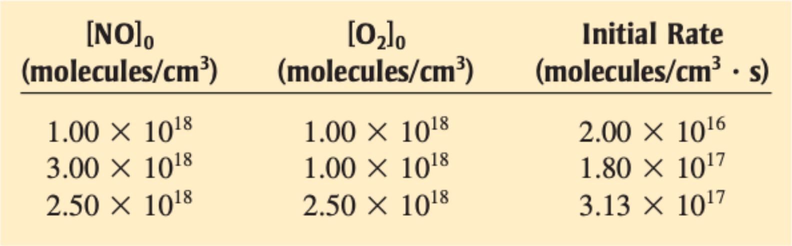
Problems Chapter 14 (Kinetics)

1. The reaction

$$2\,NO\,(g) + O_2\,(g) \rightarrow 2\,NO_2\,(g)$$

was studied, and the following data were obtained where rate = $-\frac{\Delta[O_2]}{\Delta t}$



$[NO]_0$ (molecules/cm^3)	$[O_2]_0$ (molecules/cm^3)	Initial Rate (molecules/cm$^3 \cdot$ s)
1.00×10^{18}	1.00×10^{18}	2.00×10^{16}
3.00×10^{18}	1.00×10^{18}	1.80×10^{17}
2.50×10^{18}	2.50×10^{18}	3.13×10^{17}

What would be the initial rate for an experiment where $[NO]_0 = 6.21 \times 10^{18}$ molecules/cm^3 and $[O_2]_0 = 7.36 \times 10^{18}$ molecules/cm^3?

Trial 1 → Trial 2

$[O_2]$ constant

[NO] changes by a factor of $\frac{3.00\times10^{18}}{1.00\times10^{18}} = 3$

Rate changes by a factor of $\frac{1.80\times10^{17}}{2.00\times10^{16}} = 9 = 3^{\mathbf{2}}$

Second order in [NO]

Trial 1 → Trial 3

$[O_2]$ changes by a factor of $\frac{2.50\times10^{18}}{1.00\times10^{18}} = 2.5$

[NO] changes by a factor of $\frac{2.50\times10^{18}}{1.00\times10^{18}} = 2.5$

Rate changes by a factor of $\frac{3.13\times10^{17}}{2.00\times10^{16}} = 15.65$

Second order in NO: effect of Δ[NO] by factor of 2.5 → rate changes by factor of $(2.5)^2 = 6.25$

Effect of $\Delta[O_2]$ on rate → rate changes by factor of $\frac{15.65}{6.25} = 2.5 = 2.5^{\mathbf{1}}$

First order in $[O_2]$

Rate = $k[NO]^2[O_2]$

Plug in numbers from one known trial (e.g., trial 1) to get k

2.00×10^{16} molecules cm^{-3} s^{-1} = k(1.00×10^{18} molecules cm^{-3})$^{\mathbf{2}}$ (1.00×10^{18} molecules cm^{-3})

k = 2.00×10^{-38} molecules^{-2} cm^6 s^{-1}

Rate = (2.00×10^{-38} molecules^{-2} cm^6 s^{-1})(6.21×10^{18} molecules/cm^3)^2(7.36×10^{18} molecules/cm^3)

Rate = 5.68×10^{18} molecules cm^{-3} s^{-1}

2. The gas-phase decomposition of HI

$$HI\,(g) \rightarrow \tfrac{1}{2}\,H_2\,(g) + \tfrac{1}{2}\,I_2\,(g)$$

has the rate equation $-\frac{\Delta[\mathrm{HI}]}{dt} = k[HI]^2$, where k = 30. M^{-1} min^{-1} at 443 ˚C. How much time does it take for the concentration of HI to drop from 0.010 M to 0.0050 M at 443 ˚C?

Second order kinetics: $\frac{\mathbf{1}}{[\boldsymbol{A}]} - \frac{\mathbf{1}}{[\boldsymbol{A}]_{\mathbf{0}}} = \boldsymbol{kt}$

$$\frac{1}{0.0050\,M} - \frac{1}{0.010\,M} = (30.\ M^{-1}\ min^{-1})\ t$$

t = 3.3 min

3. Radioactive decay is a first-order process. Radioactive radon-222 gas (^{222}Rn) occurs naturally as a product of uranium decay. The half-life of ^{222}Rn is 3.8 days. Suppose a flask originally contained 4.0 x 10^{13} atoms of ^{222}Rn. How many atoms of ^{222}Rn will remain after one month (30. days)?

First order kinetics: $t_{½} = \frac{ln2}{k} \rightarrow k = \frac{ln2}{3.8\ days} = 0.18\ days^{-1}$

$\ln[^{222}\mathrm{Rn}]_0 - \ln[^{222}\mathrm{Rn}] = kt \rightarrow$

$\ln(4.0 \times 10^{13}$ atoms/flask$) - \ln[^{222}\mathrm{Rn}] = (0.18$ days$^{-1})(30.$ days$) \rightarrow$

$[^{222}\mathrm{Rn}] = 1.8 \times 10^{11}$ atoms/flask

4. The decomposition of ethylene oxide, $(CH_2)_2O$ at 690 K is monitored by measuring the total gas pressure as a function of time. The data obtained are:

time (min)	**total pressure (torr)**
10	139.14
20	151.67
40	172.65
60	189.15
100	212.34
200	238.66
∞	249.88

What is the order of the reaction $(CH_2)_2O$ (g) → CH_4 (g) + CO (g)?

At infinite time, it is expected that all $(CH_2)_2O$ has decomposed to CH_4 and CO. Assume ideal gas theory, so pressure is proportional to mole amount of gas. You would have two mole equivalents of gas (one equivalent of CH_4 and one of CO) so the pressure of each gas is (249.88 torr)/2 = 124.94 torr. This also means the initial pressure of $(CH_2)_2O$ was also 124.94 torr (since one equivalent of $(CH_2)_2O$ yields one equivalent of CO and one equivalent of CH_4).

We need to find the pressure of $(CH_2)_2O$ at each time point. Here are sample calculations for how to do it for 10 min and 20 min.

10 min	$(CH_2)_2O$ (g) →	CH_4 (g) +	CO (g)
Initial	124.94 torr	0	0
Change	– x	+ x	+ x
Final	(124.94 – x) torr	x	x

Total P at 10 min = 139.14 torr = (124.94 – x + x + x) torr = (124.94 + x) torr
x = 14.20 torr
$P_{(CH2)2O}$ at 10 min = 124.94 torr – 14.20 torr = 110.74 torr

20 min	$(CH_2)_2O$ (g) →	CH_4 (g) +	CO (g)
Initial	110.74 torr	14.20 torr	14.20 torr
Change	– x	+ x	+ x
Final	(110.74 – x) torr	(14.20 + x) torr	(14.20 + x) torr

Total P at 20 min = 151.67 torr = (139.14 + x) torr
x = 12.53 torr
$P_{(CH2)2O}$ at 20 min = 110.74 torr – 12.53 torr = 98.21 torr

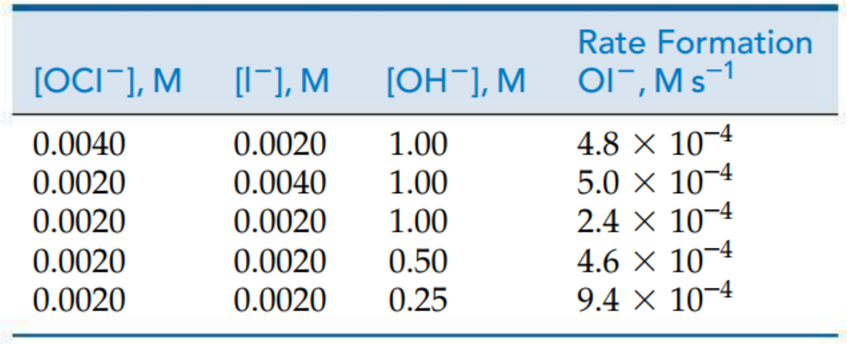
Similar calculations give $P_{(CH2)2O}$ at the other time points

Time (s)	P_{total} (torr)	$P_{(CH2)2O}$ (torr)
0	124.94	124.94
10	139.14	110.74
20	151.67	98.21
40	172.65	77.23
60	189.15	60.73
100	212.34	37.54
200	238.66	11.22

Plot $P_{(CH2)2O}$ vs. t, $\ln P_{(CH2)2O}$ vs t and 1/ $P_{(CH2)2O}$ vs t.
$\ln P_{(CH2)2O}$ vs t is linear - so it is **first order.**

5. Hydroxide ion is involved in the mechanism of the following reaction but is not consumed in the overall reaction.

$$OCl^- + I^- \xrightarrow{OH^-} OI^- + Cl^-$$



$[OCl^-]$, M	$[I^-]$, M	$[OH^-]$, M	Rate Formation OI^-, $M\,s^{-1}$
0.0040	0.0020	1.00	4.8×10^{-4}
0.0020	0.0040	1.00	5.0×10^{-4}
0.0020	0.0020	1.00	2.4×10^{-4}
0.0020	0.0020	0.50	4.6×10^{-4}
0.0020	0.0020	0.25	9.4×10^{-4}

a. From the data given, determine the order of the reaction with respect to OCl^-, I^- and OH^-.
b. What is the overall reaction order?
c. Write the rate equation and determine the value of the rate constant k.

Trial 3 → 2 (only $[I^-]$ changes)
$[I^-]$ x2 → rate x 2 → **first order in [I–]**

Trial 4 → 3 (only $[OH^-]$ changes)
$[OH^-]$ x2 → rate x 0.5 (2^{-1}) → **-1 order in $[OH^-]$**

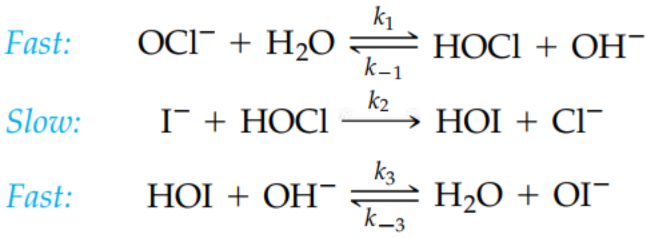
Trial 3 → 1 (only $[OCl^-]$ changes)
$[OCl^-]$ x2 → rate x 2 → **first order in $[OCl^-]$**

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

From any trial – here, trial 1:

$$\boldsymbol{k} = \frac{(rate)[OH^-]}{[I^-][OCl^-]} = \frac{(4.8 \times 10^{-4}\ M\ s^{-1})(1.00\ M)}{(0.0020\ M)(0.0040\ M)} = \boldsymbol{60.\,s^{-1}}$$

6. Show that the following mechanism is consistent with the rate law established for the iodide-hypochlorite reaction in problem 5.



Fast: $OCl^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + OH^-$

Slow: $I^- + HOCl \xrightarrow{k_2} HOI + Cl^-$

Fast: $HOI + OH^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H_2O + OI^-$

Slow step = RDS
Rate = $k_2[I^-][HOCl]$
[HOCl] is an intermediate so can't be in the rate expression

Fast equilibrium: $\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$
$k_1[OCl^-][H_2O] = k_{-1}[HOCl][OH^-]$

$$[HOCl] = \frac{k_1[OCl^-][H_2O]}{k_{-1}[OH^-]}$$

Substitute [HOCl] in the slow step:

$$rate = \frac{k_2k_1[OCl^-][H_2O][I^-]}{k_{-1}[OH^-]}$$

Water is a solvent, so its concentration remains constant throughout the experiment. So the mechanism is consistent with the rate law ($k = \frac{k_1k_2[H_2O]}{k_{-1}}$)

7. At 28 ˚C, raw milk sours in 4.0 h but takes 48 h to sour in a refrigerator at 5 ˚C. Estimate the activation energy in kJ/mol for the reaction that leads to the souring of milk.

$$lnk_2 - lnk_1 = -\frac{E_a}{R}(\frac{1}{T_2} - \frac{1}{T_1})$$

$$\text{Rate} \propto \text{k}$$

$$\text{rate}_{28\,^\circ C} = 12(\text{rate}_{5\,^\circ C}) \rightarrow k_{28\,^\circ C} = 12k_{5\,^\circ C}$$

$$\ln\frac{12k_{5\,^\circ C}}{k_{5\,^\circ C}} = -\frac{E_a}{8.314\,J\,K^{-1}mol^{-1}}(\frac{1}{301.15\,K} - \frac{1}{278.15\,K})$$

$$E_a = \frac{(ln12)(-8.314\,J\,K^{-1}mol^{-1})}{-2.485 \times 10^{-4}\,K^{-1}}$$

E_a = 75.24 kJ mol^{-1}

8. The following is a quote from an article in the August 18, 1998 issue of *The New York Times* about the breakdown of cellulose and starch: "A drop of 18 degrees Fahrenheit [from 77 ˚F to 59 ˚F] lowers the reaction rate six times; a 36-degree drop [from 77 ˚F to 41 ˚F] produces a fortyfold decrease in the rate."
   a. Calculate activation energies for the breakdown process based on the two estimates of the effect of temperature on rate. Are the values consistent?
   b. Assuming the value of E_a calculated from the 36˚ drop and that the rate of breakdown is first order with a half-life at 25 ˚C of 2.7 years, calculate the half-life for breakdown at a temperature of –15 ˚C.

$$lnk_2 - lnk_1 = -\frac{E_a}{R}(\frac{1}{T_2} - \frac{1}{T_1})$$

Estimate of E_a from 18 degree drop:
77 ˚F = 298.15 K

59 ˚F = 288.15 K

$$\ln\frac{6k_{59\,^\circ F}}{k_{59\,^\circ F}} = -\frac{E_a}{8.314\,J\,K^{-1}mol^{-1}}\left(\frac{1}{298.15\,K} - \frac{1}{288.15\,K}\right)$$

$$E_a = \frac{(ln6)(-8.314\,J\,K^{-1}mol^{-1})}{-1.164\times10^{-4}\,K^{-1}}$$

E_a = 128.0 kJ mol^{-1}

Estimate of E_a from 36 degree drop:
77 ˚F = 298.15 K
41 ˚F = 278.15 K

$$\ln\frac{40k_{41\,^\circ F}}{k_{41\,^\circ F}} = -\frac{E_a}{8.314\,J\,K^{-1}mol^{-1}}\left(\frac{1}{298.15\,K} - \frac{1}{278.15\,K}\right)$$

$$E_a = \frac{(ln40)(-8.314\,J\,K^{-1}mol^{-1})}{-2.412\times10^{-4}\,K^{-1}}$$

E_a = 127.2 kJ mol^{-1}

(the two estimates are pretty close to each other)

First order:

$$t_{½} = \frac{ln2}{k} \to 2.7\ years = \frac{ln2}{k_{25\,^\circ C}} \to k_{25\,^\circ C} = 0.257\ years^{-1}$$

$$lnk_2 - lnk_1 = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \to$$

$$\ln(0.257) - lnk_{-15\,^\circ C} = -\frac{127200\,J\,mol^{-1}}{8.314\,J\,mol^{-1}K^{-1}}\left(\frac{1}{298.15\,K} - \frac{1}{258.15\,K}\right) \to$$

$$lnk_{-15\,^\circ C} = -9.31$$

$$k_{-15\,^\circ C} = 9.0\times10^{-5}\ years^{-1}$$

$$\boldsymbol{t_{½}} = \frac{ln2}{k} = \frac{ln2}{9.0\times10^{-5}\ years^{-1}} = \mathbf{7.7\times10^3\ years}$$

9. The following mechanism has been proposed for the gas-phase reaction of chloroform ($CHCl_3$) and chlorine:

$$\text{Step 1:}\quad Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Cl(g) \quad (\text{fast})$$

$$\text{Step 2:}\quad Cl(g) + CHCl_3(g) \xrightarrow{k_2} HCl(g) + CCl_3(g) \quad (\text{slow})$$

$$\text{Step 3:}\quad Cl(g) + CCl_3(g) \xrightarrow{k_3} CCl_4 \quad (\text{fast})$$

a. What is the overall reaction?
b. What are the intermediates in the mechanism?
c. What is the molecularity of each of the elementary reactions?
d. What is the rate-determining step?
e. What is the rate law predicted by this mechanism? (Hint: the overall reaction order is not an integer.)

Overall rxn: **Cl_2 (g) + $CHCl_3$ (g) → HCl (g) + CCl_4 (g)**
Intermediates: **Cl (g), CCl_3 (g)**
Step 1: **unimolecular (forward), bimolecular (reverse)**
Step 2: **bimolecular**
Step 3: **bimolecular**
Step 2 is the RDS

Rate = $k_2[Cl][CHCl_3]$

$k_1[Cl_2] = k_{-1}[Cl]^2$

$$[Cl] = \sqrt{\frac{k_1[Cl_2]}{k_{-1}}}$$

Rate = $k_1^{0.5}k_2k_{-1}^{-0.5}[Cl_2]^{0.5}[CHCl_3]$ = **$k[CHCl_3][Cl_2]^{0.5}$**

10. Dinitrogen pentoxide decomposes in the gas phase to form nitrogen dioxide and oxygen gas. The reaction is first order in dinitrogen pentoxide and has a half-life of 2.81 h at 25 ˚C. If a 1.5 L reaction vessel initially contains 745 torr of N_2O_5 at 25 ˚C, what partial pressure of O_2 is present in the vessel after 215 minutes?

$$2\,N_2O_5\,(g) \rightarrow 4\,NO_2\,(g) + O_2\,(g)$$

First order:

$$t_{½} = \frac{ln2}{k} \rightarrow k = \frac{ln2}{2.81\ h} = 0.247\ h^{-1}$$

PV = nRT → $[N_2O_5]_0 = \frac{745\ torr}{(62.36\ L\ torr\ mol^{-1}K^{-1})(298.15\ K)} = 0.0401\ M$

ln[A]$_0$ – ln[A] = kt →

ln(0.0401 M) – ln[N_2O_5] = (0.247 h^{-1})(3.58 h) →
ln[N_2O_5] = -4.10
[N_2O_5] = 0.0166 M

	2 N_2O_5 →	4 NO_2 (g) +	O_2 (g)
Initial	0.0401 M	0	0
Change	- 2x	+ 4x	+ x
Final	0.0166 M	x	x

0.0401 M – 2x = 0.0166 M → x = 0.0118 M = [O_2]

PV = nRT → $\boldsymbol{P_{O_2}} = (0.0118\, mol\, L^{-1})(62.36\, L\, torr\, mol^{-1}K^{-1})(298.15\, K) =$
$\mathbf{219\ torr}$

11. The reaction 2 N_2O_5 (g) → 2 N_2O_4 (g) + O_2 (g) takes place at around room temperature in solvents such as CCl_4. The rate constant at 293 K is found to be 2.35 x 10^{-4} s^{-1}, and at 303 K the rate constant is found to be 9.15 x 10^{-4} s^{-1}. Calculate the frequency factor for the reaction.

$$lnk_2 - lnk_1 = -\frac{E_a}{R}(\frac{1}{T_2} - \frac{1}{T_1})$$

$$ln\frac{9.15 \times 10^{-4}\, s^{-1}}{2.35 \times 10^{-4}\, s^{-1}} = -\frac{E_a}{8.314\, J\, mol^{-1}K^{-1}}(\frac{1}{303\, K} - \frac{1}{293\, K})$$

E_a = 100.3 kJ mol^{-1}

$$lnk = -\left(\frac{E_a}{R}\right)\frac{1}{T} + lnA$$

$$\ln(9.15 \times 10^{-4}\, s^{-1}) = -\left(\frac{1.003 \times 10^5\, J\, mol^{-1}}{8.314\, J\, mol^{-1}\, K^{-1}}\right)\frac{1}{303\, K} + lnA$$

lnA = 32.8 → **A = 1.81 x 10^{14} s^{-1}**

12. A certain substance X decomposes. Fifty percent of X remains after 100 minutes. How much X remains after 200 minutes of the reaction order with respect to X is
    a. zero order?
    b. first order?
    c. second order?

Initial concentration: [X]

After 100 min: [0.5X]
After 200 min: [A]

Zero order: $[A]_0 - [A] = kt$

$$t_{½} = \frac{[A]_0}{2k} \rightarrow 2k = \frac{[X]}{100\ min} \rightarrow k = \frac{[X]}{200\ min}$$

After additional 100 min:

$$[0.5X] - [A] = \frac{[X]}{200\ min}(100\,\mathrm{min})$$

$[0.5X] - [A] = [0.5X] \rightarrow$ **$[A] = 0$**

You can also approach this by thinking how with zero order, concentration changes linearly with time (rate = constant). So if in 100 min half the [X] reacted, we know rate = [0.5X]/(100 min) and therefore the additional 100 min will mean all the remaining [0.5X] will be gone.

First order: $\ln[A]_0 - \ln[A] = kt$

$$t_{½} = \frac{ln2}{k} \rightarrow k = \frac{ln2}{100\ min}$$

After additional 100 min:

$$\ln[0.5X] - \ln[A] = \frac{ln2}{100\ min}(100\ min)$$

$$ln\frac{[0.5X]}{[A]} = ln2$$

$$\frac{[0.5X]}{[A]} = 2$$

$[A] = [0.25X]$

You can also approach this by thinking that with first order, half-life is independent of concentration. Here half life = 100 min. So after additional 100 min, another half-life will have passed, and the original [0.5X] will be halved one more time, leaving [0.25X].

Second order: $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$

$$t_{½} = \frac{1}{k[A]_0} \rightarrow k = \frac{1}{(100\text{ min})[\mathrm{X}]}$$

After additional 100 min:

$$\frac{1}{[A]} - \frac{1}{[0.5X]} = \frac{1}{(100\text{ min})[\mathrm{X}]}(100\ min)$$

$$\frac{1}{[A]} - \frac{1}{[0.5X]} = \frac{1}{[\mathrm{X}]}$$

$$\frac{1}{[A]} = \frac{1}{[\mathrm{X}]} + \frac{1}{[0.5X]}$$

$$\frac{1}{[A]} = \frac{0.5+1}{[0.5X]}$$

$$\frac{1}{[A]} = \frac{1.5}{[0.5X]}$$

1.5[A] = [0.5X] → $[\boldsymbol{A}] = [\mathbf{0.33}\boldsymbol{X}]$

13. Ethyl chloride vapor decomposes by the first-order reaction:

C_2H_5Cl (g) → C_2H_4 (g) + HCl (g)

The activation energy is 249 kJ/mol, and the frequency factor is $1.6 \times 10^{14}\ s^{-1}$.

a. Find the value of the specific rate constant at 710 K.
b. What fraction of the ethyl chloride decomposes in 15 minutes at this temperature?
c. Find the temperature at which the rate of the reaction would be twice as fast.

$$\boldsymbol{k} = Ae^{\frac{-E_a}{RT}} = (1.6 \times 10^{14}\ s^{-1})e^{-\frac{249000\ J\ mol^{-1}}{(8.314\ J\ mol^{-1}\ K^{-1})(710\ K)}} = \mathbf{7.67} \times \mathbf{10^{-5}}\ \boldsymbol{s^{-1}}$$

First order: $\ln[A]_0 - \ln[A] = kt$ →

$$ln\frac{[A]_0}{[A]} = (7.67 \times 10^{-5}\ s^{-1})(900\ s)$$

$$ln\frac{[A]_0}{[A]} = 0.0690$$

$$\frac{[A]_0}{[A]} = 1.07 \rightarrow [A] = [0.933A]_0$$

~6.7% of ethyl chloride decomposes in 15 min at 710 K.

Twice as fast = double the rate constant

$$lnk = -\left(\frac{E_a}{R}\right)\frac{1}{T} + lnA \rightarrow$$

$$\ln(1.53 \times 10^{-4}\ s^{-1}) = -\left(\frac{249000\,J\ mol^{-1}}{8.314\,J\ mol^{-1}K^{-1}}\right)\frac{1}{T} + \ln\,(1.6 \times 10^{14}\ s^{-1})$$

$$-8.783 = (-2.99 \times 10^{4})\frac{1}{T} + 32.71$$

$$\frac{1}{T} = 1.39 \times 10^{-3}\ K^{-1}$$

T = 722 K

This is consistent with the rule of a thumb (rate doubles with every 10 K temperature increase)