AN EXPERIMENTAL METHOD OF STUDYING SUBSTITUTION AND DECOMPOSITION REACTIONS BY MEANS OF PHOTOELECTRIC CELL. I. ABSORPTION OF LIGHT OF WAVE LENGTHS 3650 Å AND 4360 Å BY VAPOURS OF VARIOUS HALOGEN DERIVATIVES OF ETHANE.

By Senzo HAMAI.

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In a previous paper,[1] the author gave a suggestion as to usefulness of the phenomena of light absorption as applied to the investigation of certain chemical reactions especially where the reactions are rather slow and also an ordinary method of following the reaction fails. However, the idea requires rather an expensive apparatus[2] of infra-red analysis which, in an ordinary laboratory, can not be easily available. In order to overcome such a difficult situation, naturally we consider an alternative plan which may be used equally as well for the purpose.

Use of a photoelectric cell[3] is rather numerous, but, in the fields of chemical reactions, it is more or less limited and very scanty; for this reason it would be profitable to publish a few details of experimental apparatus and method to show its applicability.

The principle involved is rather well known. According to the law of Lambert, there exists the relation:

$$I = I_0 e^{-\beta d}, \qquad (1)$$

where I is transmitted light intensity, I_0 initial light intensity, β the specific light absorption coefficient, and d the thickness of the medium, but this can be transformed into:

$$I = I_0 e^{-\alpha c d} \quad \text{for} \quad \beta = \alpha c, \qquad (2)$$

where α is the absorption coefficient and c concentration of the medium in mol. This is a special case of Lambert's law known as the law of Beer.

(1) S. Hamai, this Bulletin, **9** (1934), 542.
(2) P. C. Cross and F. Daniels, *J. Chem. Physics*, **1** (1933), 48.
(3) N. R. Campbell and D. Ritchie, "Photoelectric Cells."

Since the laws of Lambert and Beer are valid only for monochromatic light, β and α vary with λ; furthermore, the law of Lambert presupposes only the homogeneity of the layer, whereas for the latter, because of its inclusion of the concentration of the medium, the independence of optical properties on the concentration has been assumed. Therefore in Beer's law we find several deviations as already recorded by various authors, but they do not very seriously interfere with our present purpose. By this relation, we can follow the reaction in which change of the reactants can be detected with a given λ which is absorbed by one of the constituents of the system; the amount of absorption of light directly gives the amount of substance present with known α of that substance, and with a given thickness of the medium. Batley,[4] using the light absorption with known extinction coefficient as a means of following the reaction of iodine with ethyl alcohol, investigated it spectroscopically.

The experimental apparatus and some of the experimental data will be described here in order to show the method is applicable for the purpose.

Experimental Apparatus. As shown in the diagram, the apparatus consists of a light source, colour filters,[5] absorption tube quartz-plated on both ends and inserted in a dark box, and the photoelectric cell with its recording instruments—amplifying circuit[6] of the photo-current and galvanometer.

Experimental Procedure. In the first place, the whole apparatus is set so that there is no current flowing in the galvanometer when there is no light falling on the photoelectric cell. In order that the perfect balance of the circuit is to be obtained, it is necessary to have as much similar vacuum tubes (UX 201 A) as possible; but ordinarily the characteristics of the vacuum tubes are not identical, hence we must balance the bridge by adjusting R_2. When the light from the mercury lamp is allowed to fall on the photoelectric cell, there is a steady deflection of the galvanometer depending on the photo-current which is amplified by the above bridge circuit. After the zero position in the galvanometer is obtained, to the evacuated absorption tube, the gases or vapours which are to be experimented upon, are introduced; and then the light from the mercury lamp filtered by the above combination of filters[5] are passed by opening the shutter S, and then the steady deflection of the galvanometer is read. And

(4) Batley, *Trans. Faraday Soc.*, **24** (1928), 438.
(5) (a) Wratten light filters, Eastman Kodak CO.
(b) M. Ritchie and R. G. W. Norrish, *Proc. Roy. Soc.*, **140** (1933), 99.
(6) Hughes and Dubridge, " Photoelectric Phenomena " ; see also (3).

also the deflection caused by the light through the empty tube before and after the experiment, is recorded so that we can see whether any change occurred during a run. The amount of deflection with or without gases or vapours will give the amount of the absorbing materials.

The following materials at 0° and room temperature were investigated, in the case of hydrogen chloride at various pressures, and all for wave lengths 4360 Å and 3650 Å.

(1) $C_2H_4Cl_2$ [1:2], b.p. 83°C.
(2) $C_2H_4Br_2$ [1:2], b.p. 129°C. } Takeda's products.
(3) $C_2H_3Cl_3$ [1:1:2], b.p. 113.6–114°C., Eastman's product.
(4) $C_2H_2Cl_4$ [1:1:2:2], b.p. 145°C., Kahlbaum's product.
(5) C_2HCl_5, b.p. 158.5–159.6°C., Eastman's product.
(6) C_2Cl_6, m.p. 183°C., Kahlbaum's product.
(7) HCl.
(8) Cl_2.

(1), (2), (3), (4), and (5) were all twice distilled and C_2HCl_5 was again distilled under reduced pressure.

Hydrogen chloride was prepared by dropping concentrated hydrochloric acid into concentrated sulphuric acid, washed twice through concentrated sulphuric acid, and then condensed twice with liquid nitrogen; only the middle portions were used after passing through a calcium chloride tube.

In every case, excepting (8), after the substance was exposed to the light, 3650 and 4360 Å, the vapour or gas was condensed out with liquid nitrogen and mixed with KI solution (0.1 N) in order to see whether any decomposition had occurred. None seemed to show even a trace of decomposition by having absorbed these light waves. (For corrosive gas—chlorine which has only been used in the qualitative experiment—it is expected to be investigated more thoroughly by this method; for measuring the pressure a click gage which has been described by Smith and Taylor[7] is used.)

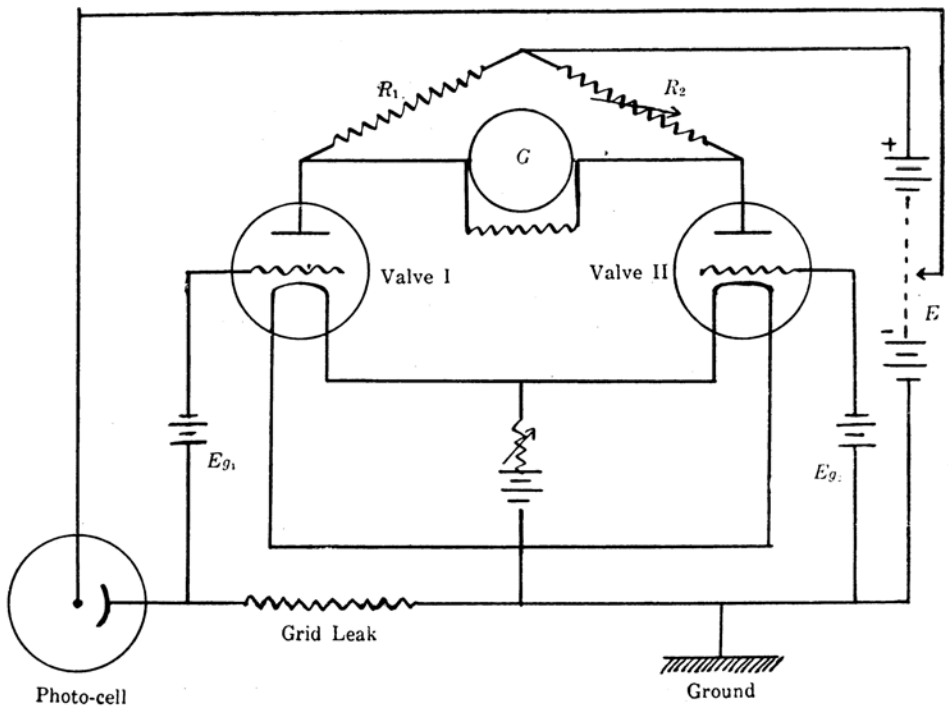
The results of these preliminary absorption experiments of above mentioned substances (including the qualitative data for chlorine) are tabulated in Tables 1–8. As shown in the tables, all of these materials except chlorine are transparent to 3650 and 4350 Å. The absorption experiments for the reaction system involving chlorine and various halogen derivatives of hydrocarbons are now under way; we hope we be able to report on these soon.

(Sample of quinine hydrochloride which has been used in the filter solutions was given generously to us by Prof. S. Fujise of the Bio-chemistry

(7) D. F. Smith and N. W. Taylor, *J. Am. Chem. Soc.*, **46** (1924), 1393.

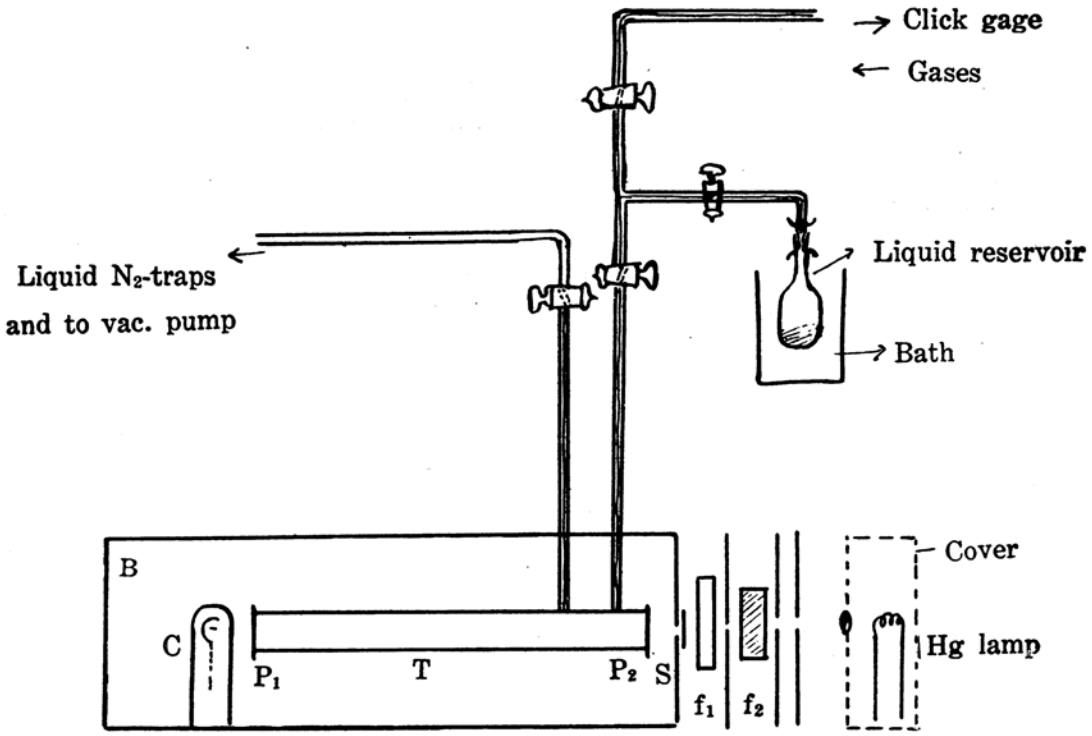
Institute of this University, to whom the author desires to thank for his kindness. Also the writer expresses very cordially his gratitude to Assist. Prof. T. Tonomura who kindly supplied a "one-stage-amplifying apparatus" used for the click gage, and to Assist. Prof. M. Arii of the Inorganic Chemistry Institute, who kindly gave $Cu(SO_4)(NH_4)_2SO_4$ used for the filter solutions.)

As shown in the case of the chlorine absorption, the present apparatus is very convenient, because only chlorine absorbs these waves and all other halogen derivatives have been found to be perfectly transparent to these waves, so that the reaction in which chlorine is substituted in these halogen derivatives of ethane as already published[1] where the amount of chlorine decreases as the reaction proceeds with no change in pressure, and where an ordinary method of following the reaction is powerless, can possibly be studied. Also for a certain decomposition reaction such as $C_2H_4I_2 \rightarrow C_2H_4 + I_2$ may easily be studied owing to the very effective absorption of these light waves, suitably selected, by halogens in general.



Valve I, II: UX 201 A

Fig. 1.



B.....Dark box
C.....Photo-cell (cesium)
T.....Absorption tube
P_1, P_2...Quartz plates
f_1, ...Wratten filter 18 A
f_2 .....Filter cell (quartz-plated) 3 cm. 6% $CuSO_4$ solution
S.....Shutter

Filters: For $\lambda = 3650$ Å, f_1 = Wratten filter 18A, f_2 = 3 cm. layer 6% $CuSO_4$ solution.
For $\lambda = 4360$ Å, without f_1, f_2 = 3 cm. $CuSO_4$ (6%) solution + 3 cm. 2/3% quinine hydrochloride + 3 cm. 1% $Cu(SO_4)(NH_4)_2SO_4$.

Fig. 2.

Table 1. Trichlorethane ($C_2H_3Cl_3$).

(1) $\lambda = 3650$ Å

Deflection			Pressure	
Vacuum	With vapour			$R_1 = 5377\ \Omega$
	Room temp.	0°C.		$R_2 = 2810\ \Omega$
cm.	cm.	cm.	mm.	$i_{Hg} = 2.0$ amp.
2.70	2.70	2.70	7.5	
2.70	2.70	2.70	7.5	$i_f = 0.26$
2.70	2.70	2.70	7.5	

(2) $\lambda = 3650$ Å

Vac.	18°C.	
cm.	cm.	$R_1 = 5377\ \Omega$
18.7	18.7	$R_2 = 4837\ \Omega$
18.7	18.7	$i_{Hg} = 2.20$ amp.
18.7	18.7	$i_f = 0.26$

(3) $\lambda = 3650$ Å

Vac.	17°C.	(The reservoir in ice bath)
cm.	cm.	$R_1 = 5377\ \Omega$
8.5	8.5	$R_2 = 4677\ \Omega$
8.5	8.5	$i_{Hg} = 2.0$ amp.
8.5	8.5	$i_f = 0.26$

(4) $\lambda = 4360$ Å

Vac.	17°C.	
cm.	cm.	$R_1 = 5377\ \Omega$
7.5	7.5	$R_2 = 4597\ \Omega$
7.5	7.5	$i_{Hg} = 2.0$-2.1amp.
7.5	7.5	$i_f = 0.26$

(i_{Hg} = the current intensity of the mercury lamp)

Table 2.

Ethylene chloride ($C_2H_4Cl_2$).

(1) $\lambda = 4360$ Å

Deflection		Pressure	
Vac.	With vapour 0°C.		$R_1 = 5377\ \Omega$
			$R_2 = 4597\ \Omega$
cm. 17.6	cm. 17.6	mm. 23.47	$i_f = 0.26$ amp.
17.6	17.6	,,	
17.6	17.6	,,	$i_{Hg} = 2.0$

(2) $\lambda = 3650$ Å

Vac.	With vapour 0°C.	Pressure	$R_1 = 5377\ \Omega$
cm. 8.5	cm. 8.5	mm. 23.47	$R_2 = 4416\ \Omega$
8.5	8.5	,,	$i_f = 0.26$ amp.
8.5	8.5	,,	$i_{Hg} = 1.85$—1.90

(3) $\lambda = 3650$ Å

Vac.	With vapour 18°C.	Pressure	$R_1 = 5377\ \Omega$
cm. 3.6	cm. 3.6	mm. 57.97	$R_2 = 4357\ \Omega$
3.6	3.6	,,	$i_f = 0.26$ amp.
3.6	3.6	,,	
3.6	3.6	,,	$i_{Hg} = 1.90$

(4) $\lambda = 4360$ Å

Vac.	With vapour 18°C.	Pressure	$R_1 = 5377\ \Omega$
cm. 3.6	cm. 3.6	mm. 57.97	$R_2 = 4357\ \Omega$
3.6	3.6	,,	$i_f = 0.26$ amp.
3.6	3.6	,,	$i_{Hg} = 2.25$—2.3

Table 3.

Pentachlorethane (C_2HCl_5).

(1) $\lambda = 3650$ Å

Deflection		Pressure	
Vac.	With vapour 20°C.		$R_1 = 5377\ \Omega$
			$R_2 = 4357\ \Omega$
cm. 3.3	cm. 3.3	mm. 6.97	$i_f = 0.26$ amp.
3.3	3.3	,,	
3.3	3.3	,,	$i_{Hg} = 2.00$

(2) $\lambda = 4360$ Å

Vac.	With vapour 20°C.	Pressure	$R_1 = 5377\ \Omega$
cm. 2.3	cm. 2.3	mm. 6.97	$R_2 = 4357\ \Omega$
2.3	2.3	,,	$i_f = 0.26$ amp.
2.3	2.3	,,	$i_{Hg} = 2.00$

(3) $\lambda = 4360$ Å

Vac.	With vapour 20°C.	Pressure	$R_1 = 5377\ \Omega$
cm. 8.5	cm. 8.5	mm. 6.97	$R_2 = 4967\ \Omega$
8.5	8.5	,,	$i_f = 0.28$ amp.
8.5	8.5	,,	$i_{Hg} = 2.10$

Table 4.

Tetrachlorethane ($C_2H_2Cl_4$).

(1) $\lambda = 4360$ Å

Deflection		Pressure	
Vac.	With vapour 18°C.		$R_1 = 5377\ \Omega$
			$R_2 = 4820\ \Omega$
cm. 4.3	cm. 4.3	mm. 35.0	$i_f = 0.28$ amp.
4.3	4.3	,,	
4.3	4.3	,,	$i_{Hg} = 2.10$

(2) $\lambda = 3650$ Å

Vac.	With vapour 16.5°C.	Pressure	$R_1 = 5377\ \Omega$
cm. 7.1	cm. 7.1	mm. 20.0	$R_2 = 4930\ \Omega$
7.1	7.1	,,	$i_f = 0.26$ amp.
7.1	7.1	,,	$i_{Hg} = 2.08$—2.15

Table 5.
Hydrogen chloride (HCl).

(1) $\lambda = 3650$ Å			
Deflection		Pressure	$R_1 = 5377\ \Omega$
Vac.	With gas 18°C.		$R_2 = 4410\ \Omega$
cm.	cm.	mm.	
6.2	—	0.0	
	6.2	37.0	$i_f = 0.26$ amp.
	6.2	79.0	
	6.2	238.0	
	6.2	421.5	$i_{Hg} = 2.02$
	6.2	760.0	
6.2	—	0.0	
(2) $\lambda = 4360$ Å			
Vac.	With gas 18°C.	Pressure	$R_1 = 5377\ \Omega$
cm.	cm.	mm.	
2.8	—	0.0	$R_2 = 4160\ \Omega$
	2.8	9.5	
	2.8	61.0	
	2.8	408.0	$i_f = 0.26$ amp.
	2.8	423.0	
	2.8	765.5	$i_{Hg} = 2.04$
2.8	—	0.0	

Table 6.
Hexachlorethane (C_2Cl_6).

(1) $\lambda = 3650$ Å			
Deflection		Pressure	$R_1 = 5377\ \Omega$
Vac.	With vapour 16°C.		$R_2 = 4336\ \Omega$
cm.	cm.	mm.	
4.5	4.5	0.15	$i_f = 0.26$ amp.
4.5	4.5	,,	
4.5	4.5	,,	$i_{Hg} = 2.20$
(2) $\lambda = 4360$ Å			
Vac.	With vapour 18°C.		$R_1 = 5377\ \Omega$
cm.	cm.		$R_2 = 4746\ \Omega$
9.0	9.0		
9.0	9.0		$i_f = 0.28$ amp.
9.0	9.0		$i_{Hg} = 2.1$

Table 7.
Ethylene bromide ($C_2H_4Br_2$).

(1) $\lambda = 3650$ Å			
Deflection		Pressure	$R_1 = 5377\ \Omega$
Vac.	With vapour 17.5°C.		$R_2 = 3506\ \Omega$
cm.	cm.	mm.	
2.1	2.1	10.0	$i_f = 0.26$ amp.
2.1	2.1	,,	
2.1	2.1	,,	$i_{Hg} = 2.1$
(2) $\lambda = 4360$ Å			
Vac.	With vapour 17°C.	Pressure	$R_1 = 5377\ \Omega$
cm.	cm.	mm.	$R_2 = 5416\ \Omega$
5.4	5.4	10.0	
5.4	5.4	,,	$i_f = 0.28$ amp.
5.4	5.4	,,	$i_{Hg} = 1.93$

Table 8. Chlorine (Cl_2).

(1) $\lambda = 3650$ Å		
Deflection	Pressure	At 18°C.
		$R_1 = 5377\ \Omega$
cm.	mm.	$R_2 = 4957\ \Omega$
15.0	0.0	$i_f = 0.28$ amp.
15.0	0.0	$i_{Hg} = 2.1$
15.0	0.0	
0.0	255.97	(Complete absorption)

(2) Chlorine is pumped out gradually		
Deflection	log I/I_0	mol/liter*
cm.		
8.0	0.2730	9.4×10^{-5}
11.5	0.11539	4.0 ,,
12.0	0.08691	3.0 ,,
12.4	0.08267	2.9 ,,
13.4	0.04899	1.7 ,,
14.0	0.02996	1.0 ,,
14.5	0.01572	5.4×10^{-6}
15.0	—	0.0

*Calculated from $I = I_0\times10^{-\alpha cd}$, where, $d = 100$ cm., $\alpha = 29$[8] at 18°C.

(8) G. E. Gibson and N. S. Baylis, *Phys. Rev.*, **44** (1933), 188–192.

Summary.

(1) An experimental technique, by which the halogen substitution reaction can be studied by using a photoelectric cell, is described. This may well also be applied to studying decomposition reaction where substances involved are susceptible to absorption of the light waves suitably selected.

(2) Absorption of light by the various organic vapours, hydrogen chloride, and chlorine has been studied by this apparatus, and it has been found that all except chlorine are transparent to 3650 and 4350 Å from the mercury lamp as a light source.

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The Laboratory of Theoretical Chemistry, Faculty of Science,
Tôhoku Imperial University, Sendai.