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by

William Reginald Sawyer

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SOME PHOTOCHEMICAL EFFECTS OF ULTRA VIOLET RADIATION

Report

Submitted to Biological Board

of Canada

by

William Reginald Sawyer

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SOME PHOTOCHEMICAL EFFECTS OF ULTRA VIOLET RADIATION.

INTRODUCTION.

In studying the physiological effects of radiation our problem is fundamentally one of photochemistry. Until we understand the fundamental processes taking place in simple photochemical reactions, it makes it extremely difficult to postulate any logical mechanism for more complicated processes.

Photochemical effects have always been a very popular subject for experimentation, and the literature abounds with experimental data. Unfortunately the fundamental principles of the subject have been very little understood and the majority of data is quite useless and often misleading. Lying as it does on the borderland of physics, chemistry and biology probably accounts for the true significance of its principles not being thoroughly appreciated, and hence the number of inconclusive and conflicting results.

Although the writer's knowledge of the fundamental principles is very limited he feels that as these points have never been emphasized in any reports to the board, and in view of the great interest in recent years taken in radiation problems at the Atlantic Biological Station, a very brief review of some of the more important principles would not be out of place here. As the review only attempts to touch the surface, the writer hopes to go into the subject more extensively at a later date.

This report has been divided into three sections.

1. On photochemistry
2. The effect of ultra violet and visible radiation on the reduction of gold chloride in silicic acid gels.
3. A few biotic effects of ultra violet radiation.

PART 1 ON PHOTOCHEMISTRY.

According to the Report of the O.S.A. Progress Committee on Spectrophotometry 1925 radiation is defined as the process in which energy is propagated through space, the possibility of propagation being unconditioned by the presence of matter (although the speed and direction of propagation, as well as the amount of energy transferred may be thus affected).

Radiant Energy is that which is transferred by radiation. It may be expressed in energy units, such as the erg or joule.

Radiant power is the time rate of transfer of energy by radiation. It has been internationally designated by the term radiant flux. The Radiant intensity in any direction from the source is the radiant power per unit solid angle in that direction. If radiant energy be incident upon a surface, the irradiation of that surface is the radiant power per unit of intercepting area. (The term specific irradiation has also been suggested for this quantity, with irradiation to be defined as the total power incident upon that surface). I have used it in this last sense.

Light is radiant energy multiplied by the visibility of the radiant energy. Or light is that agent, force, or action in nature by the operation of which on the organs of sight objects are rendered visible and luminous. In other words it is visible radiant energy. Radiant energy is emitted by every substance above absolute zero at the cost of its own heat and energy. Such radiation has been termed pure temperature radiation, since it depends only on the temperature of the body. When it is due to electrical or chemical processes in part or in entirety it is termed luminescence.

The sun the pure, metal filament lamps are pure temperature radiators emitting a continuous spectrum, the extent and distribution of which are functions of the temperature and hence the total radiant intensity. Mercury vapour lamps are luminescent radiators, the radiation originating from the atomic and molecular characteristics of the Hg vapour and consequently discontinuous, consisting of lines and bands resulting from the processes going on in the atoms and molecules.

There is no need to go into the various means and limits for the various regions of the spectrum here. When I speak of ultra violet radiation in this report I mean to include the near and middle regions (400 mu - 200 mu approximately). If I mean the near region (300 - 400 mu) alone I will refer to it as the near ultra violet.

TWO LAWS OF PHOTOCHEMISTRY.

Taylor suggests two laws of photochemistry as follows. "The First Law of Photochemistry would be the Grotthus Draper Absorption Law, embodied in the statement that: Only light that is absorbed is effective in producing chemical change.

The Second Law: The absorption of light is a quantum process involving one quantum per absorbing molecule (or atom). The photochemical yield is determined by the thermol reactions of the system produced by the light absorption."

It will be convenient to define here also the following: (Allmand 1925. Chemical Society Annual Report)

"Photosensitisers (Optical Sensitisers) By photosensitisers are understood those substances which, when added to a chemical system, by virtue of the light they themselves absorb without undergoing permanent change, make the system sensitive to light in a frequency region where it was previously non sensitive, or, less strikingly, materially increase its photosensitivity in a certain part of the spectrum.

Photocatalysts are, strictly speaking those substances which when added to an insolated system in which a photochemical reaction is already taking place, increase the speed of this reaction without in any way affecting the amount of light of effective wave-length absorbed, or undergoing any permanent change."

SOURCES OF RADIANT ENERGY. We can divide our sources of radiation into two classes according to the spectra they give; continuous or discontinuous. In the first class we have the sun, solid radiators such as incandescent filaments and magnesium, flames such as those produced by acetylene in oxygen, and finally high tension discharges under water. In the second class are the arcs such as carbon and iron, spark discharges between metallic electrodes and vapour lamps, the most common of which is the mercury vapour type.

Continuous Spectra - Solar Radiation. The sun's spectrum is a continuous one with a maximum in the yellow. Solar radiation as it reaches the earth's atmosphere extends approximately from 290 mu - 5u with very little energy beyond 2u. The solar radiation is an extremely variable quantity varying primarily in total radiation and spectral distribution from minute to minute, hour to hour, day to day, season to season and geographically and secondarily varying according to local atmospheric conditions, clouds smokes, humidity etc.

Klugh has emphasized this and gone into detail on these points in his reports to the board so that there is no need of further emphasizing them.

It would be very difficult to give the average radiation of the sun, but roughly for purposes of comparison we might take it at average heights at about 1.0 g cal/cm^2/, min. at sea level in Canada the distribution being U.V. 1 per cent, visible 40 per cent, infra red 59 - The necessity of distinguishing from daylight, sunlight and skylight is also taken up by Klugh.

Solid Radiators

Incandescent filaments such as tungsten are good sources for the near ultra violet. They have the advantages of easy operation, small cost, constancy, and finally that they can be coiled or made into a size which approximates the slit of a monochromator; a necessary condition for use with such instruments. A Nfrnst Glower (Griffiths 1925) which can be made in the laboratory is very useful with the above instrument. Magnesium burned in air was used successfully by Klugh and the writer as a source for standardising photographic plates. If magnesium could be fed uniformly into oxygen over a long period it would make a splendid source.

Flame The acetylene, oxygen (Sheppard 1914) and the carbon disulphide oxygen (Tyndall 1920) have been used for the ultra violet.

High Tension Discharges under Water.

These sources are more valuable for photographic than photochemical work (Tyndall op. cit.).

Discontinuous Spectra

Arcs Of the arcs the most common are the carbon, iron and flaming carbon types. They are all difficult to handle, fluctuate and are difficult to use with slits. Coblentz (1926-1927) gives a valuable comparison of the sun, C and mercury vapour lamp. The positive crater may be used as a source of continuous radiation (Merton 1927).

Sparks

Sparks between metallic electrodes give us the greatest intensity in the middle ultra violet. However they are unsteady unless quite an elaborate set up is used.

Mercury Vapour Lamps

These are the most popular with photochemists. These have been very much improved of late so that they run constant, with in the fraction of a per cent. Constrictions may be made in the tubes so that they may be used with a monochromator. The disadvantage of decreasing intensity with age will be considered later.

Comparison of Sun, Carbon Arc and Mercury Vapour.

The following table gives a rough comparison of the intensity and spectral distribution.

	Total Intensity g cals/cm^2/min	Spectral Distribution			U.V. g cals/cm^2/min
		U.V.	Visible per cent	I.R.	
Sun	1.2	2	49	49	40 cm
Q Hg.	0.010	30	53	17	0.024 0.030
Solarite Carc	0.91	22	43	35	0.18

(Sun average radiation for a 3 hour period at noonday for a season Solarite 25-28 A, 40-50 V). Although the intensity of the Sun and Q hg in the U.V. is practically the same the spectral distribution is entirely different. The sun has less than 5 per cent of its U.V. below 300 mu while the mercury vapour has 20. Thus we see that owing to such a great difference in their spectral distribution, any comparison between the work done in our laboratories and in nature's laboratory is subject to some uncertainty. And just as the great variation of the sun makes comparison from time to time and place to place very difficult, so the individual artificial sources (lamps of the same make and pattern) differ in a surprising degree under a number of none too well known conditions. Hence for quantitative work we must be very careful to define the irradiation, as well as the effective radiation, which can be done as in the case of many systems in physical chemistry, by two variables. These are the quality and quantity of radiation. The first is measured by the wave length and the second is the product of the time and intensity measured in absolute units. The radiation from a source may be defined if we give the total intensity plus the spectral distribution. Theoretically other variables being constant we might expect the total photochemical effect to be proportional to the product of the intensity and time. This law is called the Reciprocity Law. Unfortunately for convenience in measurement it does not seem to hold; that is it fails in many photochemical reactions under the conditions by which we choose to test it. We must remember however that what we measure in most cases is the sum total of a number of reactions which are initialed by the primary photochemical reaction. We thus have a combination of simultaneous and consecutive reactions depending on some initial primary photochemical reaction, a change in any one of which (and especially the primary reaction) will alter the whole course of events. One has only to examine critically all we know about a simple and very exhaustively studied photochemical reaction such as the effect of radiation on the H_2 and Cl_2 = 2 HC 1 equilibrium, to see how difficult or futile it is to go predicting mechanism in more complicated systems until such a time as we are in possession of a great deal more experimental evidence.

METHODS OF MEASUREMENT OF SPECTRAL DISTRIBUTION.

1. Separation of various spectral regions by:
    - (a) Quarts or fluorite prisms.
    - (b) Selective filters.
2. Measurement of the intensity of a given wave length or group of wave-lengths after having isolated them by one of the above methods. For this there are two general classes of intensimeters, selective and non-selective.
    - (a) Selective.
        1. Photographic Plates.

            Very useful and an accuracy within 1 per cent may be obtained if the fundamental principle of photographic photometry is adhered to namely:- If positions on the same plate can be found where the densities are equal, then provided the times of exposure and wave-lengths of the radiation used are identical and the development and sensitivity uniform over the plate, the intensities may be considered equal. The sensitivity of various plates has been determined by Harrison (1925) and Jones (1926).
        2. Photoelectric Cells.

            Cells free from time lag, deterioration, fatigue, and intensity current relations practically linear have been developed. Their chief drawback is that they are highly selective. They are most used as a null instrument (Goos 1926).
        3. Chemical Actinometers.

            Difficult to use. Many types quite unsatisfactory. Very few cover an extended range of the spectrum. However some types are extremely useful for self-integrating actinometry for certain specific purposes or definite regions. (Forbes 1927)

4. Selenium and Thalofide Cells. Many drawbacks.
5. Photogalvanic Cells. Little used.
6. Fluorometers. Not accurate for quantitative work (Gyement 1926)

NON-SELECTIVE.

1. Thermopile. The simplest and best for general use. They may be the surface or the linear type. (Coblenyz 1914). Moll (1920) makes an extremely useful type.
2. Bolometer. Very accurate but very expensive and difficult to operate.
3. Other types. The above two types are by far the most suitable. We can divide the remainder into thermal and electrical groups, but all having certain drawbacks such as to place them out of the field in comparison with the thermopile.
    - (a) Electrical group. Microradiometer and radiomicrometer.
    - (b) Thermal group. Torsion radiation balance - radiometers with vanes - radiocalorimeter - thermopholometer.

METHODS OF IRRADIATION.

The best method for irradiation is that using a monochromator. A very common method is the use of selective filters.

Standardization. The Hefner lamp and the Standard C lamps supplied by the Bureau of Standards are used to standardise thermopiles.

VARIATION OF THE INTENSITY OF RADIATION.

1. Nicol Prisms Cemented with glycerine may be used for the visible and ultra violet regions down to 250 mu.
2. Inverse Square Law is very often used. If lenses and slits are employed in the system this method becomes very difficult to use.
3. Neutral Wedges. Good for visible and down to 300 mu if C in gelatine used. Sputtered platinum on quartz has been used successfully recently.
4. Punched Plates or Wire Screens in irregular motion. Difficult to handle. (Harrison 1924)

5. Sector Wheels. Intermittent Effect.

6. Multiplication of Sources.

not very satisfactory.

7. Variation in Effective Area of Source.

8. Solutions of Dyes obeying Beers Law. Varying the concentration. Difficulty is in getting a satisfactory filter which is neutral to the region and will obey Beers Law.

9. Variation in Electrical Conditions. This changes quality as well as quantity.

10. Oblique Plates of Quartz. Tricky to use.

Methods 1,2,3, are the most common.

SOME SOURCES OF ERROR IN PHOTOCHEMICAL TECHNIQUE.

Errors involving the Quality of the Radiation.

1. The root of most of the evil in photochemistry probably is that due to antagonistic action. By this I mean the direct and reverse effect which may be produced by radiation from two different spectral regions, sometimes quite close together. This can be illustrated by some examples.

(a) Inorganic - OZ onization of oxygen (Goldstein 1913)

$$3O_2 = 2O_3$$

Radiation in the region 120-200 mu causes ozonization to take place. Radiation in the region 230-280 mu causes the reverse reaction to take place.

Hence the resultant effect of polychromatic radiation would be dependent on the relative proportions of the above regions present.

(b) Organic Baly (1924) in studying the synthesis of reducing sugars from carbon dioxide and water under the influence of radiation found that the maximum synthesis took place at 200 mu and that degradation was caused not only at 190 mu but for wave lengths longer than 200.

(c) Animals. Klugh and the writer showed that certain copipods which were killed by a given intensity of ultra violet radiation could withstand about twice the intensity provided it was mixed with the visible and infra red to about 1.7 u. A detailed description is given in another report.

(d) Dognon 1926 has reported an antagonistic action of X rays on the flocculation of given master sols.

(e) The quenching of fluorescence produced by ultra violet, by infra red is another well known example. It may be readily seen what errors we are open to if we deal with polychromatic radiation and then attempt to fix an effective region for a given reaction.

2. Filtering Medium and Filters.

By filtering medium I mean lenses, prisms, cells and anything that comes between the source and the system irradiated. We must be very careful to examine all these to see that certain regions are not cut out. A point often overlooked in this connection is the opacity which quarts develops to medium and near ultra violet with use. Baly (1927, 1924) among others has pointed out that with his mercury lamp he found an appreciable opacity in the quartz jacket after four hours running the opacity extending towards the longer wave lengths with time. He found similar opacity in his quartz tubes. Coblentz studied the deterioration and found it not so noticeable as Baly has reported. However it is a source of error that must be guarded against. It is difficult to obtain a filter which will transmit a narrow region of the spectrum without cutting down intensity considerably. Thus considerable radiation from the neighbouring region gets through. Sometimes a filter will have more than one transmission band and a region a considerably distance away may be also transmitted. Klugh and the writer found last summer that about three quarters of the radiation from the sun passing thru a corning G 986 A ultra violet filter was in the red and intra red.

Even in the best spectrographs and monochromators considerable false light may be present due to out-of-focus slit images formed by light re-flected and re-reflected from the lens and prism faces. Jones (1926) found that in the ultra violet this stray radiation was of wave-length longer than 400 mμ and sometimes amounted to 50 percent of the total radiation. This error would have gone unsuspected except for the fact that, instead of letting the radiation from the exit slit of their monochromator fall directly on the plate, a lens was used causing a non uniformity in the silver deposit on the plate. They found it necessary to use two monochromators in series (Helger and Bausch and Lomb) to obtain sufficiently pure monochromatic radiation for the study of the spectral distribution of the sensitivity of a photographic plate.

3. ERRORS INVOLVING THE QUANTITY OF RADIATION.

1. Reciprocity Law failure mentioned above.
2. Intensity scales. The chief errors in the methods of varying the intensity of radiation are noted above.
3. Intermittent effect. Usually a given exposure (I.T.) given intermittently is less effective than the same exposure given intermittently. We would expect this to be true from our knowledge of induction periods.
4. Filtering Medium. Just as in the case of the quality we must make the necessary criticism for reflection refraction, transmission for each wave length. The shape of the containing vessel may have a very marked effect on the intensity of the radiation. The use of spherical flasks and test tubes may often lead to a considerable error due to lens action unless two given containers are of exactly the same dimensions and the optical system identical. The lens

action formed by the curvature at the bottom of a test tube will lead to quite erroneous results.

4. ERRORS INVOLVING QUALITY AND QUANTITY.

Unfortunately for our convenience nature does not provide us with an isoenergy spectrum. The spectral distribution of continuous radiation follows a probability curve, the spectral distribution of discontinuous spectra is quite irregular. To add to this if we use a monochromator with a prism, the greater dispersion in the shorter wave lengths cuts down still further the radiant flux in the shorter wave lengths which is quite weak on account of the probability curve distribution of the source. We can get a normal spectrum by use of a grating, but such a spectrum is weak and is not satisfactory in the infra red due to the overlapping of different orders. Thus we must correct for prismatic dispersion, and variation in intensity. The correction for variation in intensity is uncertain due to the failure of the Reciprocity Law. The writer is at present using nicols in front of a quartz monochromator and cutting down the intensity at each wavelength so that a linear thermopile gives a constant deflection at the exit.

The quantum theory shows us what difference in quality will do, but the explanation of difference in intensity is not quite so obvious. Part of the effect may be due to the life of the activated molecules. If two molecules can only react when they are activated, the life in the activated state being short, the number reacting will increase at a greater rate than the increase in intensity. Thus large difference in intensity could cause very different reactions to take place in a system due to the different threshold values for each due to the above cause. So we must be very careful to find out whether a system say has its maximum sensitivity at a given wavelength or whether the increase in reaction is due to an exceptionally strong line in that region. Many errors arise of course from the incorrect use of photographic plate, by not adhering to the fundamental principle of photographic photometry enunciated above.

Part 11

THE ACTION OF VISIBLE AND ULTRA VIOLET RADIATION ON THE REDUCTION OF GOLD ION IN SILICIC ACID GELS.

Before studying the effects of ultra violet and visible radiation on organic systems I felt it would be a good idea to study a typical inorganic system not with the hope of establishing the mechanism of the reactions but more the effect of a combination of factors. The system chosen was that represented by the following equation:

$$2\ AuCl_3 + H_2C_2O_4 = 2\ Au^{\circ} + 6\ HCl + 6\ CO_2$$

taking place in a silicic acid gel. The advantage of this gel being its transmission to the near ultra violet and its general inertness. This system was taken as the writer had previously done some work on it, was familiar with the technique and had access to the necessary materials. If oxalic acid is placed on top of a silicic acid gel containing gold chloride and left for a week or two the tube will be filled with colored bands or green blue and red colloidal gold.

For many years the fact that changing light was the cause of the colored gold bands in silicic acid gels went unnoticed. They were always classed as Liesegang phenomena. Davies (1922) came to the conclusion that light was a factor in the formation of the bands. Later in 1923 (op. cit.) he clearly demonstrated that the banding was entirely a matter of the changing light conditions. Cadenhead (op. cit.) also pointed out the fact that these were not Liesegang rings but rhythmic banding due to changing light conditions.

PREPARATION OF SILICIC ACID GELS

The silicic acid gels were obtained by mixing equal volumes of sodium silicate and some acid, pouring the sodium silicate into the acid with constant stirring. The sodium silicate used was Bakers 40 per cent sol. gave Na_2O 8.28 per cent SiO_2 27.13 per cent. ratio Na_2O $Si\ O_3$ 1: 3.39. The density was 1.378. This sodium silicate was similar to that used by Holmes (1917) Davies (1922) Cadenhead (1926).

The sodium silicate density 1.378 was diluted to 1.160. If the water was added to the sodium solute a white precipitate formed. But when the sodium silicate was slowly stirred into the water a clear solution was obtained. It was found best to remove the carbon dioxide from the water and to keep the air from the solution afterwards. Unless prepared very carefully a milkiness will form which will have a profound influence on the formation of crystals in the gels.

The acids used were 3N HCL, H_2SO_4, HNO_3, and acetic. It was found necessary to pour the sodium silicate into the acid otherwise bits of gel would be formed in mixing.

$$Na_2SiO_3 + 2\ HCl\ =\ H_2SiO_3 + 2\ NaCl$$

For the diffusion experiments 1.16 sodium silicate and $3N\ H_2\ S\ O_4$ gave the best results. Most of the experiments involve the following mixtures which I will always refer to as standard tubes. Ten ml of 1.160 Sodium Silicate was added to 10 ml of 3N HCL containing 0.2 g of oxalic acid. To this mixture 0.8 ml of 1 per cent gold chloride was added. This mixture set in about six hours showing a slight opalescence on setting.

METHODS OF EXPOSURE

In order to compare the effects of radiation on gel mixtures it is necessary that tubes of the same glass of equal diameters and equal thicknesses of glass be used. Tubes may be placed so that the gel acts as a lens and in which cases reaction will start on the side farthest from the source of radiation. Normally reduction started on the side nearest the source. The bottom of the tube could be pointed at the sun in such a way that reduction would take place only when the rays were concentrated in the centre. Reaction always started at the bottom of the tubes and in the meniscus. For comparing the effect of light the tubes were covered with heavy paper so that only the same and equal portions of the tubes were exposed. The tubes were laid on a piece of white paper.

EXPERIMENTAL

VARYING THE CONCENTRATION OF GOLD CHLORIDE.

It was thought that the concentration of the gold in the gels would be an important factor in determining the color of the colloidal gold bands. In order to show this the following experiment was performed. Eight tubes containing 10 ml of standard gel containing oxalic acid were made up and varying amounts of gold chloride as shown in Table 1 were added to the gels. The tubes werekept for 4 days in the dark and exposed to the sun at noon. All tubes were given 30 min. exposure except No. 8 which was given 60 min.

TABLE 1.

5 ml sodium silicate, 5 ml 2.945 HCL and 0.1 g oxalic acid

No.	Amount of AuCL added ml	Time to set	First appearance of color min	Color
1	0.001	8 hrs.		colorless
2	0.01	8 hrs.		colorless
3	0.1	8 hrs.	1.25	blue red in and near meniscus
4	0.2	8 hrs.	2.33	ruby red all through
5	0.4 STD.	8 hrs.	4.66	darker ruby red all through
6	0.8	8 hrs.	7.20	opaque centre not reduced
7 1	1.6	14 hrs.	15.00	side nearest light only blue
8	4.0	2 days		crystals only syneresis

6,7,8, showed crystals

No. 3 became slightly redder in the dark

2. VARYING THE CONCENTRATION OF OXALIC ACID.

Experiments showed that decreasing the concentration of oxalic acid increased the time necessary to obtain reduction and when decreased sufficiently blue bands were obtained.

3. VARYING THE H ION CONCENTRATION.

Davies (1923) showed that changing the H ion concentration greatly affected the rate of reaction and hence the color of the gold formed as we would predict from the equation.

$$2\ AuCl_3 + 3\ H_2C_2O_4 = 2\ Au^{\circ} + 6\ HCl + 6\ CO_2$$

That a decrease in the H ion concentration would bring about more rapid reduction. This was found to be the case. The concentration of the standard tubes was about 0.6 N. If this concentration was lowered to 0.03 N reduction took place in the dark giving a purple band. A blue band was obtained with 0.6 N Acetic acid in the dark. Lowering the acidity to 0.01 N gave a wine colored band. Potassium and ammonium oxalate gave more rapid reduction than oxalic acid. This was again probably due to lowered acidity.

4. THE EFFECT OF TEMPERATURE.

The following table shows the effect of temperature of standard tubes exposed to noon sunlight.

TABLE 2.

Temperature OC	Time taken to obtain standard tint. min	Hue obtained
90	2.00	red
20	2.10	red
0	2.25	red
-13	2.66	red

The above experiment showed that the temperature coefficient was small. Most photochemical reactions have a small temperature coefficient. Allmand (1925)

Increasing the temperature in the dark to 95 C was alone not sufficient to give colored bands.

5. AGEING OF THE STANDARD TUBES.

Davies (1926) showed that the age of a gel had a marked effect on the color of the gel and the time taken to show color. Before setting it required ten times the exposure to obtain color as that required to obtain color after the tubes had remained in the dark for eleven days. He got reduction to a blue sol at four weeks and a light blue sol at 37 days. He did not report when he ceased to get reduction.

In a similar experiment the writer got the same general results except that all the gold had been reduced at the end of 26 days.

A slight opalescence was always observed upon the setting of the silicic acid gels with or without gold chloride. This probably had a bearing on the marked decrease in the time taken for reduction after setting.

The writer has tubes which have been exposed to daylight including direct sunlight every day for eight months without syneresis or any marked change in the gels having taken place.

6. VELOCITY OF REACTION AND INTENSITY OF RADIATION.

Standard tubes were placed at 10,20 and 30 cm from a 300 W Mazda lamp. The tubes were kept cool by means of an electric fan. The time taken for a given color to be formed at the various distances by various intensities is shown in Table 3.

TABLE 3.

No. of tube	Distance from the lamp	Time taken to obtain a given color. hours	Color	Intensity g/cals/cm/min
1	10	1.25	blue	0.00306
2	20	7.00	blue	0.01224
3	30	11.45	blue	0.02754

The effect produced on a standard tube by direct sunlight 11 am pyrheliometer value 1.36 g/cals/cm^2/min was compared with the effect produced by a 300 Watt Mazda lamp at 20 cm. Taking the value of the sunlight as 100 per cent the value of the intensity of radiation from the lamp at this point was found to be 0.9 per cent. This value was determined by means of an ecological photometer invented by Klugh (1925). The results are shown in table 4.

TABLE 4.

No. of tube	Time taken to obtain given reduction min	Light source	Ratio of Intensities
1	2.1	sun	111
2	263	300 Watt Mazda 20 cm	

These are the mean values of three determinations.

7. INTERMITTENT EFFECT.

If the velocity of nuclear formation is autocatalytic the same quantity of light given intermittently should have produced greater reduction for the same total quantity of radiation. A number of experiments to study this were carried out. The same general result was obtained from each, namely that there was very little difference in the effect of the same quantity continuously or intermittently. If there were any difference the greater effect was due to the continuous light. In one of the experiments a tube was exposed continuously to the sun for three minutes developing considerable reduction. A similar tube was exposed for a total period of three minutes but in 6 exposures of 30 seconds at 30 second intervals. The resulting effects were almost identical. If there was any difference, there was a slightly greater reduction in the tube exposed to the continuous radiation. Such differences as might exist were very difficult to judge.

Another set of tubes was exposed in 20 second exposures followed by 20 second intervals. The tube exposed to continuous radiation gave visible reduction first in 3 min 57 seconds, the other gave visible reduction in 3 min 59 seconds.

8. INDUCTION PERIOD AND PHOTOCHEMICAL AFTER EFFECT.

The question arose, would a reduction once started in any part of a gel spread in the dark to the other portions of the gel. To show this the whole of a tube was covered with paper except a small slit on one side. This was given an exposure to direct sunlight whereupon an area in the gel corresponding to the area of the opening was reduced to a depth of about 3mm. This portion kept the same dimensions for thirty minutes even when kept for thirty minutes at a temperature of 80 degrees. Further experiments in which banding was effected by covering parts of the tubes with paper showed that the bands did not spread.

Of course we must not confuse this with the induction period, which takes place before we can actually see evidence of reduction. We would naturally expect that the gold nuclei when first formed would be too small to absorb selectively visible radiation, but when once formed would grow in the dark to give a colored gel. The writer observed a number of cases of this and many cases in which a color previously formed greatly intensified afterwards; sometimes to such an extent that the gel became quite opaque.

9. RHYTHMIC BANDING.

A set of 24 tubes was made up containing 1 ml 1 per cent gold chloride per 25 ml of gel made by mixing equal volumes of sodium silicate 1.160 and 21962 N H_2 SO_4. Saturated oxalic acid was placed on the tops of the gels after setting. These were exposed an hour a day, each day for two weeks. The remaining ten were exposed similarly at one month intervals. In every case during the first hour exposure, a heavy band average width of 5 mm formed. The band was a heavy ruby color but not transparent. During the first 24 hours in the dark, a greenish band, varying in depth from 14-19 mm was formed. The subsequent exposure of one hour produced a band of ruby, shading to blue of an average depth of 8 mm. During the second and remaining dark periods no large green band formed but between the clear space 2 mm between the previous day's exposure a tinge of green was noticed. In all cases the red was formed at the top shading into blue at the bottom. On a bright day the band would be four-fifths red. Dull light increased the proportion of blue. In no case did we get either an all blue or an all red band. The greater the intensity of light, the wider was the band. But acting against this, the deeper the diffusion on the narrower the band so that the tube contained bands of varying sizes.

The depth to which the oxalic acid had diffused was shown by gleaming crystals of gold. Whenever a band formed it formed approximately 1 cm above the lowest point where crystals could be seen. Both Davies and Cadenhead made a similar observation. The depth of gel in the tubes was 11 cm. In two weeks crystals of gold filled the tube from top to bottom. When this had taken place no bands were formed on exposure. For example, if we place the saturated oxalic acid above the gel and kept it in the dark for two weeks subsequent exposure a band at the very bottom of the tube. The usual green band formed during the period in the dark following the first exposure, was formed in every case. But between it and the bottom only gold crystals could be observed. If the tube were kept longer than two weeks in the dark no band would form on exposure.

An outstanding feature in the formation of a band was the fact that it formed uniformly throughout its depth and did not build up from the top downward.

The actual age from time of setting of the gel made very little difference in the nature of the bands formed.

10. CRYSTALIZATION VELOCITY AND DIFFUSION.

In the course of my experiments I observed that when a band was formed it became heavier in the dark and that if the band was large enough it removed all the gold chloride so the further exposure gave no reduction and time gave no crystal growth. In order to test this out I made a set of 10 tubes 4 mm in diameter and 19 mm long as follows: Standard reaction mixture was drawn up into 4 mm glass tubing in lengths of 1 cm. The ends were plugged and the gels allowed to harden in the dark. After the gels had set the tubing was cut in the required lengths and sealed. The central portions of the tubes were covered with paper leaving 4 mm on both ends uncovered. The whole set was then exposed to the sun for 7 min at 11 a.m. Bright ruby bands developed leaving the central portions colorless. These portions were then covered with 1 cm bands of paper in such a way that on exposure to the sun 5 colored bands would form, one in the centre of the tube with two on either side of it, separated in each case by colorless zones. The tubes were given a second exposure for 7 min at the times shown in the Table 5. The time taken for the middle and outer bands to become visible and also the color is recorded in the table

TABLE 5.

No.	Times between 1st and 2nd exposure days	Time when reduction first observed		Color
		Outer bands min	Middle bands seconds	
1	1	2.10	2.10	both red
2	2	2.26	2.46	both red
3	3	2.10	2.41	both red
4	4	2.25	2.52	both red
5	5	2.02	2.50	both red
6	7	1.56	2.24	both red
7	11	2.11	2.35	both red

TABLE 5. (continued)

No.	Time between 1st and 2nd exposure days	Time when reduction first observed		Color
		Outer bands min	Middle band seconds	
8	13	1.42	2.21	both red
9	17	1.30	2.03	outer bluish inner reddish blue
10	19	1.22	2.03	all bluish outer bands fainter

It was quite hazy when No. 7 was exposed. The others were exposed to continuous clear sunlight as near to 11 a.m. as possible. The light was constant for three minutes at least in every case. In no case did the time vary 45 minutes each way from 11 a.m. The time given for 7,8,9, and 10, was closen on account of favorable weather on those dates.

11. THE EFFECT OF GRAVITY ON THE DIFFUSION OF OXALIC ACID.

Two diffusion tubes were made up and saturated with oxalic acid, poured on the top of the gel and allowed to remain for 10 min. and then poured off. One tube was formed upside down and the two were placed side by side where they would be subjected to changing light. In a week's time both had developed the usual bands, except that they were less dense and contained a greater proportion of blue. The remarkable thing about the experiment is the fact that bands of the same color developed exactly the same place in each tube. It was difficult to tell them apart.

12. ABSORPTION SPECTROGRAMS OF THE REACTION.

Absorption spectrograms of glass filters, gelatin filters, 1 per cent solutions of various dyes and different stages of the reaction in a standard mixture, were taken with both a glass prism and a quartz prism spectrograph.

A 1 cm thickness of gel containing gold chloride in the concentration used in the tubes showed a heavy absorption band starting at 390 Mu becoming very dense from 365 Mu to the end of the transmission of the glass at about 325. We might expect this from the color of a solution of gold chloride.

The other interesting feature is shown in Table 6 which was drawn up from the results of an experiment the spectrograms of the gel alone, the gel plus gold chloride, the gel plus oxalic acid no gold chloride the gel plus oxalic and gold chloride, the various stages of the reaction. The spectrograms were taken by means of an iron ARC and a glass prism spectrograph. The mixtures were placed in a glass cell of 1 cm inside thickness, and wells 1 mm.

In the Table the mixtures are shown as follows:

A - gel

B - gold chloride

C - oxalic acid

TABLE 6.

No.	Mixture	Length of exposure to direct sunlight min	Region in which absorption took place Mu
1	A		None down to 325
2	A B		325-390, 410-480
3	A B C		Same as 1.
4	A B C	3.0	325-340
5	A B C	5.2	Same as 1 ruby color in the meniscus but not opposite slit
6	A B C	6.25	Slight absorption in the blue only. Ruby opposite the slit.
7	A B C	8.5	Heavy ruby all over. Exposure too short. Absorption everywhere a few lines shown in the ultra violet.

The reaction was produced by exposure to a bright sun at 4.30 p.m. through a closed window.

13. REGION OF THE PHOTOSENSITIVITY OF GOLD CHLORIDE.

In order to determine this the following experiment was carried out. A box was constructed containing a number of compartments 2.5 by 2.5 by 1 cm depth. The compartments were lined with white paper, and the top was covered with various filters. The liquid filters were contained in low glass cells open at the top, the glass being 1 mm thick. Small tubes of thin glass were used so that there was only 1.5 cm of glass above the gel. The exposures were made to direct sunlight at noon. The times taken to develop bands the color of the bands and the transmission of the filters are shown in Table 7. The maximum transmission is shown between the underlined wave lengths.

TABLE 7.

Filter	Transmission between the following wave lengths Mu	Time to develop band min. secs.	Color
Direct sun	298-556-730	4 : 00	red
Corning Uviol 3 mm	298-310-410-435	5 : 25	red
Corning Noviol 3 mm	365-390-730	8 : 40	red
Indigo 0.1 per cent sol 3 mm	385-395-425-430	9 : 25	red
Acid green 0.1 per cent sol 3 mm	346-350-396-400 450-340	7 : 33	red
Tartrazine	490-700	3 hours	Nil
Gold Chloride	260-270	3 hours	Nil

Absorption Max. 290-325

Transmission increases towards 500

DISCUSSION OF RESULTS.

COLOR OF THE BANDS.

The results outlined in Experimental showed that the size and shape of the gold particles and hence the color of the bands was a function of the rate of reaction. Red bands were formed when the reaction was rapid due to

1. Intense radiation
2. High concentration of reducing agent
3. Low acidity
4. Optimum concentration of gold chloride

On the other hand blue bands formed under the following conditions, giving a slower rate of reaction.

1. Weak radiation
2. Low concentration of the reducing agent
3. High acidity
4. Concentration of gold chloride greater or less than the optimum.

Green bands were observed only in the case of rhythmic banding. They formed in the night when the visible radiation was at a minimum, but when a fairly high concentration of reducing agent was present.

The yellow macroscopic crystals formed when all factors were favourable with the exception of the radiation or when intense radiation without any added reducing agent was present. It follows of course that purple bands are due to a mixture of a red and a blue. In such sols centrifuging Freundlich (op. cit.) has separated the mixture. The effect of grain size of gold on its color is shown in the following table (Mellor 1923). To these is added Zsigmondys estimate (1917) of grain size.

Conc. of Sol	Color of liquid	Opacity	Average size of grain Mu
1: 1,000	Deep purple red	Opaque in thin layers	75
1: 10,000	Purple red	Opaque in 14 cm Layers	38
1: 100,000	Rose-red	Perceptible in 1 cm layer	10

Conc. of Sol	Color of liquid	Opacity	Average size of grain mu
1: 200,000	Very pale rose	14 cm layers rose color	6
1: 500,000	Scarcely perceptible	14 cm layers perceptible	3
1: 1,000,000	Colorless	Colorless	

THE THEORY OF THE COLORED SOLS.

The question of the color of gold sols has attracted a considerable amount of attention. Svedberg (1924) stated : "There is no simple relationship between the size of the particles and the light absorption and scattering respectively but it is possible to find out experimentally certain emperical relations."

The color of the gold sols may be traced to the fact that gold has an absorption maximum in the green and a reflection maximum in the yellow. With small particles absorption preponderates: with large particles reflection. (Freundlick 1926).

It is often taken for granted that particles in a blue sol are larger than those in a red sol. This is true in a good many cases bit not necessarily always so. Steubing (1908) prepared blue sols by the reduction of gold chloride by hydrazine in the cold. Reduction in the hot gave the usual ruby sol. He obtained curves for the absorption and radiation of these sols.

If we illuminate a sol with unpolarised light, the state of polarisation of the diffracted light varies with the angle of observation and the size of the particles. With very small particles, the light diffracted at right angles to the original direction is completely polarised: at all other angles the proportion of light polarized decreases symmetrically towards the direction of entry and exist of the original beam. For particles larger, the diameter of which approaches the wave-length of visible radiation, the maximum is displaced, that is the angle at which light contains a maximum proportion of polarised light: the angle becomes greater, the polarisation maximum approaches the direction of the exit.

This gives us a very good means of determining the size of the particles. If the particles are 50 mu or less the polarization maximum is at 90 degrees. Steubing's blue sols were of this type. The absorption curve was of a distinctly different form and much lower radiation was shown. The light radiated laterally appeared greyish-green.

Garnett (1904) and Mie 1905 calculated the absorption maximum for different sizes of gold particles assumes to be spherical on the Basis of Rayleigh's absorption formula.

$$J = \text{constant} - \frac{v^2}{\lambda^4}$$

where v is the volume of the particle, the intensity of scattered light. His calculations showed that a sol with particles of 25 mu would be red absorption maximum at 530 mu and the radiated light would constitute only a small fraction. His calculations also showed that increasing the size would shift the absorption maximum and the radiated light to the longer wave lengths thus giving blue or green sols both having a greater proportion of radiated light.

Steubing showed that experiment agreed with the calculations except in the case mentioned above.

Gans 1912 extended Mie's theory to non-spherical particles with the result that for both discs and rods the absorption maximum compared with spherical particles was displaced towards the red. Hence we see a reason for Stuebing's blue sols.

The conclusions drawn from the above elsewhere may be summed up in the following table.

TABLE 10.

Size	Color by Transmitted light	Radiated light	Plane of max. polarization	Probable shape
6 Mu	Red	very faint green	90	octahedra
25 Mu	Red 534	Green 560	90	octahedra
100 Mu	Blue 605	Yellowish brown	90	irregular
150 Mu	Green	Brownish	90	irregular
50 Mu	Blue	Greyish green	90	disc.

Massive gold when compact reflects yellow.

Massive gold when porous reflects brown to black.

Thin films of gold transmit green.

Thus we see that in the case of selective reflection some or all of the light which is absorbed by a given metal is reflected or radiated from the surface if compact.

Davies (1922) and Cadenhead (op. cit.) stated that the blue bands contained larger particles than the red, due to the slower rate of reaction building up larger particles. The writer is in complete accord with this. A glance at the radiated light containing red and blue bands will show the more intense and yellowish brown radiated light from the blue particles.

The writer has observed blue bands in which the particles are smaller than those in the red. They were observed under the following conditions: A tube containing less than the optimum amount of gold chloride was exposed to strong radiation from the sun. When reaction first started the band was blue by transmitted light and feebly radiated greyish green. It then slowly became slightly reddish and remained so, but never became intense. The reverse of a red changing to a blue was never observed. Apparently when any amount of colloidal gold is formed it soon removes most of the gold chloride so that the bands do not grow into blue. The phenomenon of the blue bands containing the smaller particles looks like another case of Steubing's (op. cit.) blue sols, which contained disc shaped particles. Reference to a suggested reason for these will be made later.

SHAPE OF THE MACROSCOPIC CRYSTALS.

The small gleaming yellow crystals appeared to have macroscopically the form of octahedra and tetrahedra. However when a hand lens was used it was found that the crystals were really flat hexagonal and triangular flakes. Most of the tubes contained approximately equal numbers of both forms. A few transitions forms were found. A great many of the crystals were twinned. The triangular twinned looked very much like tetrahedra, but in more careful examination showed that such was not the case.

An attempt was made to examine the crystals by means of a microscope. The writer was unable to cut a section of the gel without it crumbling to pieces so that it could not be examined between a slide and coverglass. An examination of pieces of the gels placed on the slide without a coverglass yielded no further information. For the same reason the writer was unable to study the colloid particles with the ultramicroscope.

VELOCITY OF NUCLEAR FORMATION AND VELOCITY OF CRYSTALLIZATION.

The reduction of gold chloride to colloidal and macroscopic gold crystals gives a good illustration of the difference between velocity of nuclear formation and velocity of crystallization. Velocity of crystallization here appeared to be independent of light. It obviously was not the same for every face of the crystal. Once the nuclei were formed they developed in the light or dark until all the gold was used up.

In contrast to this the intensity of radiation along with the other well-known factors was the controlling power in the velocity of nuclei formation. Radiation increased the rate of reduction and billions of nuclei were formed at once and crystallization was able to proceed even in the dark, but the particles could not grow to any size before all the gold ions were used up. This tells us why when a tube is given a sufficiently long exposure, though not long enough to produce visible crystals, growth of colored bands will take place in the dark.

INTERPRETATION OF RESULTS.

I interpret the results of the observations as follows:
The photosensitivity begins in the neighborhood of 450 mu and increases with the frequency down past 325. The fact that the reaction is more rapid when insolated in a quartz tube as compared with glass shows that in spite of the lower intensity ofthe sun below 325, the reaction was the more rapid due, of course, to the increased transmission by the uviol and the lower wave-lengths. Table 7 gives the transmission of the filters, showing how far the uviol and noviol deviate from

the regions wanted and thus accounting for the reaction found under the noviol filter. The greater effect of the near ultra violet is made more definite still when we consider that the transmission of the uviol to the near ultra violet of the sun was only 65.2 whereas the total transmission of the noviol was over 80. Another point clearly brought out in Table 7 is that in spite of the fact that the maximum radiation of the sun is in the region near 550 mu (at Washington Bigelow 1918) if the portion below 490 was cut out no reduction took place in an exposure of three hours.

CONCLUSION.

In conclusion the results of this very brief investigation point out a very instructive and important field in photo and colloid chemistry the surface of which has only been scratched. The effect of radiations on the reduction of gold ion in silicic acid gels affords a splendid method of studying the rates of reaction, velocity of nuclear formation, velocity of crystallisation, and their relations to radiation, due chiefly to, the following facts: that the reactions are slow; that we have considerable reliable information as to the relation of color and particle size of gold and lastly a silicic acid gel has the very necessary features namely, high transmission of ultra violet and visible radiation, stability, inertness to many reagents and reproducibility.

The writer is quite well aware of how far the above methods and technique depart from an exact quantitative method. It might be called semi-quantitative but that is all.

SUMMARY.

1. A number of points in connection with the photochemistry of the reduction of gold ion by oxalic acid in silicic acid gels have been studied with the conclusion that:

(a) The maximum sensitivity is in a region of lower wave-length than 330 mu.

(b) This maximum corresponded with the maximum (290-325) in the absorption curve of gold chloride.

(c) This maximum in the absorption curve shifted towards and into visible as the size of the particles increased.

(d) What is true for a number of photochemical reactions is also true for this system namely: that the velocity of reaction increased more rapidly than the intensity of radiation, the temperature coefficient was low and irradiation given intermittently has less effect than an equal irradiation given continuously.

2. The relations between size of particles and color; the rate of nuclear formation and velocity of crystallization; and the equilibrium represented by the equation, have been investigated and the results applied in explaining the mechanism of the formation of the diurnal and pseudo-bands investigated by Davies and Cadenhead.

PART 111

A FEW BIOTIC EFFECTS OF ULTRA VIOLET RADIATION.

The results of the work on the "Light Tower" have been given in a separate report. In this section I will deal only with several attempts by Klugh and the writer to observe the physiological effects. These experiments are very rough and incomplete, due to lack of time, material and apparatus.

Having observed that the near ultra violet was lethal to a certain species of copepods, it occurred to us that it would be a good idea to see if we could find out what was absorbing the radiation, as it follows from the first law that something must be absorbing the lethal radiation.

Attempts were made to remove the liquid constituents of copepods, fish eggs, etc., and place them in a tiny quartz cell in order to obtain the absorption spectrum. The greatest difficulty in this connection lay in the fact that it was extremely difficult to get pure samples and also that changes in the phase relations took place before a spectrogram could be taken. In order to get around this latter difficulty we mounted a copepod on the slit of the spectrograph and took the absorption through the animal. It was surprising how definite an absorption band was found in the near ultra violet. This region of the spectrum we had previously proved was lethal. Just what was giving the absorption we do not know. The constituent causing the absorption may be a photosensitiser.

Examination of the colloidal nature of these systems was rendered very difficult owing to the fact that their phase relations changed so rapidly with time.

The writer had a dark field condenser and a Jentzch condenser for examining sols, but found the former unsatisfactory for examining sols which changed rapidly with time, while the latter condenser required a considerable quantity of sol.

A very satisfactory scheme was found to be a combination of the Jentzch condenser without the window and a water or oil immersion objective. The condenser gave a concentrated disc of light orthogonal to the axis of the objective. A drop of sol was placed on the objective and the drop lowered into the disc of light.

By this means very small quantities of a given sol could be examined in less than ten seconds. Obviously this method has the further advantage in the case of cleaning and hence the number of samples examined in a short time can be made quite large.

MECHANISM.

From the very limited experimental work carried out by the writer it is impossible to attempt to hypothecate any sort of mechanism. It was observed that the death of the animal was accompanied by an opacity in the sol portion caused by some sort of coagulation. Further than that it is very difficult to postulate.

However it would not seem fitting to leave off this section without saying a few words about the mode of action in general. I will merely quote a few statements from the work of those who have studied the problem.

"Hinrichs has briefly reviewed the various views as to the action of ultra violet radiation. It produces primarily a surface effect, it inhibits the action of harmones and enzymes; it kills protoplasm by coagulation and not by the inhibition of enzyme action; its effect is due to sensitization to heat; its action interferes with the time relations in a system of interdependent, progressive processes; its effect is due to the precipitation of the proteins of protoplasm following electron emission; certain constituents of protoplasm, as tyrosin and phenylalanin, act as optical sensitizers rendering living cells susceptible to the toxic action of ultra violet radiation.

The majority of reactions caused by radiation are due to oxidations and reductions, or processes in which changes in valency take place and there is some evidence to show that the biological action of short waved radiation is due to its reducing properties, to the splitting off of O_2 molecules from the easily deoxidizable plasma compounds.

Clark elaborates a theory of the formation of images on photographic plates which in its application to the living cell may be summarized as follows: Energy shorter than 300 mu acts on the living cell by ionising its photo-electric constituents thereby leading to photochemical action. Energy longer than 300 mu acts in the same way in the presence of sensitizers which so affect the surface conditions of these constituents that their photoelectric threshold is shifted into the visible, and they therefore become ionised with resulting chemical action when illuminated by visible or near ultra violet energy."

It is rather difficult to develop any theory to fit the experimental facts when our knowledge of the energy⇒matter equilibrium of the simplest systems we know in the gaseous phase are not clearly understood. Perhaps we will have to wait awhile and see what wave-mechanics will bring forth. Our conception of such fundamentals as radiation and electrons is none too certain at the present time. However theories are very necessary right or wrong because of the old experimental evidence that is gathered together and because of the wonderful stimulus that is given for the collection of new experimental data . Otherwise we would only have scattered here and there a number of isolated experimental facts. The more theories that are put forth, the more evidence from widely scattered sources will be gathered together and hence the more comprehensive the theory we temporarily choose to fit the evidence we have in hand.

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NOTE. Particle size in Water at St. Andrews

The writer attempted to determine the size of the larger colloidal particles found in the water immediately after a storm by measuring the rate of settling and calculating the size from the following formula of Stokes:

$$V = \frac{2r^2\ (s-s0)\ \ g}{9\ n}$$

Where r is the radius of the particle
ssis the specific gravity of the particle
s0 is the specific gravity of the water
n is the viscosity of the water
g is the gravity constant
V is the rate of settling

The writer tried to locate and follow the horizons by means of the Tyndall cone from a strong incandescent lamp which could be focussed on any portion of a tall cylinder containing the water. There did not appear to be a sufficient enough concentration of colloidal material, of the various sizes to give any clear cut horizons. Most of the suspended matter settled out in 24 hours.

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McGill University.
April 1928