

5.08 KINETICS OF ATOMIC OXYGEN REACTIONS BY A FLOW METHOD

(5 points)

Background information

Relevant lecture courses: Introduction to Kinetics (year 1), Kinetics and Mechanism (year 2), Atmospheric Chemistry (year 3). The theory behind this experiment does not depend strongly on the Atmospheric Chemistry course; it should be possible to complete the experiment at any stage in years 2 or 3.

Aim of the experiment

Early this century, Lord Rayleigh discovered that atomic oxygen is one of the products of an electric discharge through molecular oxygen. (The Rayleigh referred to is R.J.Strutt, 4th Lord Rayleigh, known as 'airglow Rayleigh' to distinguish him from the 3rd Baron, or 'scattering Rayleigh'.) Relative concentrations of up to 10% may easily be produced in this way, although in this experiment we shall use smaller values at low total pressure to simplify the reactions in the system. Atomic oxygen is not, of course, an intrinsically unstable species, but it is highly reactive. It is therefore not possible to study it in an ordinary static system, and a flow method must be employed instead [1,2].

Atomic oxygen is detected by doping the molecular oxygen with 10% nitrogen. Then not only is atomic oxygen formed in the electric discharge, but also nitric oxide. The latter reacts with the atomic oxygen to form electronically excited nitrogen dioxide, which emits light as it decays to its ground state. The greenish emission, observed by Rayleigh, is known as the air afterglow, and its intensity, at fixed [NO], is proportional to the atomic oxygen concentration, since it is this which determines the amount of NO₂ which is formed. Thus the kinetics of oxygen atom decay can be

calculated from measurements of emission intensity at measured intervals along a flow tube positioned downstream of the discharge.

In this experiment we derive two rate constants. The first is for the combination of atomic oxygen with molecular oxygen. The second is for the recombination of oxygen atoms at the wall of the flow tube, and is used to calculate the fraction of wall collisions at which the atoms are lost.

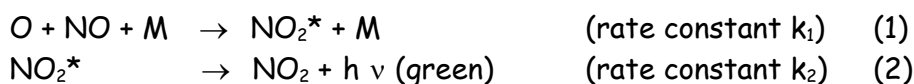
Safety

The power supply used to create the discharge in this experiment generates a lethal voltage. Do not handle the power unit or the electrodes connected to it under any circumstances. Wear safety glasses throughout the experiment to protect yourself against the possibility of the glass vacuum line collapsing.

Theory

Detection of atomic oxygen

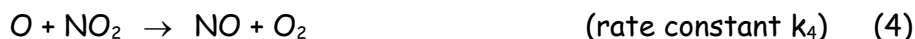
Before considering the kinetics of the oxygen atom reactions, we must measure the relative concentration of atomic oxygen. The air afterglow used to detect atomic oxygen is caused by the chemiluminescent process



where NO_2^* represents electronically excited nitrogen dioxide. There is also a non-radiative recombination process



Low concentrations of NO give a clearly visible chemiluminescence but do not appreciably affect the concentration of atomic oxygen. It is fortunate, for our purposes, that the process



is an exceptionally rapid reaction with a rate constant of $9.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature [3]. Thus every time an NO molecule changes to NO_2 in reaction (1) or (3), it is almost immediately regenerated by reaction (4). The effect of this is that the concentration of nitric oxide does not decay down the flow tube.

It may be shown that the intensity I of the air afterglow is proportional to the product of the NO and O concentrations, but independent of total pressure:

$$I = I_0 [\text{NO}] [\text{O}] \quad (5)$$

where I_0 is the intensity at unit concentration of NO and O. Since [NO] is constant, the intensity of the air afterglow at selected points down the tube is a relative measure of [O].

Measurement of linear flow velocity

In this experiment, the system rapidly settles to a stationary state after the discharge is turned on. Under these conditions, the atomic oxygen concentration measured at a point downstream from the discharge is the concentration remaining after a time t given by $t = x/V$, where x is the distance down the flow tube and V is the linear flow velocity.

Two approximations are required to find V . First, the oxygen atom concentration is sufficiently small for us to assume that its flow velocity is the same as that of the oxygen/nitrogen mixture passing from the cylinder into the discharge. Secondly, we assume that the gas flows as a 'plug' with an axial diffusion rate which is negligible compared with the flow velocity, and that the tube is wide enough for there to be no appreciable pressure drop along its length. The linear flow velocity V of the gases in the tube is then

$$V = \frac{F}{Ay} \quad (6)$$

where A is the cross-sectional area of the tube (cm^2). The total concentration y (molecule cm^{-3}) is calculated from the total pressure in the flow line. The bulk flow rate F (molecule s^{-1}) is determined with a capillary flow meter, which measures the difference in pressure across a capillary mounted in the inlet line. The Poiseuille equation for the bulk flow rate F through a uniform tube of radius r and length l is

$$F = \frac{\pi r^4}{16\eta l RT} (p_1^2 - p_2^2) \quad (7)$$

in which p_1 is the pressure at the high pressure end of the tube and p_2 the pressure at the low pressure end. The capillary tube used in this apparatus (situated immediately above tap A in Figure 1) is simply a drawn-out jet, and so is not of uniform bore. It must therefore be calibrated before the experiment. We rewrite equation 7 in the form

$$F = \text{const} (p_1 + p_2) (p_1 - p_2) \quad (8)$$

Then if $(p_1 - p_2) = \Delta p$ is small, to a good approximation

$$F = K p_1 \Delta P \quad (9)$$

and the flow meter calibration is expressed in terms of a value of K . Δp is then the difference in pressure between the two sides of the drawn-out capillary and is measured with an oil manometer.

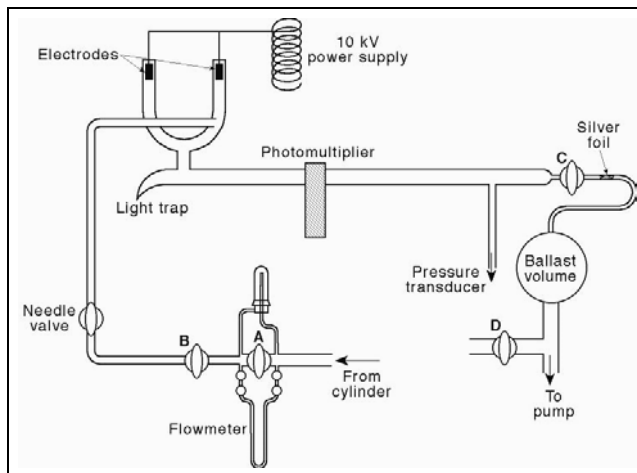
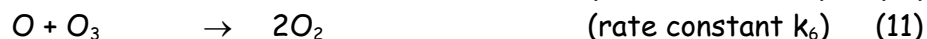


Fig. 1. The oxygen atom flow apparatus.

The volume of gas swept out per second by the vanes of the rotary pump is constant at all pressures used in the experiment. Thus the linear flow velocity V should remain constant and independent of the mass flow velocity F , provided the setting of the tap between the rotary pump and flow line is not altered. In practice the connecting pipes offer increasing relative impedance to flow as the pressure drops. As a result, the flow velocity decreases somewhat with decreasing pressure.

Kinetics of oxygen atom decay

At the concentrations used in this experiment, all the reactions removing oxygen atoms are first order in oxygen atom concentration $[O]$:



Recombination reactions, second order in $[O]$, such as



can be neglected at the low concentrations of atomic oxygen produced in this experiment. Reactions 10 and 13 need a third body M to stabilize the reaction products, and are kinetically third order overall. In the present instance M is molecular oxygen, since this is the major component of the reaction mixture. It is

evident from the reaction scheme that the rate of decay of atomic oxygen, $-d[O]/dt$, is given by

$$\frac{d[O]}{dt} = k_5 [O][O_2][M] + k_6 [O][O_3] + k_7 [O] \quad (14)$$

We now apply the steady-state approximation to ozone, i.e. we assume that its concentration does not change with time. Then

$$\frac{d[O_3]}{dt} = 0 = k_5 [O][O_2][M] - k_6 [O][O_3] \quad (15)$$

and thus

$$[O_3] = \frac{k_5}{k_6} [O_2][M] \quad (16)$$

Substituting this expression into equation (14)

$$-\frac{d[O]}{dt} = 2k_5 [O][O_2][M] + k_7 [O] \quad (17)$$

After integrating, and replacing $[M]$ by $[O_2]$ as explained previously, we obtain

$$-\ln [O] = (2k_5[O_2]^2 + k_7) t + \text{const} \quad (18)$$

This equation shows what measurements are necessary for the determination of k_5 and k_7 . We fix $[O_2]$, which we assume is equal to the total gas concentration in the flow line, and require a series of measurements of $[O]$ as a function of t . A plot of $-\ln[O]$ against t gives a straight line of slope $(2k_5[O_2]^2 + k_7)$. (In fact we can plot $-\ln(\text{intensity})$ rather than $-\ln[O]$, as shown by equation 5). We then carry out further measurements at different values of $[O_2]$, and thus obtain a series of slopes $(2k_5[O_2]^2 + k_7)$. These are plotted against $[O_2]^2$ to obtain a straight line of slope $2k_5$ and intercept k_7 .

Interpretation of k_1 and k_5

The newly formed molecule in an atom association reaction such as reaction 1 or 3 is energy rich by an amount equivalent to the energy of the new bond. Unless this excited molecule is stabilized by collisions decreasing the internal energy, it can (and will) redissociate. The overall process can be represented by the (simplified) scheme



A steady state treatment leads to the result

$$\text{Rate of reaction} = \frac{k_a k_s [A][B][M]}{k_s [M] + k_r} \quad (19)$$

If $k_r \gg k_s [M]$ (which is the case for reactions (1) and (5) at the values of $[M]$ used here) then the expression simplifies to

$$\text{Rate of reaction} = \frac{k_a k_s}{k_r} [A] [B] [M] \quad (20)$$

i.e. third order, and the rate constant measured actually corresponds to $k_a k_s / k_r$. As a first approximation both k_a and k_s can be taken as equal to the gas collision frequency factor Z' , so that the third order rate constants k_1 and k_5 can be used to provide estimates of the respective redissociation rate constants k_r from the relation

$$k_1 \text{ or } k_5 = (Z')^2 / k_r \quad (21)$$

Hence k_r may be calculated.

Interpretation of k_7

If γ is the fraction of oxygen atoms which recombine on striking the wall, then the rate of wall recombinations is $\gamma nca/4$ where n is the number of oxygen atoms per unit volume, and c their mean speed. a , the area of the wall, is $2\pi rl$ where r is the radius of the tube and l its length. Then the rate constant k_7 will be the ratio of the rate of wall recombinations per unit length to the number of oxygen atoms per unit length, i.e.

$$k_7 = \frac{(\gamma nc/4)2\pi r}{n\pi r^2} = \frac{\gamma c}{2r} \quad (22)$$

The value of c may be obtained from the kinetic theory of gases:

$$c = (8RT/\pi M)^{\frac{1}{2}} \quad (23)$$

Thus a value of γ may be calculated from the value of k_7 by using equations (22) and (23).

Apparatus

The apparatus, shown in Fig. 1, is installed in a dark room. A mix of 90% oxygen and 10% nitrogen is supplied from a cylinder with a regulator set to a pressure slightly above atmospheric. There is also a small control valve which is used as an on/off tap and a pressure-release valve in the line leading to the manometer set to minimize the possibility of overpressuring the apparatus. The pressure of the gas entering the apparatus is measured on a mercury manometer in the form of a short U-tube. (Note that the actual pressure of the incoming gas at this point is not just the difference between the two mercury columns, but is that pressure *plus* atmospheric pressure, since the right-hand arm of the manometer is open to the atmosphere.)

The gas then passes through a flow meter, in which the pressure drop across an orifice is measured by a manometer filled with dibutyl phthalate ('oil'). The flow meter also incorporates a by-pass tap (tap A). From the flow meter the gas passes through another tap (tap B), through a needle valve, and then into the discharge, the details of which are shown in the diagram. The excited gas then passes into the flow tube via a 'light trap' - a drawn-down end of tubing to prevent the passage of stray light from the discharge.

A photomultiplier, draped in black cloth to minimize stray light, can be slid along the flow tube to detect light output. It is supplied by a high voltage ('EHT') power supply, which has switches both for the mains input and the high voltage output. The photomultiplier anode current is measured by a digital ammeter. Connected to the flow tube is an electronic pressure transducer. From the flow tube the gas passes through a large tap (tap C) which can be used to adjust the flow velocity. The gas passes over a piece of silver foil, which acts as a catalyst for the recombination of oxygen atoms to molecular oxygen, thus protecting the pump oil against oxidation. The gas then passes through a large globe which smooths out pressure pulses produced by the pump, and finally to the rotary vacuum pump itself. There is the usual air-leak (tap D) to prevent suck-back of pump oil when the pump is turned off.

Procedure

It is easy to ruin this apparatus by the careless turning of taps. Taps turned too fast or too roughly may crack the glassware, or may cause mercury or oil to be blown out of the manometers. If air is sucked into the system, the discharge intensity may change for several hours. So be gentle and be wary!

The high voltages used in this experiment are potentially lethal - do not touch the leads associated with the discharge or photomultiplier. Photomultipliers are easily destroyed by being made to pass too high a current, so do not turn on the room lights, while the photomultiplier is energized.

Start up

You will need to know atmospheric pressure later on, so start by recording the ambient atmospheric pressure, p_{atm} , on the barometer beside the service room in the lower teaching laboratory.

Check the small control valve on the gas cylinder is turned off (fully clockwise) and that the flow tube is closed off from the vacuum pump globe (tap C). Close the air leak (tap D) and start the vacuum pump. Check that the needle valve between the flow meter and flow tube is closed (fully clockwise) but light finger tight only. (Needle valves such as the one you will use can be ruined by being overtightened, so do not

close it beyond the point at which gentle resistance is felt.) Evacuate the flow tube by opening it to the pump (tap C). Tap C should be opened several turns to ensure rapid passage of gas down the flow tube. Note the falling pressure on the flow line pressure transducer.

Experiment

Open the by-pass to the flow meter (tap A) and the tap between the flow meter and its needle valve (tap B), but do not open the needle valve itself yet.

Turn on the cylinder supply. Slowly turn on the valve on the cylinder regulator to give a slight positive output pressure, making sure that the mercury in the manometer does not blow over. Now close the by-pass tap (tap A). There should be no pressure difference on the oil manometer of the flow meter. If there is, the needle valve or flow meter is leaking - seek assistance.

Open the flow control needle valve by the flow meter until the pressure difference on the flow meter is between 10 and 100 mm oil. Keep the mercury head between 10 and 15 mm Hg.

Turn on the discharge power supply. A mauve discharge should be struck between the aluminium electrodes. Turn out the room lights and wait for a steady faint green air afterglow to be established in the main part of the flow tube; adjust the flow needle valve if necessary. The discharge will not be apparent at very low pressures (too few O atoms excited to give a detectable emission), or at high pressures (rapid deactivation). It is likely to be strongest in the range 1-3 Torr, as measured by the pressure transducer. Switch off the discharge and estimate the time for the tail end of the glowing gas column to move down the tube. The flow velocity should be of the order of 200 cm s^{-1} ; if it is not, adjust the tap between the flow tube and the pump. Switch on the discharge again, and leave the flow to stabilize for a few minutes.

Cover the photomultiplier with the black cloth provided, then switch it on. Read the oil, mercury and flow-line manometer pressures. Measure the "dark current" (background reading) at about a dozen different positions along the tube. Now turn on the discharge and repeat the measurements. Check that the manometer readings have not changed significantly.

At the voltage used in this experiment, the discharge is stable at pressures of a few torr as measured on the flow tube pressure transducer. Carry out from six to eight experiments at pressures which give a suitable discharge. Allow the pressure to settle each time, and measure the dark current along the tube before turning on the discharge and measuring the discharge intensity at the same positions. Use only the needle valve between the flow meter and flow tube to adjust the pressure. Be very careful not to blow over oil or mercury in the flow meter - keep an eye on their levels whenever you move a tap or needle valve. A small low-voltage bulb is available to help you monitor these levels in the darkened room.

Shut down

Turn off the discharge and photomultiplier supplies at all switches. Leave the pump running for the present. Open the bypass to the flow meter (tap A). Close the small control valve on the gas cylinder, and shut off the cylinder. If the pressure registered on the mercury manometer is higher than about 50 mm Hg, reduce the pressure in the flow meter by opening the needle valve between it and the flow tube. This is to prevent mercury being blown over when the apparatus is left unattended.

Close the needle valve between the flow meter and flow tube, and the tap between it and the flow meter.

Close off the flow tube from the pump (tap C). Open the air leak (tap D), then turn off the pump.

Calculation [4]

1. For each experiment, find the bulk flow rate F from equation 9; K is 8.55×10^{14} molecule s^{-1} (mm Hg) $^{-1}$ (mm oil) $^{-1}$, when p_1 is recorded in mm Hg and Δp in mm oil. Do not forget that the pressure at the high-pressure side of the drawn-out tip is related to both the pressure provided by the small mercury column, and atmospheric pressure.
2. Convert the flow line pressures to units of molecule cm^{-3} , given that 1.00 torr (which equals 1 mm Hg and is the unit in which the Pirani gauge reports the pressure) is equivalent to 3.24×10^{16} molecule cm^{-3} of gas at 298 K.
3. Calculate the linear flow velocity V from equation 6. (A is 3.80 cm^2) Check that each linear flow velocity is compatible with your original visual estimate, and that this parameter is reasonably constant from experiment to experiment.
4. Correct your intensities for the effect of any dark current.
5. Knowing the distance between observation points on the tube, tabulate relative oxygen atom concentration (from equation 5) against contact time t for each experiment.
6. Hence find k_5 and k_7 graphically, as described in the THEORY section. Express them in the conventional units of cm^6 molecule $^{-2}$ s^{-1} , and s^{-1} respectively. (Make a careful check of the units used in the calculations for this experiment.)
7. Given that the collision frequency factor Z' is approximately 2×10^{10} cm^3 molecule $^{-1}$ s^{-1} , find the rate constant for the redissociation of ozone from equation 21.

Find k_r for the redissociation of NO_2 given that k_1 is $7.0 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ at 298K [5].

8. Calculate c from equation 23. Hence from equation 22 find γ , the fraction of wall collisions at which oxygen atoms are lost.

9. Comment on the source and size of experimental errors in your results. No allowance has been made in the treatment given above of the fact that oxygen atoms are consumed by reaction (1). Discuss how this omission might affect your results.

Comment

If known concentrations of nitric oxide are admitted through a jet at the upstream end of the flow tube, the rate constant k_1 for the combination of NO with O in the presence of a third body may be measured. Flow experiments are a powerful method of studying simple gas reactions. Recent experiments employ sensitive detection methods such as mass spectrometry, resonance fluorescence and laser magnetic resonance which allow very low radical concentrations to be measured [7]. The use of low concentrations minimizes interference by second order reactions and secondary chemistry in the flow tubes.

References

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