to concentration) vs time to find the reaction order.

First, find the initial pressure of A. At "infinite" time, when you can assume all the $\text{C}_2\text{H}_4\text{O}$ has reacted, $P = P_b + P_c = 2P_b = 249.88$ torr. Therefore, $P_b = 124.94$ torr. From the stoichiometry of the reaction, that means the initial pressure $P_0 = 124.94$ torr.

Now find an expression for P_a in terms of the initial pressure and the total pressure.

$$P_a = P_o - x$$

$$P = P_a + P_b + P_c = P_a + 2x$$

Plug in the expression for P_a to get

$$P = P_o - x + 2x = P_o + x.$$

Solve this for $x = P - P_o$.

Then plug this back into the expression for P_a to get

$$P_a = P_o - (P - P_o) = 2P_o - P$$

Now construct a table of pressures of C_2H_4O at given times in the reaction, by plugging in the initial pressure and the given total pressures. Also include $\ln(P_a)$ and $1/P_a$ to obtain:

time (min)	10	20	40	60	100	200	"infinity"
P (torr)	139.14	151.67	172.65	189.15	212.34	238.66	249.88
P_a (torr)	110.74	98.21	77.23	60.73	37.54	11.22	0
$\ln(P_a)$	4.707	4.587	4.347	4.106	3.625	2.418	
$1/(P_a)$.00903	.0102	.0129	.0165	.0266	.0891	

By inspection, the plot of $\ln(P_a)$ vs time is linear, and the plot of $1/P_a$ vs time is not. Therefore, the reaction is **first order in C_2H_4O** .

$$\text{Rate} = k[C_2H_4O]$$

To find the rate constant k , use the first order integrated rate law

$$c = c_o e^{-kt}$$

and plug in values for c , c_o and t at a given time. [You can use pressures instead of concentration since they are directly proportional with the fixed volume and temperature assumed.] At 100 min,

$$37.54 \text{ torr} = 124.94 \text{ torr } e^{-k(100\text{min})}$$

$$\ln(37.54/124.94) = -(100k)\text{min} \quad \text{so} \quad k = 1.20 \times 10^{-2} \text{ min}^{-1}$$

3. (a) **Step 1 is initiation, 2 and 3 are propagation, and 5 is termination.**

The intermediates are Br and H.

(b) From the steady-state approximation,

$$d/dt[\text{Br}] = 0 = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2$$

where the factors of 2 are included because of the stoichiometry of these steps.

That is, since you are making 2 equivalents of Br in the k_1 step, you must account for it with the factor of 2.

next

$$d/dt[\text{H}] = 0 = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

(c) add these up, many terms cancel out!

$$0 = 2k_1[\text{Br}_2] - 2k_5[\text{Br}]^2$$

$$[\text{Br}] = \{k_1[\text{Br}_2]/k_5\}^{1/2}$$

Plug this back into the expression for $d/dt[\text{H}]$ to get

$$d/dt[\text{H}] = 0 = k_2\{k_1[\text{Br}_2]/k_5\}^{1/2}[\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

Solve this for [H]

$$[\text{H}] = (k_2\{k_1[\text{Br}_2]/k_5\}^{1/2}[\text{H}_2]) / (k_3[\text{Br}_2] + k_4[\text{HBr}])$$

To find the rate

$$\text{Rate} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{HBr}][\text{H}]$$

Now plug in the expressions for H and Br and solve.

4. (a) **Rate = k [Cl₂][H₂S] This is consistent with experiment.**

(b) Rate = k[HS⁻][Cl₂]

Find an expression for [HS⁻] from the first, equilibrium step:

$$[\text{HS}^-][\text{H}^+]/[\text{H}_2\text{S}] = K_{\text{eq}}$$

so [HS⁻] = $K_{\text{eq}}[\text{H}_2\text{S}]/[\text{H}^+]$ Plug this in:

Rate = kK_{eq}[H₂S][Cl₂]/[H⁺] This is NOT consistent with experiment.

$$(c) \text{ Rate} = k[\text{Cl}^+][\text{HS}^-]$$

Find expressions for these concentrations from the first 2 equilibrium steps.

$$[\text{Cl}^+][\text{Cl}^-][\text{H}^+]/[\text{H}^+][\text{Cl}_2] = K_2$$

$$\text{so } [\text{Cl}^+] = K_2[\text{Cl}_2]/[\text{Cl}^-]$$

$$[\text{HS}^-][\text{H}^+]/[\text{H}_2\text{S}] = K_1$$

$$\text{so } [\text{HS}^-] = K_1[\text{H}_2\text{S}]/[\text{H}^+] \quad \text{Plug these in:}$$

$$\text{Rate} = kK_2[\text{Cl}_2]/[\text{Cl}^-](K_1[\text{H}_2\text{S}]/[\text{H}^+])$$

$$= kK_2K_1[\text{Cl}_2][\text{H}_2\text{S}]/[\text{Cl}^-][\text{H}^+] \quad \text{This is also not in agreement with experiment.}$$

$$5. (a) \text{ Arrhenius equation: } k = Ae^{-E_a/RT}$$

$$\text{for the catalyzed reaction, } k' = Ae^{-E_a'/RT}$$

Divide these to get:

$$k/k' = e^{-\Delta E_a/RT} \text{ where } \Delta E_a = E_a - E_a'$$

$$\ln(k/k') = -\Delta E_a/RT$$

$$\ln(1/4.1 \times 10^4)(8.31 \text{ J/molK})(298 \text{ K}) = -\Delta E_a$$

$$\Delta E_a = 26.3 \text{ kJ/mol}$$

$$(b) \text{ From the stoichiometry, Rate} = (-1/2)d/dt [\text{NH}_3] = k$$

$$\text{Let } [\text{NH}_3] = c, \text{ then } dc/dt = -2k$$

To transform this differential form into an integrated rate law, integrate from the initial concentration c_0 to concentration c , and from initial time (0) to time t , to get:

$$c - c_0 = -2kt$$

$$c = c_0 - 2kt$$

$$(c) \text{ At } t_{1/2}, c = 1/2c_0$$

$$c_0/2 = c_0 - 2kt$$

$$c_0 = 2c_0 - 4kt \quad \text{so} \quad t = c_0/4k$$

NOTE. An equivalent answer would use a different rate constant k' , i.e. $c = c_0 - k't$ and $t = c_0/2k'$. (This is similar to our discussion of the general 2nd-order rate expression in class).

6. Data is given for concentration of the product B, but you need it in terms of the reactant A to find the order in A.

To convert the data to this form, let x be the number of mol of A that are consumed (equal to the number of mol B formed) at a given time in the reaction. Then $[A] = [A]_0 - x = [A]_0 - [B]$. Add some more calculations to the table of data like so:

time(s)	0	10	20	30	40	50	60	70	80
[B] (M)	0	0.202	0.330	0.412	0.478	0.526	0.562	0.588	0.612
[A] (M)	0.840	0.638	0.510	0.428	0.362	0.314	0.278	0.252	0.228
ln[A]	-.174	-.449	-.673	-.849	-1.02	-1.16	-1.28	-1.38	-1.48
1/[A]	1.19	1.57	1.96	2.34	2.76	3.18	3.60	3.97	4.39

There is a little scatter in the data, but the $\ln[A]$ vs time plot is NOT linear and the $1/[A]$ one is. So the reaction is **2nd order in A**. This means that the elementary step that determines the rate involves collision of 2 A molecules, so the standard 2nd order rate law applies.

(b) You can find k in several ways. The easiest might be the slope, of the $1/[A]$ vs time plot. Pick any 2 points, I chose $t=0$ and $t=80s$ for convenience:

$$k = \text{slope} = (4.39 - 1.19\text{M}^{-1}) / (80 - 0\text{s})$$

$$\text{so } k = \mathbf{0.04\text{M}^{-1}\text{s}^{-1}}$$

Alternatively, Rate = $-1/2d[A]/dt = k[A]^2$ for the 2nd order reaction.

The integral form of this is

$$1/c = 1/c_0 + kt \text{ as usual}$$

Plug in some data, at 10s, to find k :

$$1/.638M - 1/.840M = 10ks$$

k = 0.038M⁻¹s⁻¹; this is the same as the result from the (less precise) slope above

7. First, find the rate constant at 500K.

$$\text{Rate} = k[\text{NO}_2][\text{CO}] = k[0.250M]^2 = 1.26 \times 10^{-7} \text{Ms}^{-1}$$

$$k = 2.02 \times 10^{-6} \text{M}^{-1} \text{s}^{-1}$$

Use the Arrhenius equation to find the value of A

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

$$2.02 \times 10^{-6} \text{M}^{-1} \text{s}^{-1} = Ae^{-(132 \text{kJ/mol})/(8.31 \text{J/molK})(500 \text{K})(1 \text{kJ}/1000 \text{J})}$$

$$A = 1.27 \times 10^8 \text{M}^{-1} \text{s}^{-1}$$

Plug this back in to find k at 600K:

$$k = (1.27 \times 10^8 \text{M}^{-1} \text{s}^{-1})e^{-132 \text{kJ/mol}/(8.31 \text{J/molK})(600 \text{K})(1 \text{kJ}/1000 \text{J})}$$

$$\mathbf{k = 4.04 \times 10^{-4} \text{M}^{-1} \text{s}^{-1}}$$

You can also do this directly from

$$\ln(k_2/k_1) = -E_a/R (1/T_2 - 1/T_1)$$

8. (a) $PV=nRT$ or $P = nRT/V$

$$P = (10 \text{ atoms}) (1 \text{ mol}/6.02 \times 10^{23} \text{ atoms})(0.0821 \text{Latm/molK})(100 \text{K})$$

$$/(1 \text{cm}^3)(1 \text{L}/1000 \text{cm}^3)$$

$$\mathbf{= 1.36 \times 10^{-19} \text{ atm}}$$

(b) The reaction should proceed much **more quickly on Earth** than under these conditions.

From the collision theory, reactions occur when particles collide with enough energy to overcome the activation energy. **Because the pressure is so low, there will be very few collisions** (actually, about 1 every 30 YEARS), greatly slowing the rate. Less importantly, the lower temperature in space will reduce

the average speed of the atoms, thereby reducing the energy of collision and also reducing rate.

9. (a) **FALSE** (b) **3** (c) **2** (d) **2** (e) **2 and 4**