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 · 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?

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?

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 4.0×10^{13} atoms of ^{222}Rn. How many atoms of ^{222}Rn will remain after one month (30. days)?

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 $(CH_2)_2O\ (g) \rightarrow CH_4\ (g) + CO\ (g)$?

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.

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

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.

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.

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

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

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

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

   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.)

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?

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 2.35×10^{-4} s^{-1}, and at 303 K the rate constant is found to be 9.15×10^{-4} s^{-1}. Calculate the frequency factor for the reaction.

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?

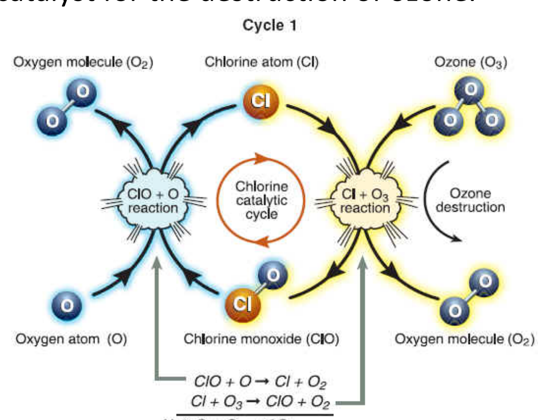
13. Ethyl chloride vapor decomposes by the first-order reaction:

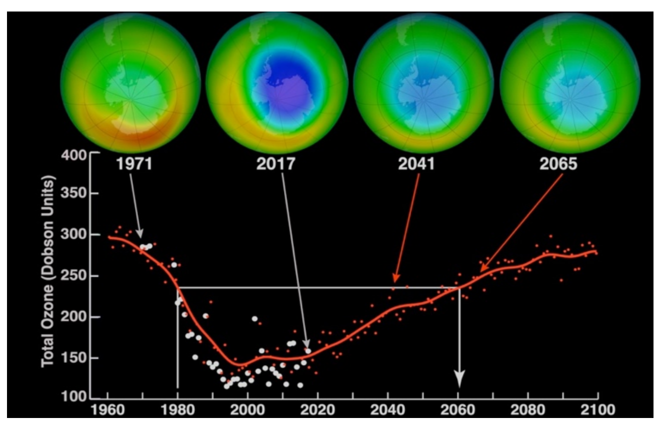
    C_2H_5Cl (g) → C_2H_4 (g) + HCl (g)

    The activation energy is 249 kJ/mol, and the frequency factor is 1.6×10^{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.

Mario Molina: a chemist who saved our planet

Chlorofluorocarbons (CFCs or Freons) are a class of chemicals that were widely used as aerosols and refrigerants – up until it was discovered that CFCs contribute to the destruction of the ozone layer. The UV light from the sun possesses enough energy to break the C–Cl bonds in CFCs, causing the formation of “loose” chlorine atoms possessing unpaired electrons. Such atoms are known as radicals and are extremely reactive. They react with ozone (O_3), thus stripping our planet from its natural protective layer against harmful high energy UV light. Even more concerningly, these chlorine radicals are regenerated though the mechanism, acting as a catalyst for the destruction of ozone.





This shocking discovery was made by the Mexican chemist Mario José Molina-Pasquel Henríquez. Mario Molina was fascinated by chemistry since he was a child; he admired his aunt Esther Molina, who was a chemist, and with her help performed various experiments in a makeshift little laboratory of his own creation. He went on to study chemical engineering and applied and physical chemistry, building his career in the United States. While doing postdoctoral research at UC Irvine, Molina published a paper in the leading scientific journal *Nature* with his adviser Sherwood Rowland, in which they calculated the threat that the CFCs pose to stratospheric ozone. Molina used his knowledge of ozone and CFC chemistry along with computer models to develop the ozone depletion theory. He worked extensively to spread public awareness about the harmful effects of CFCs on the atmosphere; his efforts led to the signing of the Montreal protocol, an international agreement to phase out CFC production, in 1987. He served as a scientific adviser to the US presidents Bill Clinton and Barack Obama and to the Mexican president Enrique Peña Nieto. For his role in elucidating the process of ozone depletion Molina was awarded the Nobel Prize in chemistry in 1995.

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