Ozone Decomposition Data for Kinetics Exercises

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Abstract: The goal of this paper is to provide data that can be used in a variety of exercises ranging from kinetics in general chemistry to advanced problems in physical chemistry. The data provided relates to ozone-decay kinetics in various atmospheres (O_2, N_2, Ar) as measured by ultraviolet/visible absorbance spectroscopy (UV/vis) at 254 nm. The absorbance of ozone is monitored over a 75-min time period, and by using Beer's law the concentration is calculated. Nine data sets, each repeated three times, of absorbance measurements are provided for student exercises, and prelaboratory and postlaboratory questions are suggested.

Introduction

Ozone (O_3) has become a very influential molecule in our industrialized society. This allotrope of molecular oxygen regularly grabs headlines for its decreasing quantities in the stratosphere. Ozone also has a large number of expanding applications including in water and wastewater treatment, as a food preservative, in chemical etching, for odor control, as a disinfectant, and in chemical synthesis.

The word ozone comes from the Greek word ozein, which means to smell. Ozone was first noticed because of its characteristic pungent odor. The odor is detectable in air at levels of about 0.1 parts per million, and exposure to ozone becomes fatal to humans at levels of about 100 ppm for 10,000 min or 10,000 ppm for 30 s. Ozone is a blue-colored gas at ambient temperature, but this color is not seen at the low concentrations at which it is usually generated. In the liquid and solid states ozone is dark blue. Liquid ozone boils at –111.3 °C and solid ozone melts at –192.5 °C. Ozone is an unstable gas and an explosive liquid. The ozone molecule has a bent structure with O–O bond lengths of 1.278 Å and a bond angle of 116.8° as shown in Figure 1.

Second only to fluorine in its oxidizing power (see Table 1), ozone has many applications including, but not limited to, water purification, bleaching of materials such as paper, synthetic fibers, Teflon, waxes, flour, treatment of wastes in industry, and deodorization and sterilization. Previously, chlorine products have been used for many purposes, but chlorine products may produce carcinogens such as trihalomethanes and chloramines. Ozone is a safe alternative to chlorine products, and it performs the same functions without the undesirable side effects; ozone is not harmful to the environment because it is made from oxygen (O_2) and decomposes back into O_2. Perhaps the most common use of commercially produced ozone is in the treatment of water and wastewater. Ozone has been used in water treatment worldwide for more than 100 years. Tables 2 and 3 illustrate ozone's ability to decompose organic structures and in the disinfection of various microbes.

Drinking water, when untreated, often contains undesirable sediments, microbes and organic contaminants, unwanted colors, and residual tastes and odors, which may be successfully removed by treatment with ozone. Treatment of drinking water with ozone disinfects the water by killing bacteria and deactivating viruses present in the water. Ozone has been demonstrated to effectively inactivate strains of poliovirus, adenoviruses, rotaviruses, and the viruses that cause vesicular stomatitis and encephalomyocarditis. The oxidative properties of ozone are useful in the removal of soluble iron and manganese; the removal of unwanted colors, tastes, and odors; the decomplexing of bound heavy metals; the destruction of inorganic components such as sulfides, cyanides, and nitrites; and the removal of suspended solids. One invention even provides a means for maintaining a degree of residual ozone in the water after treatment in order for the water to remain pure during storage.

Although many methods exist for producing ozone, there are three main categories of ozone production: corona discharge methods, electrochemical methods, and methods involving ultraviolet radiation. In the corona discharge method, the most common method, oxygen or an oxygen-containing gas, most commonly air, is passed through the space between two electrodes separated by a dielectric material, which is usually glass (Figure 2). The electrodes are most often either concentric metallic tubes or flat, plate-like electrodes that are connected to a source of high voltage. When a voltage is supplied to the electrodes, a corona discharge forms between the two electrodes, and the oxygen in the discharge gap is converted to ozone (eq 1). A corona discharge is characterized by a low-current electrical discharge across a gas-containing gap at a voltage gradient, which exceeds a certain threshold value. First, oxygen molecules, O_2, are split into oxygen atoms, O, (eq 2) by impact with electrons(e^-), and then the individual oxygen atoms combine with the remaining oxygen molecules to form ozone, O_3 (eq 4). In the stratosphere, instead of electrons splitting the O_2 double bond, ultraviolet light (uv) dissociates the molecule.

$$3O_2(g) \rightarrow 2O_3(g) \tag{1}$$

$$O_2(g) + e^- \rightarrow 2O(g) + e^- \tag{2}$$

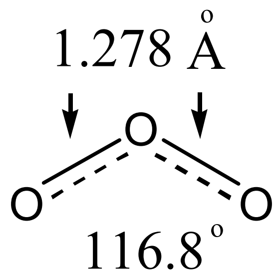

Figure 1. Structure of ozone, an allotrope of oxygen.

Table 1. The Reduction Potentials for Oxidizing Agents Commonly Used

$O_2 + 4H_3O^+ + 4e^- \rightarrow 6H_2O$	$E^o = +1.23$ V
$Cl_2 + 2e^- \rightarrow 2Cl^-$	$E^o = +1.36$ V
$HClO + H_3O^+ + e^- \rightarrow 2H_2O + 1/2Cl_2$ (g)	$E^o = +1.63$ V
$HClO_2 + 2H_3O^+ + 2e^- \rightarrow HClO + 2H_2O$	$E^o = +1.63$ V
$H_2O_2 + 2H_3O^+ + 2e^- \rightarrow 4H_2O$	$E^o = +1.77$ V
$O_3(g) + 2H^+ + 2e^- \rightarrow O_2(g) + H_2O$	$E^o = +2.07$ V
$F_2 + 2e^- \rightarrow 2F^-$	$E^o = +2.87$ V

Table 2. The Impact Kinetics That Three Different Oxidizing Agents Have in Decomposing a Range of Organic Compounds

Compound	Chlorine	Permanganate	Ozone
Acetophenone	26 days	43 days	25 minutes
Benzaldehyde	>3.2 days	36 minutes	28 minutes
Camphor	>3.2 days	>5.8 days	12 minutes
p-Nitrophenol	2.1 hours	1.1 days	2 minutes
Borneol	1.4 days	7 days	53 minutes
Methyl-m-toluate	>20 days	22 days	5.5 minutes
Diacetone-L-sorbose	100 days	14 days	2.8 minutes

$$O_2(g) + uv \rightarrow 2O(g) \tag{3}$$

$$O(g) + O_2(g) \rightarrow O_3(g) \tag{4}$$

Usually, in the electrochemical method of ozone production, an electrical current is applied between an anode and cathode in an electrolytic solution containing water and a solution of highly electronegative anions. A mixture of oxygen and ozone is produced at the anode. Another common method of ozone generation involves bombarding oxygen with ultraviolet radiation, which splits oxygen molecules into oxygen atoms that then combine with other oxygen molecules to form ozone. As with the corona discharge method, many modifications of the electrochemical method of ozone production and the ultraviolet radiation method exist.

In the chemical education literature, Allen et al. outline a UV/vis absorption experiment that measures a number of atmospheric gases [1]. Manning et al.'s past work in this laboratory centered on the impact that various gas mixtures have on ozone production from an electric discharge [2–4]. Information on the generation and application of ozone can be found in various articles in the chemical literature [5–9]. It should be noted that ozone decomposition is well-known to be dependent on the material of the container walls. This means that the kinetic data taken is specific to the system measured and cannot be universally applied (atmospheric chemistry, high pressure storage, etc.). For example, the kinetics (rate constants) of ozone's decomposition back to oxygen in a quartz cell is different than those measured in a stainless steel container. This exercise does provide data that can be used for pure kinetic exercises or to teach the basics of gas-phase ozone chemistry. Depending on the depth at which the material is covered, the data can be used in general chemistry, environmental chemistry, or physical chemistry classes.

Experimental

A 5-cm quartz cell was filled with ozone and the following gaseous compositions: pure O_2 (Exercise 1), 20% Ar and 80% O_2 (Exercise 2), 40% Ar and 60% O_2 (Exercise 3), 60% Ar and 40% O_2 (Exercise 4), 80% Ar and 20% O_2 (Exercise 5), 20% N2 and 80% O_2 (Exercise 6), 40% N_2 and 60% O_2 (Exercise 7), 60% N_2 and 40% O_2 (Exercise 8), and 80% N_2 and 20% O_2 (Exercise 9). The ozone decay was monitored at 254 nm by the Perkin Elmer Lambda 11/Bio UV/vis spectrometer over a 75-min time period. The absorbance was determined at 5-min time intervals and recorded. Using this data, the concentration of ozone can be determined using Beer's Law:

$$A = \varepsilon l c \tag{5}$$

where A is the absorbance, l is the path length of the quartz cell (l = 5 cm), c is the concentration, and ε is the extinction coefficient (ε = 3000 M^{-1} cm^{-1}) for ozone. By rearranging the equation we get

$$c = A/(15000 \text{ M}^{-1}) \tag{6}$$

The ozone generator is shown in Figure 3. It operates at 7500 V and 30 milliamps and was built in this laboratory.

Discussion

Prelaboratory Questions. The purpose of the prelaboratory questions is to expand the students' general knowledge of principles associated with the generation and use of ozone. Typically, general chemistry classes, as well as upper level classes, contain students with a wide range of majors from premedicine to engineering and chemistry majors. Students are encouraged to use the Internet to find answers.

1. Why is ozone such a good oxidizing agent? Cite E^o versus H_2O_2, Cl_2, O_2, MnO_4^-, and two chlorine–oxide compounds. Give some half-lives ($t_{½}$) for organic destruction.
2. How is ozone made (diagram, equation)? What role do electrons in a corona discharge or UV light from the strastophere play in making ozone?
3. List and briefly describe the equations for zero, first, and second order reactions. Specifically:
   a. rate of reaction (r = ?),
   b. concentration versus time relationship,
   c. half-life expression ($t_{1/2}$ = ?),
   d. plot to obtain a straight line for each order.
4. Ozone is often injected into water with equipment that takes advantage of the Venturi effect. What is the Venturi (Bernoulli Principal) effect? Include diagrams.
5. Describe how chlorofluorocarbons (CFCs) destroy ozone in the atmosphere. What are the primary sources of CFCs? (Include reactions)
6. Ozone is used in the Cuban health care system (see Google.com search engine, search "Havana, Cuba, Ozone Research Center"). What medical applications can ozone be used for? Describe these applications.

Table 3. *ct* Values (m g m in L^{-1}) for 99% Inactivation of Microorganisms with Various Chemical Disinfectants (c = concentration, t = time)

Microorganism	Chlorine	Chloro-amine	Chlorine Dioxide	Ozone
E. Coli	0.05	95–180	0.75	0.02
Polio 1	2.5	3740	6.7	0.2
Rotavirus	0.05	6480	2.1	0.006
G. lamblia cysts	1.50			0.6
G. muris cysts	6.30	1400	18.5	2.0
Phage f2	0.18			

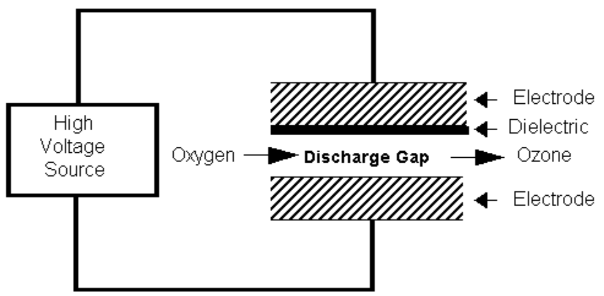

Figure 2. Schematic diagram of a typical corona discharge ozone generator.

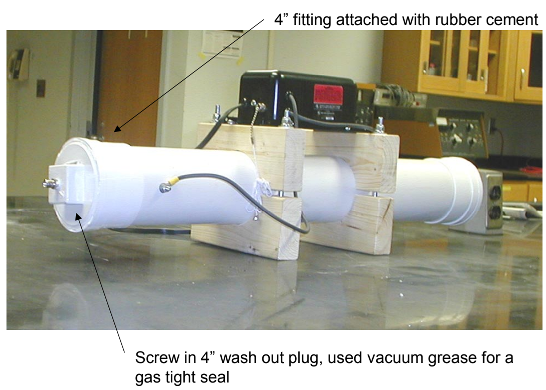

Figure 3. Ozone generator used in this work uses a 7500 V, 30-milliamp power supply to charge a corona discharge that is contained inside the PVC tube. Most plastics and metals react with ozone but PVC and stainless steel are resilient to the strong oxidizng agent. Gas is pumped in one end and leaves the other through stainless steel compression fittings.

7. Because the Cuban health care system, which is based on preventive care, rivals the US system in results (i.e., life expectancy, vaccinations of children, etc.), its "alternative" approaches to health should be evaluated scientifically, not politically.

The students are provided with the data for exercises 1–9 as listed in Tables 4–12, respectively. A student performing an exploratory laboratory in physical chemistry determined each data set. In each case, the same set of conditions was run three times for accuracy and precision concerns. The data is provided on a disk so students can cut and paste it into spreadsheets for calculations and graphing.

Exercise 1. Ozone decomposition data is monitored by a UV spectrometer at 254 nm. (This is in a 5-cm quartz cell and the gas mixture is 100% oxygen, 0% argon.)

Exercise 2. Ozone decomposition data is monitored by a UV spectrometer at 254 nm. (This is in a 5-cm quartz cell and the gas mixture is 80% oxygen, 20% argon.)

Exercise 3. Ozone decomposition data is monitored by a UV spectrometer at 254 nm. This is in a 5-cm quartz cell and the gas mixture is 60% oxygen, 40% argon.)

Exercise 4. Ozone decomposition data is monitored by a UV spectrometer at 254 nm. (This is in a 5-cm quartz cell and the gas mixture is 40% oxygen, 60% argon.)

Exercise 5. Ozone decomposition data is monitored by a UV spectrometer at 254 nm. (This is in a 5-cm quartz cell and the gas mixture is 20% oxygen, 80% argon.)

Exercise 6. Ozone decomposition data is monitored by a UV spectrometer at 254 nm. (This is in a 5-cm quartz cell and the gas mixture is 80% oxygen, 20% nitrogen.)

Exercise 7. Ozone decomposition data is monitored by a UV spectrometer at 254 nm. (This is in a 5-cm quartz cell and the gas mixture is 60% oxygen 40% nitrogen.)

Exercise 8. Ozone decomposition data is monitored by a UV spectrometer at 254 nm. (This is in a 5-cm quartz cell and the gas mixture is 40% oxygen, 60% nitrogen.)

Exercise 9. Ozone decomposition data is monitored by a UV spectrometer at 254 nm. (This is in a 5-cm quartz cell and the gas mixture is 20% oxygen 80% nitrogen.)

Laboratory Questions. With the aid of a spreadsheet, the students are asked to answer the following questions using the data provided in Exercises 1–9. The concentration of ozone produced in the corona discharge varies, in a predictable fashion, with the gas mixtures entering the ozone generator. This can be, for example, the argon/oxygen mixtures produced more ozone than the other mixtures. For details of argon's catalytic effect on the production of ozone inside a corona discharge, please see references 2 through 4.

For the questions below, those labeled "general" are for freshmen laboratories and only need the information provided here, and those labeled "advanced" were used in physical chemistry and need references 2 and 3 for details about the mechanisms associated with ozone formation and decomposition, particularly question 9.

1. For each data set, calculate the average of the absorbance and the standard deviation for a given time interval and plot the absorbance versus time with error bars. (general)
2. Using Beer's law (5-cm path length, 3000 M^{-1} cm^{-1}), calculate the concentration of ozone in the gas phase. (general)
3. For each data set, do a first order plot, calculate the correlation coefficient and slope for each average absorbance. (general)
4. Use this slope to determine the rate constant for each mixture. Also, using the first-order rate constant, calculate the half-life. (general)
5. Plot the rate constants (y axis) versus the oxygen concentration (mole fraction, 1.0, 0.8, 0.6, 0.4, 0.2) There should be two plots, one using the argon/oxygen data and one for nitrogen/oxygen. Use the pure O_2 data for both graphs. (advanced)

Table 4. Data for Exercise 1

Time (min)	Abs	Abs	Abs
0	0.291	0.297	0.297
3	0.271	0.242	0.252
5	0.257	0.225	0.237
10	0.226	0.197	0.209
15	0.201	0.179	0.189
20	0.181	0.162	0.172
25	0.159	0.147	0.157
30	0.145	0.132	0.143
35	0.130	0.119	0.131
40	0.117	0.108	0.118
45	0.104	0.097	0.108
50	0.093	0.087	0.098
55	0.086	0.078	0.092
60	0.077	0.073	0.083
65	0.069	0.066	0.073
70	0.061	0.057	0.070
75	0.055	0.053	0.064

Table 5. Data for Exercise 2

Time (min)	Abs	Abs	Abs
0	0.681	0.677	0.685
3	0.568	0.573	0.581
5	0.537	0.558	0.562
10	0.481	0.518	0.524
15	0.445	0.487	0.494
20	0.413	0.457	0.466
25	0.383	0.429	0.440
30	0.364	0.402	0.415
35	0.334	0.371	0.390
40	0.305	0.343	0.369
45	0.285	0.321	0.347
50	0.264	0.297	0.326
55	0.251	0.290	0.307
60	0.239	0.271	0.289
65	0.222	0.254	0.272
70	0.206	0.234	0.254
75	0.190	0.219	0.235

Table 6. Data for Exercise 3

Time (min)	Abs	Abs	Abs
0	1.321	1.246	1.309
3	1.098	1.043	1.117
5	1.023	0.988	1.041
10	0.935	0.908	0.943
15	0.879	0.865	0.904
20	0.833	0.826	0.863
25	0.789	0.788	0.825
30	0.747	0.746	0.773
35	0.708	0.712	0.733
40	0.670	0.679	0.699
45	0.637	0.647	0.655
50	0.603	0.617	0.635
55	0.571	0.590	0.606
60	0.541	0.559	0.578
65	0.513	0.525	0.549
70	0.485	0.503	0.524
75	0.464	0.476	0.497

Table 7. Data for Exercise 4

Time (min)	Abs	Abs	Abs
0	2.082	2.175	1.890
3	1.793	1.894	1.670
5	1.674	1.780	1.556
10	1.501	1.559	1.388
15	1.411	1.482	1.314
20	1.339	1.426	1.256
25	1.275	1.357	1.205
30	1.203	1.297	1.151
35	1.169	1.233	1.100
40	1.112	1.187	1.050
45	1.059	1.141	0.991
50	1.013	1.078	0.973
55	0.963	1.034	0.936
60	0.902	0.973	0.888
65	0.864	0.947	0.856
70	0.841	0.907	0.826
75	0.800	0.865	0.789

Table 8. Data for Exercise 5

Time (min)	Abs	Abs	Abs
0	3.370	3.569	3.306
3	3.073	3.221	2.930
5	2.920	3.031	2.797
10	2.612	2.754	2.702
15	2.490	2.630	2.536
20	2.390	2.521	2.436
25	2.297	2.391	2.337
30	2.202	2.350	2.251
35	2.107	2.264	2.163
40	2.042	2.144	2.077
45	1.947	2.093	1.997
50	1.852	2.016	1.920
55	1.771	1.938	1.843
60	1.727	1.862	1.771
65	1.644	1.779	1.709
70	1.582	1.713	1.658
75	1.522	1.644	1.594

Table 9. Data for Exercise 6

Time (min)	Abs	Abs	Abs
0	0.915	0.801	0.820
3	0.773	0.671	0.685
5	0.718	0.624	0.636
10	0.652	0.570	0.596
15	0.631	0.541	0.555
20	0.610	0.519	0.520
25	0.568	0.496	0.502
30	0.543	0.473	0.488
35	0.512	0.452	0.466
40	0.498	0.431	0.445
45	0.476	0.412	0.423
50	0.454	0.402	0.401
55	0.433	0.386	0.394
60	0.415	0.369	0.379
65	0.395	0.352	0.361
70	0.376	0.336	0.336
75	0.356	0.321	0.325

Table 10. Data for Exercise 7

Time (min)	Abs	Abs	Abs
0	0.909	0.999	1.041
3	0.758	0.823	0.852
5	0.707	0.769	0.794
10	0.648	0.708	0.734
15	0.619	0.678	0.703
20	0.592	0.650	0.671
25	0.568	0.625	0.656
30	0.543	0.60	0.632
35	0.530	0.577	0.618
40	0.508	0.553	0.581
45	0.487	0.530	0.563
50	0.465	0.501	0.531
55	0.447	0.474	0.509
60	0.425	0.455	0.485
65	0.408	0.437	0.451
70	0.399	0.420	0.443
75	0.375	0.402	0.421

Table 11. Data for Exercise 8

Time (min)	Abs	Abs	Abs
0	0.291	0.297	0.297
3	0.271	0.242	0.252
5	0.257	0.225	0.237
10	0.226	0.197	0.209
15	0.201	0.179	0.189
20	0.181	0.162	0.172
25	0.159	0.147	0.157
30	0.145	0.132	0.143
35	0.130	0.119	0.131
40	0.117	0.108	0.118
45	0.104	0.097	0.108
50	0.093	0.087	0.098
55	0.086	0.078	0.092
60	0.077	0.073	0.083
65	0.069	0.066	0.073
70	0.061	0.057	0.070
75	0.055	0.053	0.064

Table 12. Data for Exercise 9

Time (min)	Abs	Abs	Abs
0	1.465	1.497	1.379
3	1.172	1.266	1.089
5	1.074	1.138	1.024
10	1.005	1.052	0.952
15	0.935	1.012	0.923
20	0.895	0.969	0.890
25	0.859	0.926	0.858
30	0.825	0.912	0.834
35	0.790	0.875	0.807
40	0.759	0.842	0.773
45	0.729	0.811	0.743
50	0.702	0.783	0.716
55	0.674	0.746	0.687
60	0.646	0.72	0.662
65	0.622	0.693	0.634
70	0.595	0.665	0.607
75	0.572	0.642	0.583

6. Plot the half-life (*y* axis) versus the oxygen concentration for all data sets. Discuss the role that the oxygen/argon ratio plays in the decomposition of ozone. (advanced)
7. Discuss the effect that argon, and/or nitrogen, and/or oxygen have on the decomposition kinetics of ozone as outlined in plots 5 and 6. (advanced)
8. Plot the first ozone concentration (time = 0) versus the rate constant (5 points total) of each experiment. Does ozone play a role in its own decay? For example, does $O_3 + O_3 \rightarrow$ product (O_2) or $O_3 + O_2 \rightarrow$ product (O_2) appear to be the predominant mechanism? (advanced)
9. Plot the starting ozone concentration versus the argon fraction (5 points). Does argon play a role in the production of ozone in an electrical discharge? Explain (use references 2 and 3 for details). (advanced)

Conclusion

The purpose of this exercise is not to describe a laboratory where the kinetics data is measured but rather to provide data that can be used in exercises.

Ozone is not only a scientifically and industrially prominent molecule but also a socially and politically charged species. Ozone's decay back to oxygen is slow enough to be easily measured with a single-beam or double-beam UV spectrometer with a quartz cell. Varying simple parameters such as gas mixture can provide interesting experimental data that can be related to a variety of undergraduate classes including fundamental kinetics in general chemistry, three-body reactions in physical chemistry, and atmospheric reactions in environmental chemistry.

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