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# ON THE BECQUEREL EFFECT OF COPPER OXIDE ELECTRODE IN ALKALI SOLUTION.*

## Some Considerations from the Stand-points of Reaction Kinetics and Thermodynamics.

By Nagao Hayami.

Since the discovery of the Becquerel effect[1] of a copper oxide electrode, many studies[2] have been made on the effect and yet there was no satisfactory theory to elucidate the mechanism of the effect because of disagreement in experimental results. Several years ago, Prof. S. Horiba and the author[3] found that the disagreement was due to the fact that those studies were undertaken with the copper oxide electrodes not in complete equilibrium, and so they investigated the effect with the copper oxide electrode considered to be in complete equilibrium and proposed a theory on the effect. Long after cuprous oxide film was immersed in alkali solution, a black cupric oxide film was obtained by the catalytic action of alkali. The copper oxide electrode thus obtained presented a constant voltage in the dark, that is, it was regarded as an electrode in such an equilibrium as $2CuO \rightleftarrows Cu_2 + \frac{1}{2}O_2$. Using this electrode, Prof. S. Horiba and the author studied the Becquerel effect of the following two cells:

$$[A] \quad Cu \left| \underset{\text{equilibrium film}}{Cu_2O,\ CuO}\ \frac{N}{10}\ NaOH \right| 3N \cdot NaOH \left| \frac{N}{10}\ KCl,\ Hg_2Cl_2 \right| Hg,$$

$$[B] \quad Cu \left| \underset{\text{equilibrium film}}{Cu_2O,\ CuO,}\ \frac{N}{10}\ NaOH, HgO \right| Hg,$$

and observed that the effect was simply owing to the photo-reversible reaction:

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* This paper is the English translation of the same article which appeared in *this journal*, 9, 38 (1934).

1) Becquerel '*La Lumiere*' 11, 121; C. R., 9, 561 (1839).

2) Rigollot, *Annalis de l'Universite de Lyon*, 29, Mai (1891).
Goldmann & Brodsky, *Ann. Physik.*, [4], 849 (1914); ibid, 44, 914 (1914).
Bauer, *Z. Physik. Chem.*, 66, 683 (1908); *ibid*, 72, 323 (1910).
A. D. Garrison, *J. phys. Chem.*, 27, 601 (1923).
A. Tucker, *ibid.* 31, 1356 (1927).
Wildermann, *Z. physik. Chem.*, 59, 708 (1906); *ibid*, 62, 70 (1907).

3) S. Horiba and N. Hayami, *Rev. Phys. Chem. Japan*, 4, 55 (1930).

$$2\,CuO \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} Cu_2O + \frac{1}{2}O_2.$$

The present research is undertaken to study the chemical kinetics and the thermodynamical relation of the photochemical reaction from Becquerel effect and to verify the above mentioned theory on the effect.

## Experimental.

### 1) Material and Procedure.

The materials used for electrodes and electrolytes, and the method of measuring in the present experiments were the same as used in the preceding. In the above mentioned cell (A) as a copper oxide electrode a black copper oxide film was used, which was turned by the action of alkali electrolyte from cuprous oxide film prepared on a copper plate by electrolysis of the Fehling solution. When the cell (A) showed a constant voltage-0.2322- at 25°C., the electrode could be regarded as the equilibrium electrode of $CuO \cdot Cu_2O$, and it was exposed to light to examine its photo-effect.

## Experimental Results.

### Expt. I. Measuring Instrument and Change of Photovoltaic Potential with Time.

The photovoltaic potentials calculated by means of a potentiometer are given in Table I, a, and those by means of a quadrant electrometer in Table I, b; these are compared in Fig. 1.

Table I, a.

The Influence of the Measuring Instrument on the Photovoltaic Potential.

| Time (mins.) | E. M. F. of Cell [A] (volts.) | Photovoltaic Potential (mili-volt.) | Ea ((E. M. F. of $Cu \mid Cu_2O, CuO, \frac{N}{10}NaOH \mid H_2$)[4] (volts) | $P_{O_2}$ (oxygen-pressure) (atm) |
|---|---|---|---|---|
| Exposure | | | | |
| 0 | 0.2322 | 0 | 0.8425 | $1.000 \times 10^{-26}$ |
| 1 | 0.2476 | 15.4 | 0.8579 | $1.096 \times 10^{-25}$ |
| 2 | 0.2525 | 20.3 | 0.8628 | 2.399 „ |
| 4 | 0.2568 | 24.6 | 0.8671 | 5.754 „ |
| 6 | 0.2586 | 26.4 | 0.8689 | 6.310 „ |
| 8 | 0.2595 | 27.3 | 0.8698 | 7.244 „ |
| 10 | 0.2601 | 27.9 | 0.8704 | 7.762 „ |
| 12 | 0.2607 | 28.5 | 0.8710 | 8.710 „ |
| 15 | 0.2607 | 28.5 | 0.8710 | 8.710 „ |
| 30 | 0.2607 | 28.5 | 0.8710 | 8.710 „ |

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[4] The E. M. F. of $Cu/Cu_2O$, $CuO \frac{N}{10} NaOH \mid H_2$ at 25°±0.02°C. (See S. Horiba and N. Hayami, *ibid.*,) can be calculated from the E. M. F. of the cell (A) and Eh as follows:

| | E. M. F. of Cell (A) | Eh |
|---|---|---|
| °C | $\left[Cu \mid Cu_2O, CuO \frac{N}{10}NaOH \mid 3N.NaOH \mid \frac{N}{10}KCl, Hg_2Cl_2 \mid Hg\right]$ | $\left[Hg \mid Hg_2Cl_2, \frac{N}{10}KCl \mid 3N.NaOH \mid \frac{N}{10}NaOH \mid H_2\right]$ |
| 0° | 0.2446 volt | 1.0986 volt |
| 25° | 0.2326 „ | 1.0747 „ |

| | |
|---|---|
| °C | E. M. F. of $Cu \mid Cu_2O, CuO \mid \frac{N}{10}NaOH \mid H_2$ |
| 0° | 0.8540 volt |
| 25° | 0.8421 „ |

| | | | | |
|---|---|---|---|---|
| Light off | | | | |
| 0 | 0.2607 | 28.5 | 0.8710 | 8.710×10$^{-25}$ |
| 2.5 | 0.2555 | 23.3 | 0.8658 | 3.802 " |
| 3 | 0.2523 | 20.1 | 0.8626 | 3.396 " |
| 5.5 | 0.2495 | 17.3 | 0.8598 | 1.489 " |
| 7 | 0.2477 | 15.5 | 0.8580 | 1.125 " |
| 7.5 | 0.2462 | 14.0 | 0.8565 | 1.038 " |
| 8.5 | 0.2450 | 12.8 | 0.8553 | 7.379×10$^{-26}$ |
| 10 | 0.2432 | 11.0 | 0.8535 | 5.152 " |
| 11 | 0.2413 | 9.1 | 0.8516 | 4.140 " |
| 12.5 | 0.2392 | 7.0 | 0.8495 | 2.980 " |
| 14.5 | 0.2370 | 4.8 | 0.8473 | 2.113 " |

25°±0.02°C. Light source: a 100V–200W Tungsten-filament lamp, operating from a battery supply. The light was passed through a 80 mm. layer of a Solution $(CuSO_4+1080\ NH_3)/90$ (Normal). Intensity of Light: 0.2364 cal/cm$^2$/sec. The measuring instrument: Leads & Northrup Potentiometer

Table II, b.

The Influence of the Measuring Instrument on the Photovoltaic Potential.

| Time (mins.) | E. M. F. of Cell [A] (volts) | Photovoltaic Potantial (milli-volts) | $E_a$ $\left(\text{E. M. F. of Cu}\,\middle|\,Cu_2O,\ CuO\ \frac{N}{10}NaOH\,\middle|\,H_2\right)$ (volts) | $P_{O_2}$ (oxygen pressure) (atm) |
|---|---|---|---|---|
| Exposure | | | | |
| 0 | 0.2322 | 0 | 0.8425 | 1.000×10$^{-26}$ |
| 1 | 0.2522 | 20.0 | 0.8625 | 2.239×10$^{-25}$ |
| 2 | 0.2550 | 22.8 | 0.8653 | 3.467 " |
| 4 | 0.2583 | 26.1 | 0.8686 | 5.754 " |
| 6 | 0.2599 | 27.7 | 0.8702 | 7.567 " |
| 8 | 0.2611 | 28.9 | 0.8714 | 9.084 " |
| 10 | 0.2621 | 29.9 | 0.8724 | 1.072×10$^{-24}$ |
| 15 | 0.2621 | 29.9 | 0.8724 | 1.072 " |
| 30 | 0.2621 | 29.9 | 0.8724 | 1.072 " |
| Light off | | | | |
| 0 | 0.2621 | 29.9 | 0.8724 | 1.072×10$^{-24}$ |
| 1.2 | 0.2598 | 27.6 | 0.8701 | 7.413×10$^{-25}$ |
| 2 | 0.2585 | 26.3 | 0.8688 | 6.025 " |
| 3 | 0.2561 | 23.9 | 0.8664 | 4.169 " |
| 4 | 0.2530 | 21.8 | 0.8643 | 3.020 " |
| 5.5 | 0.2516 | 19.4 | 0.8619 | 2.042 " |
| 6.5 | 0.2474 | 17.2 | 0.8597 | 1.479 " |
| 7.5 | 0.2472 | 15.0 | 0.8575 | 1.047 " |
| 8.5 | 0.2452 | 13.0 | 0.8555 | 7.585×10$^{-26}$ |
| 10 | 0.2428 | 10.6 | 0.8531 | 5.370 " |
| 12 | 0.2405 | 8.3 | 0.8508 | 3.631 " |
| 13.5 | 0.2383 | 6.1 | 0.8486 | 2.571 " |

25°±0.02°C. Light source: a 100V—200W Tungsten-filament lamp, operating from a battery supply. The light was passed through a 80 mm. layer of a Solution $\frac{(CuSO_4+1080NH_3)}{90}$ (Normal). Intensity of light: 0.2364 cal/cm$^2$/sec. The measuring instrument: Quadrant electrometer.

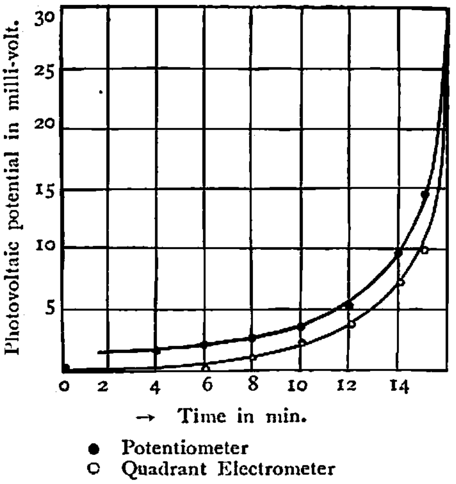


Fig. 1.
The Influence of the Measuring Instrument on the Photovoltaic Potential.

As is seen, variation in the measuring instruments used gives rise to slight variation in photovoltaic potentials for the same intensity of light. This may be because some electric current is taken out in the case of a potentiometer. Even in this case, however, the difference was limited within 1% in such a degree of light intensity. Accordingly, a potentiometer was used in the present experiment.

### Expt. II. Intensity of Light and Change of Photovoltaic Potential with Time.

The change of the photovoltaic potential was measured with a monochromatic light of 492 $\mu\mu$ and three kinds of intensities of light—0.004054, 0.02843, and 5.575 cal/cm$^2$/sec. The results obtained are given in Table II, a, b, c, and Fig. II.

Table II, a.
The Change of Velocity in the Photochemical Reaction with Intensity of Light at 25±0.02°C.

| Time (mins). | E. M. F. of Cell [A] (volts) | Photovoltaic Potential (milli-volts) | $E_a$ (E. M. F. of Cu\|Cu$_2$O, CuO$\frac{N}{10}$NaOH\|H$_2$) (volts) | $P_{O_2}$ (oxygen-pressure) (atm) |
|---|---|---|---|---|
| Exposure | | | | |
| 0 | 0.2322 | 0 | 0.8425 | $1.000\times10^{-26}$ |
| 1 | 0.2734 | 41.2 | 0.8837 | $0.581\times10^{-23}$ |
| 2 | 0.2767 | 44.5 | 0.8870 | 0.981 ,, |
| 3 | 0.2783 | 46.1 | 0.8886 | 1.293 ,, |
| 5 | 0.2799 | 47.7 | 0.8902 | 1.652 ,, |
| 6 | 0.2803 | 48.1 | 0.8906 | 1.773 ,, |
| 9 | 0.2805 | 48.3 | 0.8908 | 1.994 ,, |
| 10 | 0.2809 | 48.7 | 0.8912 | 2.041 ,, |
| 14 | 0.2809 | 48.7 | 0.8912 | 2.041 ,, |
| 20 | 0.2809 | 48.7 | 0.8912 | 2.041 ,, |
| 24 | 0.2809 | 48.7 | 0.8912 | 2.041 ,, |
| 30 | 0.2809 | 48.7 | 0.8912 | 2.041 ,, |
| Light off | | | | |
| 0 | 0.2809 | 48.7 | 0.8912 | $2.041\times10^{-23}$ |
| 3 | 0.2740 | 41.8 | 0.8855 | $8.128\times10^{-24}$ |
| 5 | 0.2697 | 37.5 | 0.8812 | 4.266 ,, |
| 7 | 0.2668 | 34.6 | 0.8783 | 2.692 ,, |
| 8.5 | 0.2635 | 31.3 | 0.8750 | 1.585 ,, |
| 11 | 0.2593 | 27.1 | 0.8708 | $8.511\times10^{-25}$ |
| 12 | 0.2573 | 25.0 | 0.8687 | 5.888 ,, |
| 13.5 | 0.2539 | 21.7 | 0.8654 | 3.548 ,, |
| 15 | 0.2509 | 18.7 | 0.8624 | 2.239 ,, |
| 18 | 0.2457 | 13.5 | 0.8572 | 1.000 ,, |
| 20 | 0.2444 | 12.2 | 0.8559 | $8.128\times10^{-26}$ |

25°±0.02°C. Light source: a 100V–1000W Tungsten-filament lamp, operating from a battery supply. The light monochromatic(492 $\mu\mu$) was passed through a Wratten light filter. Intensity of light: 5.575 cal/cm$^2$/sec. The measuring instrument: Potentiometer.

Table II, b.

The Change of Velocity in the Photochemical Reaction with Intensity of Light at 25°±0.02°C.

| Time (mins) | EM.F. of Cell [A] (volts) | Photovoltaic Potential (milli-volts) | $E_a$ $\left(\text{E. M. F. of Cu}\middle\vert \text{Cu}_2\text{O, CuO}\frac{\text{N}}{10}\text{NaO}\middle\vert \text{H}_2\right)$ (volts) | $P_{O_2}$ (oxygen-pressure) (atm) |
|---|---|---|---|---|
| Exposure | | | | |
| 0 | 0.2322 | 0 | 0.8425 | $1.000\times10^{-26}$ |
| 1 | 0.2412 | 9.0 | 0.8515 | 4.169 ,, |
| 2 | 0.2450 | 12.8 | 0.8553 | 7.418 ,, |
| 4 | 0.2464 | 14.2 | 0.8567 | 9.120 ,, |
| 6 | 0.2471 | 14.9 | 0.8574 | $1.023\times10^{-25}$ |
| 8 | 0.2476 | 15.4 | 0.8579 | 1.096 ,, |
| 10 | 0.2478 | 15.6 | 0.8581 | 1.148 ,, |
| 12 | 0.2477 | 15.5 | 0.8580 | 1.122 ,, |
| 14 | 0.2478 | 15.6 | 0.8581 | 1.148 ,, |
| 20 | 0.2478 | 15.6 | 0.8581 | 1.148 ,, |
| 24 | 0.2478 | 15.6 | 0.8581 | 1.148 ,, |
| 30 | 0.2478 | 15.6 | 0.8581 | 1.148 ,, |
| Light off | | | | |
| 0 | 0.2478 | 15.6 | 0.8581 | $1.148\times10^{-25}$ |
| 2 | 0.2449 | 12.7 | 0.8544 | $6.310\times10^{-26}$ |
| 3 | 0.2422 | 10.0 | 0.8525 | 4.784 ,, |
| 4 | 0.2412 | 9.0 | 0.8515 | 4.074 ,, |
| 5 | 0.2401 | 7.9 | 0.8504 | 3.467 ,, |
| 6 | 0.2390 | 6.8 | 0.8493 | 2.884 ,, |
| 7 | 0.2374 | 5.2 | 0.8477 | 2.291 ,, |
| 8.5 | 0.2360 | 3.8 | 0.8463 | 1.950 ,, |
| 10 | 0.2354 | 3.2 | 0.8457 | 1.660 ,, |

25°±0.02° C. Light source: a 100V—1000W Tungsten-filament lamp, operating from a battery supply. The light monochromatic (492 $\mu\mu$) was passed through a Wratten light filter. Intensity of light: 0.02843 cal/cm²/sec.

Table II, c.

The Change of Velocity in the Photochemical Reaction with Intensity of Light at 25°±0.02°C.

| Time (mins.) | E. M. F. of Cell [A] (volts) | Photovoltaic Potential (milli-volts) | $E_a$ $\left(\text{E.M.F. of Cu}\middle\vert \text{Cu}_2\text{O, CuO}\frac{\text{N}}{10}\text{NaOH}\middle\vert \text{H}_2\right)$ (volts) | $P_{O_2}$ (oxygen-pressure) (atm) |
|---|---|---|---|---|
| Exposure | | | | |
| 0 | 0.2324 | 0 | 0.8423 | $9.729\times10^{-27}$ |
| 1 | 0.2355 | 3.1 | 0.8454 | $1.570\times10^{-26}$ |
| 2 | 0.2362 | 3.8 | 0.8461 | 1.754 ,, |
| 3 | 0.2368 | 4.4 | 0.8467 | 1.941 ,, |
| 4 | 0.2373 | 4.9 | 0.8472 | 2.089 ,, |
| 5 | 0.2376 | 5.2 | 0.8475 | 2.168 ,, |
| 6 | 0.2379 | 5.5 | 0.8478 | 2.249 ,, |
| 7 | 0.2381 | 5.7 | 0.8480 | 2.355 ,, |
| 8 | 0.2382 | 5.8 | 0.8481 | 2.399 ,, |
| 9 | 0.2383 | 5.9 | 0.8482 | 2.443 ,, |
| 10 | 0.2383 | 5.9 | 0.8482 | 2.443 ,, |
| 11 | 0.2383 | 5.9 | 0.8482 | 2.443 ,, |
| 12 | 0.2383 | 5.9 | 0.8482 | 2.443 ,, |
| 30 | 0.2383 | 5.9 | 0.8482 | 2.443 ,, |
| Light off | | | | |
| 0 | 0.2383 | 5.9 | 0.8482 | $2.443\times10^{-26}$ |
| 1 | 0.2373 | 4.9 | 0.8472 | 2.022 ,, |
| 2 | 0.2362 | 3.8 | 0.8461 | 1.723 ,, |
| 3.5 | 0.2352 | 2.8 | 0.8451 | 1.503 ,, |
| 4 | 0.2346 | 2.2 | 0.8445 | 1.373 ,, |
| 5 | 0.2342 | 1,8 | 0.8441 | 1.273 ,, |
| 6 | 0.2338 | 1.4 | 0.8437 | 1.213 ,, |
| 7 | 0.2335 | 1.1 | 0.8434 | 1.153 ,, |
| 8 | 0.2333 | 0.9 | 0.8432 | 1.123 ,, |

25°±0.02°C. Light source: a 100V—100W Tungsten-filament lamp, operating from a battery supply. The monochromatic light (492$\mu\mu$) was passed through a Wratten light filtener. Intensity of light: 0.004055 cal/cm²/sec.

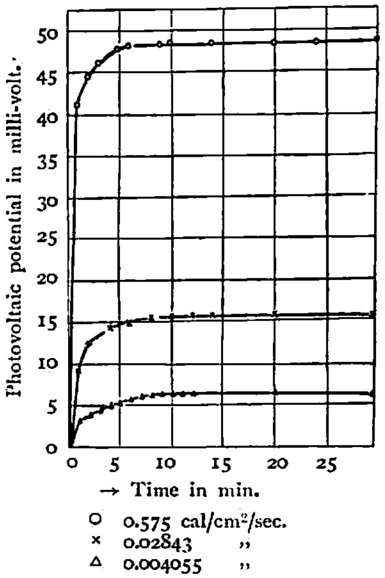


Fig. II

The Change of Velocity in the Photochemical Reaction with Intensity of Light at 25°±0.02°C.

The experimental results show that the time taken before the equilibrium of the Becquerel effect is established is not influenced by the intensity of light and the thee quilibrium photovoltaic potential is proportional to light. It is also shown that the reaction velocity after the exposure increases in proportion to light intensity.

### Expt. III. Wave Length and Change of Photo-electrode with Time.

The effect of wave length upon the change of the photovoltaic potential was examined. The change of the photovoltaic potential with time was measured with a given intensity of such monochromatic lights as 430 $\mu\mu$ (violet), 492 $\mu\mu$ (green), 550$\mu\mu$ (yellow), and 640 $\mu\mu$ (red). The reeults are given in Table III a, b, c, d, and in Fig. III.

Table III, a.

The Change of Velocity in the Photochemical Reaction with Wave Length of Light at 25°C.

| Time (mins.) | E. M. F. of Cell [A] (volts) | Photovoltaic Potential (milli-volts) | $Ea$ $\left(\text{E. M. F. of Cu}\middle|\text{Cu}_2\text{O, CuO, }\frac{\text{N}}{10}\text{NaOH}\middle|\text{H}_2\right)$ (volts) | $P_{O_2}$ (oxygen-pressure) (atm) |
|---|---|---|---|---|
| Exposure | | | | |
| 0 | 0.2324 | 0 | 0.8423 | $9.727\times10^{-27}$ |
| 1 | 0.2349 | 2.5 | 0.8449 | $1.432\times10^{-26}$ |
| 2 | 0.2359 | 3.5 | 0.8458 | 1.675 „ |
| 3 | 0.2364 | 4.0 | 0.8463 | 1.803 „ |
| 4 | 0.2368 | 4.4 | 0.8467 | 1.905 „ |
| 5 | 0.2371 | 4.7 | 0.8470 | 2.014 „ |
| 6 | 0.2373 | 4.9 | 0.8472 | 2.089 „ |
| 7 | 0.2376 | 5.2 | 0.8475 | 2.168 „ |
| 8 | 0.2377 | 5.3 | 0.8476 | 2.228 „ |
| 9 | 0.2379 | 5.5 | 0.8478 | 2.291 „ |
| 10 | 0.2379 | 5.5 | 0.8478 | 2.291 „ |
| 11 | 0.2379 | 5.5 | 0.8478 | 2.291 „ |
| 12 | 0.2379 | 5.5 | 0.8478 | 2.291 „ |
| Light off | | | | |
| 0 | 0.2379 | 5.5 | 0.8478 | $2.291\times10^{-26}$ |
| 1.2 | 0.2364 | 4.0 | 0.8463 | 1.803 „ |
| 3 | 0.2352 | 2.8 | 0.8451 | 1.500 „ |
| 4 | 0.2348 | 2.4 | 0.8447 | 1.393 „ |
| 5 | 0.2343 | 1.9 | 0.8442 | 1.294 „ |
| 5.5 | 0.2340 | 1.6 | 0.8439 | 1.236 „ |
| 6.5 | 0.2338 | 1.4 | 0.8437 | 1.159 „ |
| 7.5 | 0.2334 | 1.0 | 0.8433 | 1.133 „ |
| 8 | 0.2333 | 0.9 | 0.8432 | 1.107 „ |
| 8.5 | 0.2331 | 0.7 | 0.8430 | 1.086 „ |

25°±0.02°C. Light source: a 100V—200W Tungsten-filament lamp, operating from a battery supply. The monochromatic light (550$\mu\mu$) was passed through a Wratten light filler. Intensity of light: 0.004055 cal/cm²/sec.

### Table III, b.

The Change of Velocity in the Photochemical Reaction with Wave Length of Light at 25°C.

| Time (mins.) | E. M. F. of Cell [A] (volts) | Photovoltaic Potential (mili-volts) | E*a* (E. M. F. of Cu\|Cu$_2$O, CuO, $\frac{N}{10}$NaOH\|H$_2$) (volts) | P$_{O_2}$ (oxygen-pressure) (atm) |
|---|---|---|---|---|
| Exposure | | | | |
| 0 | 0.2324 | 0 | 0.8423 | $9.729\times10^{-27}$ |
| 1 | 0.2355 | 3.1 | 0.8454 | $1.570\times10^{-26}$ |
| 2 | 0.2362 | 3.8 | 0.8461 | 1.754 " |
| 3 | 0.2368 | 4.4 | 0.8467 | 1.941 " |
| 4 | 0.2373 | 4.9 | 0.8472 | 2.089 " |
| 5 | 0.2376 | 5.2 | 0.8475 | 2.168 " |
| 6 | 0.2379 | 5.5 | 0.8478 | 2.249 " |
| 7 | 0.2381 | 5.7 | 0.8480 | 2.355 " |
| 8 | 0.2382 | 5.8 | 0.8481 | 2.399 " |
| 9 | 0.2383 | 5.9 | 0.8482 | 2.443 " |
| 10 | 0.2383 | 5.9 | 0.8482 | 2.443 " |
| 11 | 0.2383 | 5.9 | 0.8482 | 2.443 " |
| 12 | 0.2383 | 5.9 | 0.8482 | 2.443 " |
| 30 | 0.2383 | 5.9 | 0.8482 | 2.443 " |
| Light off | | | | |
| 0 | 0.2383 | 5.9 | 0.8482 | $2.443\times10^{-26}$ |
| 1 | 0.2373 | 4.9 | 0.8472 | 2.022 " |
| 2 | 0.2362 | 3.8 | 0.8461 | 1.723 " |
| 3 | 0.2352 | 2.8 | 0.8451 | 1.503 " |
| 4 | 0.2346 | 2.2 | 0.8445 | 1.373 " |
| 5 | 0.2342 | 1.8 | 0.8441 | 1.273 " |
| 6 | 0.2338 | 1.4 | 0.8437 | 1.213 " |
| 7 | 0.2335 | 1.1 | 0.8434 | 1.153 " |
| 8 | 0.2333 | 0.9 | 0.8432 | 1.123 " |

25°±0.02°C. Light source: a 100V—200W Tungsten-filament lamp, operating from a battery supply. The monochromatic light (492 μμ) was passed through a Wratten light filter. Intensity of light: 0.004055 cal/cm$^2$/sec.

### Table III, c.

The Change of Velocity in the Photochemical Reaction with Wave Length of Light at 25°C.

| Time (mins.) | E. M. F. of Cell [A] (volts) | Photovoltaic Potential (mili-volts) | E*a* (E. M. F. of Cu\|Cu$_2$O, CuO, $\frac{N}{10}$NaOH\|H$_2$) (volts) | P$_{O_2}$ (oxygen-pressure) (atm) |
|---|---|---|---|---|
| Exposure | | | | |
| 0 | 0.2324 | 0 | 0.8423 | $9.727\times10^{-27}$ |
| 1 | 0.2346 | 2.2 | 0.8445 | $1.387\times10^{-26}$ |
| 2 | 0.2352 | 2.8 | 0.8451 | 1.500 " |
| 3 | 0.2357 | 3.3 | 0.8456 | 1.614 " |
| 4 | 0.2360 | 3.6 | 0.8459 | 1.694 " |
| 5 | 0.2362 | 3.8 | 0.8461 | 1.754 " |
| 6 | 0.2365 | 4.1 | 0.8464 | 1.820 " |
| 7 | 0.2366 | 4.2 | 0.8465 | 1.854 " |
| 8 | 0.2367 | 4.3 | 0.8466 | 1.892 " |
| 9 | 0.2368 | 4.4 | 0.8467 | 1.923 " |
| 10 | 0.2368 | 4.4 | 0.8467 | 1.923 " |
| 11 | 0.2368 | 4.4 | 0.8467 | 1.923 " |
| 12 | 0.2368 | 4.4 | 0.8467 | 1.923 " |
| Light off | | | | |
| 0 | 0.2368 | 4.4 | 0.8467 | 1.923 |
| 1.5 | 0.2338 | 3.4 | 0.8457 | 1.660 |
| 2.5 | 0.2350 | 2.6 | 0.8449 | 1.445 |
| 3.5 | 0.2345 | 2.1 | 0.8444 | 1.330 |
| 4 | 0.2341 | 1.7 | 0.8440 | 1.259 |
| 5 | 0.2338 | 1.4 | 0.8437 | 1.202 |
| 6.5 | 0.2334 | 1.0 | 0.8433 | 1.127 |
| 7.5 | 0.2331 | 0.7 | 0.8430 | 1.076 |

25°±0.02°C. Light source: a 100V—200W Tungsten-fiament lamp, operating from a battery supply. The monochromatic light (430 μμ) was passed through a Wratten light filter. Intensity of light: 0.004055 cal/cm$^2$/sec.

Table III, d.

The Change of Velocity in the Photochemial Reaction with Wave Length of Light at 25°C.

| Time (mins.) | E. M. F. of Cell [A] (volts.) | Photovoltaic Potential (milli-volts.) | Ea $\left(\text{E. M. F. of Cu}\middle|\text{Cu}_2\text{O, CuO,}\frac{\text{N}}{10}\text{NaOH}\middle|\text{H}_2\right)$ (volts) | $P_{O_2}$ (oxygen-pressure) (atm) |
|---|---|---|---|---|
| Exposure | | | | |
| 0 | 0.2324 | 0 | 0.8423 | $9.727\times10^{-27}$ |
| 1 | 0.2343 | 1.9 | 0.8442 | $1.306\times10^{-26}$ |
| 2 | 0.2350 | 2.6 | 0.8449 | 1.459 " |
| 3 | 0.2354 | 3.0 | 0.8453 | 1.542 " |
| 4 | 0.2357 | 3.3 | 0.8456 | 1.570 " |
| 5 | 4.2360 | 3.6 | 0.8459 | 1.670 " |
| 6 | 0.2361 | 3.7 | 0.8460 | 1.722 " |
| 7 | 0.2362 | 3.8 | 0.8461 | 1.745 " |
| 8 | 0.2363 | 3.9 | 0.8462 | 1.786 " |
| 9 | 0.2363 | 3.9 | 0.8462 | 1.786 " |
| 10 | 0.2363 | 3.9 | 0.8462 | 1.786 " |
| 11 | 0.2363 | 3.9 | 0.8462 | 1.786 " |
| 12 | 0.2363 | 3.9 | 0.8462 | 1.786 " |
| Light off | | | | |
| 0 | 0.2363 | 3.9 | 0.8462 | $1.786\times10^{-26}$ |
| 1.2 | 0.2354 | 3.0 | 0.8453 | 1.542 " |
| 2.5 | 0.2347 | 2.3 | 0.8446 | 1.328 " |
| 3 | 0.2343 | 1.9 | 0.8442 | 1.294 " |
| 4 | 0.2339 | 1.5 | 0.8438 | 1.225 " |
| 5 | 0.2334 | 1.0 | 0.8433 | 1.138 " |
| 6 | 0.2332 | 0.8 | 0.8431 | 1.096 " |
| 7.5 | 0.2330 | 0.6 | 0.8429 | 1.057 " |

25°±0.02°C. Light source: a 100V—200W Tungsten-filament lamp, operating from a battery supply. The monochromatic light (640$\mu\mu$) was passed through a Wratten light filter. Intensity of light: 0.004055 cal/cm$^2$/sec.

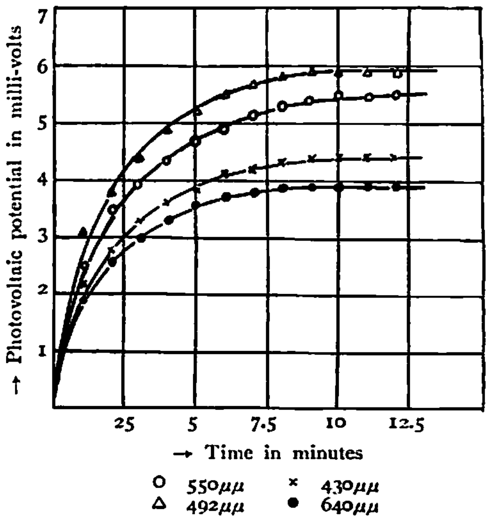


Fig. III

The Change of Velocity in the Photochemical Reaction with Wave Length of Light at 250°C.

It is apparent from these that the time elapsing before the equilibrium of the Becquerel effect is established is almost uniform, regardless of the wave-length, and that variation in the wave-length gives rise to variation in the photo-effect.

## Expt. IV. Wave Length and Maximum Photovoltaic Potential.

The relation between the wave length and the maximum photovoltaic potential was examined. The examination was made with three electrodes —No. 1, No. 2 and No. 3. The copper oxide electrodes which had been in equilibrium in the dark were exposed to six kinds of monochromatic lights, and their maximum photovolatic potentials measured. During the experiment the electric current and voltage were regulated by means of a thermopile so that the intensity of light might be kept constant. The experimental results are given in Table IV and Fig. IV, which show that the photovoltaic potential of Cu | $Cu_2O$, CuO $\frac{N}{10}$ NaOH has a selective effect on different wave lengths of light, and that its maxium photo-effect lies between 450-500μμ.

Table IV.
The Influence of the Wave Length of Light on the Maximum Photovoltaic Potential

| Number of Cell. / Monochromatic Light (μμ) | | $\mathrm{I}_{Ed}$. Maximum Photovoltaic Potential (volts) | $\mathrm{II}_{Ed}$. Maximum Photovoltaic Potential (volts) | $\mathrm{III}_{Ed}$. Maximum Photovoltaic Potential (volts) | Mean. (volts) |
|---|---|---|---|---|---|
| U. V. | 380 | 0.0035 | 0.0036 | 0.0036 | 0.0036 |
| Violet | 430 | 0.0044 | 0.0043 | 0.0043 | 0.0043 |
| Green | 492 | 0.0058 | 0.0058 | 0.0058 | 0.0058 |
| Yellow | 550 | 0.0055 | 0.0056 | 0.0055 | 0.0055 |
| Red | 640 | 0.0039 | 0.0040 | 0.0039 | 0.0039 |
| I. R. | 810 | 0.0030 | 0.0031 | 0.0031 | 0.0031 |

25°±0.02°C. Light source: a 100V—500W Tungsten-filament lamp, operating from a battery supply. The monochromatic lights, 380, 492, 550, 640 and 810 μμ, were passed through a Wratten light filter. Intensity of light: 0.004055 cal/cm²/sec.

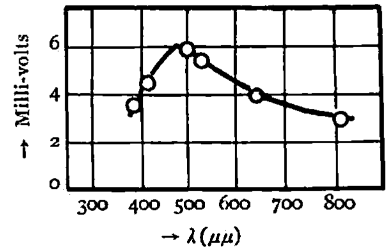


Fig. IV

The Influence of the Wave Length of Light on the Maximum Photovoltaic Potential (Intensity of Light: 0.004055 cal/cm²/sec. 25°±0.02°C.)

## Expt. V. Intensity of Light and Saturated Maximum Photovoltaic Potential.

An electrode, Cu | $Cu_2O$, CuO $\frac{N}{10}$ NaOH, which had been in equilibrium in the dark,

Table V.
The Influence of Intensity of Light on the Maximum Photovoltaic Potential

| Intensity of light (cal/cm²/sec.) | E. M. F. of Cell [A] (obs.) | $E_a$ (E. M. F. of Cu \| $Cu_2O$, CuO, $\frac{N}{10}$NaOH \| $H_2$) (calc.) | Maximum Photovoltaic Potential |
|---|---|---|---|
| 0 | 0.2323 volt | 0.8424 volt | —— |
| 0.002318 | 0.2298 | 0.8449 | +0.0025 |
| 0.004055 | 0.2282 | 0.8465 | +0.0041 |
| 0.008130 | 0.2233 | 0.8514 | +0.0090 |
| 0.02843 | 0.2174 | 0.8573 | +0.0149 |
| 0.1042 | 0.2087 | 0.8660 | +0.0236 |
| 5.575 | 0.1848 | 0.8899 | +0.0475 |
| 14.100 | 0.1628 | 0.9119 | +0.0695 |

25°±0.02°C. Light source: a 100V—1000W Tungsten-filament lamp, operating from a battery supply. The monochromatic light (492 μμ) was passed through a Wratten light filter.

---

5) Photochemical equilibriums corresponding to intensities of light can be established. The photovoltaic potential in equilibrium will be called the maximum photovoltaic potential for convenience' sake,

was exposed to light of various intensities and its saturated maximum photovoltaic potentials were measured. The results are given in Table V and Fig. V.

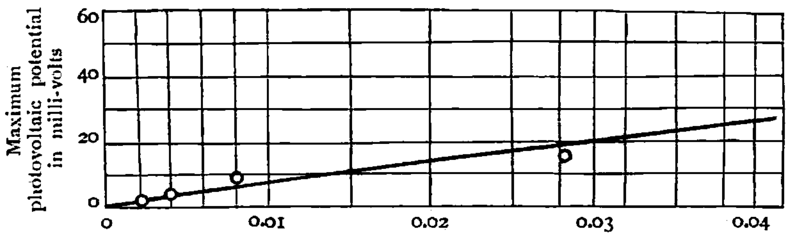


Fig. V.

The Influence of the Intensity of Light on the Maximum Photovoltaic Potential.

### Expt. VI. Temperature and Change of Photovoltaic Potential.

The influence of temperature on the photovoltaic potential was examined with the copper oxide electrodes which reached equilibrium at 0°, 10°, 25°, 35° and 45°C. respectively. The results are given in Table VI and Fig. VI.

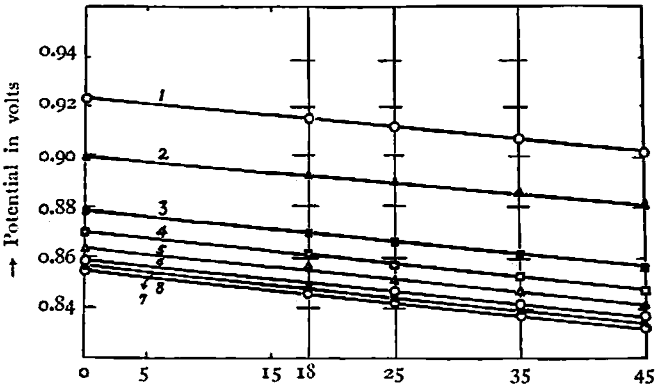
Table VI.

The Influence of Temperature on the Maximum Photovoltaic Potential

| Intensity of light (cal/cm²/sec). | 0 | | 0.002318 | | 0.004055 | | 0.00818 | |
|---|---|---|---|---|---|---|---|---|
| $E_{\alpha t}$ & $\Delta E_t$ (milli-volts) / Temp. °C | E | ΔE | E | ΔE | E | ΔE | E | ΔE |
| 0 | 855.07 | —— | 857.32 | —— | 859.00 | —— | 863.85 | —— |
| 18 | 845.99 | 9.12 | 848.37 | 8.95 | 850.00 | 9.00 | 856.87 | 8.98 |
| 25 | 842.40 | 12.67 | 844.90 | 12.42 | 846.50 | 12.50 | 851.40 | 12.45 |
| 35 | 837.32 | 17.75 | 838.92 | 17.40 | 841.50 | 17.50 | 846.41 | 17.44 |
| 45 | 832.27 | 22.80 | 834.97 | 22.35 | 836.40 | 22.50 | 841.45 | 22.40 |
| $-\frac{\Delta E}{\Delta T}$ (mean) | | 5.07 | | 4.97 | | 5.00 | | 4.98 |

| Intensity of light (cal/cm²/sec.) | 0.02843 | | 0.1042 | | 5.575 | | 14.100 | |
|---|---|---|---|---|---|---|---|---|
| $E_{\alpha t}$ & $\Delta E_t$ (milli-volts) / Temp. °C | E | ΔE | E | ΔE | E | ΔE | E | ΔE |
| 0 | 869.80 | —— | 878.50 | —— | 902.27 | —— | 924.20 | —— |
| 18 | 860.80 | 9.00 | 869.50 | 9.00 | 893.37 | 8.90 | 915.36 | 8.84 |
| 25 | 857.30 | 12.50 | 866.00 | 12.50 | 889.90 | 12.37 | 911.90 | 12.30 |
| 35 | 852.28 | 17.52 | 861.15 | 17.50 | 884.92 | 17.35 | 907.00 | 17.20 |
| 45 | 847.34 | 22.51 | 856.15 | 22.50 | 879.97 | 22.30 | 902.10 | 22.10 |
| $-\frac{\Delta E}{\Delta T}$(mean) | | 5.01 | | 5.00 | | 4.95 | | 4.92 |

Light source: a 100V—1000V Tungsten-filament lamp, operating from a battery supply. The monochromatic light (492 $\mu\mu$) was passed through a Wratten light filter.



1. 14.100 cal/cm²/sec.
2. 5.575 ,,
3. 0.1042 ,,
4. 0.02843 ,,
5. 0.00813 cal/cm²/sec.
6. 0.004055 ,,
7. 0.00218 ,,
8. 0.00 ,,

Fig. VI.
The Influence of Temperature on the Maximum Photovoltaic Potential.

As is seen, the photo-electrode potential which is in equilibrium in the dark decreases with the increase of temperature.

The photovoltaic potential for the the same intensity of light is not correlated to the rise of temperature. Therefore the temperature coefficients of voltage are equal both in the dark and in the light.

## Theoretical.

### 1) Consideration from the Standpoint of the Reaction Kinetics.

1) Copper Oxide Electrode as a Reaction System.

An electrode, Cu | $Cu_2O$, $CuO\frac{N}{10}NaOH$, which has reached equilibrium in the dark is expressed as a heterogeneous reversible reaction thus,

$$\underset{\text{(solid)}}{2CuO} \rightleftarrows \underset{\text{(solid)}}{Cu_2O} + \underset{\text{(gas)}}{\frac{1}{2}O_2}. \qquad (1.1)$$

When this system is exposed to light, it reaches photochemical equilibrium according to a reaction,

$$2\,CuO \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} Cu_2O + \frac{1}{2}O_2, \qquad (1.2)$$

as already said in the preceding report. It is apparent from the experimental results that when light is shut off the reaction proceeds to the direction indicated by ←, and equilibrium is restored in the dark. As far as this photochemical reaction velocity is concerned, it is clear that the reaction must be treated as a reversible reaction. The question whether the reverse reaction is affected by light or not has not been solved yet, and so the author intends to make discussion under the assumption that the reverse reaction has no influence upon light, and if it has any influence, further consideration will have to be made.

In equation (1.2), supposing that the density of the solids is constant, the following velocity equation is assumed:

$$\frac{d\Delta p}{dt}=k_1\cdot J_{abs}-k_d'\cdot[O_2], \qquad (1.3)$$

where $P$ is the oxygen pressure during exposure, $k$, and $kd'$ the reaction velocity constants in the light and the dark respectively, and $J_{abs}$ the intensity of light.

First we shall calculate the velocity from this equation. The relation is graphically shown in Fig. VII, in which the height of A shows the equilibrium pressure of oxygen in the dark.

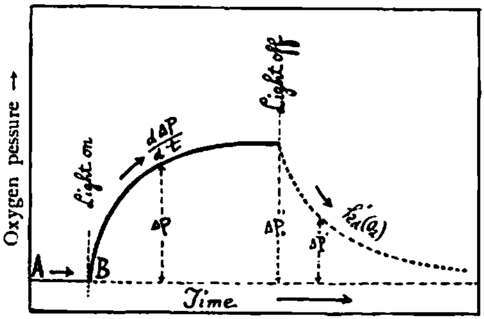


Fig. 7

2) Photovoltaic Potential.

Before the calculation of $\frac{d\Delta p}{dt}$ from equation (1.3) it is necessary to make clear the photovoltaic potenital. As has been mentioned in the preceding report, when the copper oxide electrode was combined with hydrogen electrode, an oxy-hydrogen cell was formed. Therefore E. M. F. can be obtained from the following equation:

$$E_a=E_\beta+\frac{0.059}{4}\log P_{O_2}, \qquad (1.4)$$

at 25±0.02°C. Here,

$E_a$: E. M. F. of $\mathrm{Cu}\,\big|\,\mathrm{Cu_2O, CuO}\,\frac{N}{10}\,\mathrm{NaOH}\,\big|\,\mathrm{H_2}$ (at 25°C.)
(x atm) (1 atm)

$E_\beta$: E. M. F. of $\mathrm{O_2}\,\big|\,\frac{N}{10}\,\mathrm{NaOH}\,\big|\,\mathrm{H_2}$ (at 25°C.).
(1 atm) (1 atm)

Putting $E_\beta=a$ and $\frac{0.059}{4}=b$, we have

$$E_a=a+b\log P_{O_2}. \qquad (1.5)$$

The photovoltaic potential $\Delta E_q$ is determitned by the difference between the potential in the light, $E_a'$, and that in the dark, $E_a$; hence

(dark) $E_a = \mathrm{a} + b \log P_{O_2}$

(light) $E_a' = \mathrm{a} + b \log P_{O_2}'$

$$\therefore \quad E_a' - E_a = b(\log P_{O_2}' - \log P_{O_2}) \qquad (1.6)$$

$$\log \frac{P_{O_2}'}{P_{O_2}} = \frac{E_a' - E_a}{b} = \frac{\Delta E_a}{b}$$

$$\Delta E_a = b \log \frac{P_{O_2}'}{P_{O_2}}$$

$$\frac{P_{O_2}'}{P_{O_2}} 10^{\frac{E_a' - E_a}{b}} \quad \text{or} \quad \frac{P_{O_2}'}{P_{O_2}} - 1 = 10^{\frac{E_a' - E_a}{b}} - 1$$

$$\therefore \quad \frac{P_{O_2}' - P_{O_2}}{P_{O_2}} = 10^{\frac{E_a' - E_a}{b}} - 1.$$

$$\Delta P = P_{O_2}\left\{10^{\frac{E_a' - E_a}{b}} - 1\right\}, \ldots\ldots\ldots \text{(at 25°C.)} \qquad (1.7)$$

where $P_{O_2}$ is the equilibrium oxygen pressure of the electrode in the dark. The electrode oxygen pressure $\Delta p$ equivalent to the photovolaic potential $\Delta Ea = Ea$ can be calculated from the equation.

3) Reaction Velocity after Shutting off Light.

When light was shut off, equiation (1.2), the equlibrium system during exposure, proceeded to the direction indicated by ←. This is the case where $K_1 \cdot J_{abs} = 0$ in equation (1.3), and it may be rewritten as follows:

$$-\frac{d(\Delta P')}{dt} = k_d'[O_2], \qquad (1.8)$$

where $\Delta P'$ is the difference of the pressure of oxygen after shutting off light,

$$\text{or} \qquad -\ln \Delta P = k_d t + C. \qquad (1.9)$$

In equation (1.9), if $t=0$, that is, the value of $\Delta P'$ at the instant of shutting off light is taken to be $\Delta P_0'$, we have

$$C = -\ln \Delta P_0', \qquad (1.10)$$

$$\therefore \quad -2.303 \log \frac{\Delta P_0'}{\Delta P'} = k_d' t. \qquad (1.11)$$

In order to see if this equation gives the observed values of the curve of oxygen pressure decrease, the author calculated $kd'$ through equation (1.11) from several points on the curves of the oxygen pressure decrease obtained by Expts. II and III, and obtained 0.306 as the mean value, which proved to be a constant in each case. As one of those examples Expt. II, c is given in Table VII and graphically in Fig. VIII.

Table VII.

$k_d'$: velocity constant of the dark reaction.

| Time (mins.) | $\Delta P'$ (atm) (obs.) | $k_d'$ | $\Delta P'$ (atm) (calc.) |
|---|---|---|---|
| 0 | $1.47 \times 10^{-26}$ | —— | $1.470 \times 10^{-26}$ |
| 1 | 1.05 " | 0.314 | 1.053 " |
| 2 | 0.75 " | 0.324 | 0.775 " |
| 3 | 0.53 " | 0.331 | 0.571 " |
| 4 | 0.40 " | 0.319 | 0.420 " |
| 5 | 0.30 " | 0.313 | 0.309 " |
| 6 | 0.24 " | 0.298 | 0.228 " |
| 7 | 0.18 " | 0.296 | 0.168 " |
| 8 | 0.15 " | 0.275 | 0.123 " |
|  |  | mean 0.308 |  |

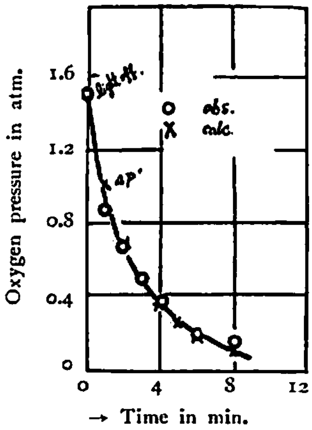


Fig. 8

The relation between the velocity constants of the reaction in the dark and the intensity of light is given in Table VIII, and that between the constants and the wave length in Table IX. As is seen in these tables, both the mean values are precisely 0.306. This shows that the velocity constants after the shutting off of light is fairly constant in each case, regardless of the intensity of light and wave length. $P'$ was calculated from this mean value and Fig. VIII shows that it is in good agreement with the observed value $\Delta P'$.

Table VIII.

$k_d'$: velocity constant of the dark reaction.

| Wave length ($\mu\mu$) | $J_{abs.}$ The light energy absorbed, before light off. (cal/cm$^2$/sec.) | $k_d'$ (atm/sec) | mean. (atm/sec) |
|---|---|---|---|
| 492 | 5.575 | 0.300 |  |
| 492 | 0.02843 | 0.302 | 0.306 |
| 492 | 0.004055 | 0.316 |  |

Table IX.

$k_d'$: velocity constant of the dark reaction.

| Wave length ($\mu\mu$) | $J_{abs.}$ | $k_d'$ | mean. |
|---|---|---|---|
| 430 | 0.004055 | 0.303 |  |
| 492 | " | 0.316 | 0.306 |
| 550 | " | 0.291 |  |
| 640 | " | 0.315 |  |

4) Reaction Velocity after Exposure.

A) Calculation of the Reaction Velocity during Exposure. When the copper oxide electrode which had been in equilibrium in the dark was exposed to light, a photochemical reversible reactions:

$$4\,CuO \rightleftarrows 2\,Cu_2 + O_2$$

took place and from this chemical relation the velocity equation (1.3) was assumed. (See Theroretical, 1.)

In this expression, $k_1 \cdot J_{abs}$, the first term in the side, is a constant for a given intensity of light, according to the author's assumptions.

When the reaction system reached a stationary state during the course of exposure,

$$\frac{d\Delta P}{dt} = 0.$$

Therefore,

$$k_1 \cdot J_{abs} = k_4'[O_2], \qquad (1.12)$$

the right side of which can be obtained from the observed value, because the mean value of the reaction velocity constant, $k_4'$, is already given as 0.306, and the value of $O_2$ which is the oxygen pressure equivalent to the photovoltaic potential is calculated from the observed value at the time when the system has reached a stationary state. Accordingly, $k_1 \cdot J_{abs}$ can be easily calculated from equation (1. 12); the values obtained are given in Table X.

Table X.

$k_1$ $J_{abs.}$: specific constant of the light reaction at 25°C.

| Wave length ($\mu\mu$) | $J_{abs}$ The light energy absorded (cal/cm²/sec) | Oxygen pressure in equilibrium (atm/min) | $k_1$ $J_{abs}$ (atm/min) |
|---|---|---|---|
| 492 | 5.575 | $2.04 \times 10^{-23}$ | $0.623 \times 10^{-23}$ |
| 492 | 0.02843 | $1.028 \times 10^{-25}$ | $0.317 \times 10^{-25}$ |
| 492 | 0.004055 | $1.470 \times 10^{-26}$ | $0.452 \times 10^{-26}$ |
| 430 | 0.004055 | $0.950 \times 10^{-25}$ | $0.292 \times 10^{-26}$ |
| 492 | 0.004055 | 1.470 ,, | 0.452 ,, |
| 550 | 0.004055 | 1.318 ,, | 0.404 ,, |
| 640 | 0.004055 | 0.813 ,, | 0.250 ,, |

The values of $k_1$ for variation in the wave length and intensity of light are given in Table XI, a, and b.

Table XI, a.

$k_1$: velocity constant of the light reaction at 25°C.

| Wave length ($\mu\mu$) | $J_{abs}$ The light energy absorbed (cal/cm²/sec) | $k_1$ (atm/sec) |
|---|---|---|
| 492 | 0.004055 | $1.86 \times 10^{-26}$ |
| 492 | 0.02843 | $1.85 \times 10^{-26}$ |
| 492 | 5.575 | $1.88 \times 10^{-26}$ |
|  |  | mean $1.863 \times 10^{-26}$ |

Table XI, b.

$k_1$ : velocity constant of the light reaction at 25°C.

| Wave length ($\mu\mu$) | $J_{abs}$ The light energy absorbed (cal/cm²/sec) | $k_1$ (atm/sec) |
|---|---|---|
| 430 | 0.004055 | $0.120 \times 10^{-26}$ |
| 492 | 0.004055 | 0.186 " |
| 550 | 0.004055 | 0.166 " |
| 640 | 0.004055 | 0.103 " |

This shows that $k_1$ which is the so-called photochemical velocity constant, is constant regardless of the intensity of light, and has a selective effect on the change of wave length, its maximum value being between 400 $\mu\mu$ and 500 $\mu\mu$.

(B) The Reaction Velocity during Exposure, $\frac{d\Delta P}{dt}$. As above said, from the values of $k_1$, $J_{abs}$ and $kd'$ and equation (1.7), the reaction velocity $\frac{d\Delta P}{dt}$ can be easily calculated. As one of the examples, Expt. III, c is shown in Table XII, where the calculated values agree quite well with the observed ones. This justifies equation (1.2) proposed by the author.

Table XII.

| t (minutes) | $\Delta P$ ($10^{-26}$atm/min) | $k_d'(\Delta P)=k_d'[O_2]$ ($10^{-26}$atm/min) | $k_1 \cdot J_{abs}$ ($10^{-26}$atm/min) | $\frac{d\Delta P}{dt}$ ($10^{-26}$atm/min)(calc.) | $\frac{d\Delta P}{dt}$ $10^{-26}$atm/min)(obs.) |
|---|---|---|---|---|---|
| 0 | 0 | —— | —— | —— | —— |
| 1 | 0.414 | 0.127 | 0.292 | 0.165 | 0.124 |
| 2 | 0.527 | 0.162 | 0.292 | 0.130 | 0.111 |
| 3 | 0.641 | 0.197 | 0.292 | 0.095 | 0.095 |
| 4 | 0.721 | 0.221 | 0.292 | 0.071 | 0.076 |
| 5 | 0.781 | 0.240 | 0.292 | 0.050 | 0.060 |
| 6 | 0.847 | 0.260 | 0.292 | 0.032 | 0.049 |
| 7 | 0.881 | 0.271 | 0.292 | 0.021 | 0.039 |
| 8 | 0.919 | 0.282 | 0.292 | 0.010 | 0.032 |
| 9 | 0.950 | 0.292 | 0.292 | 0 | 0.019 |
| 10 | 0.950 | 0.292 | 0.292 | 0 | 0 |
| 11 | 0.950 | 0.292 | 0.292 | 0 | 0 |
| 12 | 0.950 | 0.292 | 0.292 | 0 | 0 |

### 5) Photochemical Reaction Velocity, Light Intensity, and Wave Length.

In the preceding section the reaction velocity equation (1.3) was experimentally-proved. Accordingly, the pure photochemical reaction excluding the dark reaction is apparently of the zero order from equation (1.3):

$$\frac{dP}{dt} k_1 \cdot J_{abs} = k_1' , \qquad (1.13)$$

where $K_1$ is a particular constant including the intensity of light, $P$, the oxygen pressure equivalent to

$$P = \Delta P + \Delta p \qquad (1.14)$$

as is shown in Fig. IX.

Hence

$$P = k_1 \cdot J_{abs} \cdot t$$

$$= k_1' \cdot t \qquad (1.15)$$

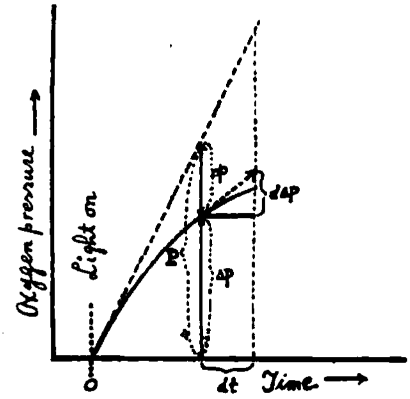


Fig. 9

The values obtained are given in Table XIII and XIV, and graphically in Figs. X and XI, which prove that the photochemical reaction is of the zero order, and also show that the stronger the intensity of light the

Table XIII.

| Time (mins.) | Wave length ($\mu\mu$) | P (atm) | | |
|---|---|---|---|---|
| | | J=5.575 cal/cm²/sec | J=0.02843 cal/cm²/sec | J=0.004055 cal/cm²/sec |
| 0 | 492 | 0 | 0 | 0 |
| 1 | 492 | $0.623 \times 10^{-23}$ | $0.317 \times 10^{-25}$ | $0.452 \times 10^{-26}$ |
| 2 | 492 | 1.246 ,, | 0.634 ,, | 0.904 ,, |
| 3 | 492 | — | — | 1.356 ,, |
| 4 | 492 | 2.492 ,, | 1.268 ,, | 1.808 ,, |
| 5 | 492 | — | — | 2.260 ,, |
| 6 | 492 | 3.738 ,, | 1.902 ,, | 2.712 ,, |
| 7 | 492 | — | — | 3.164 ,, |
| 8 | 492 | 4.984 ,, | 2.536 ,, | 3.616 ,, |
| 9 | 492 | — | — | 4.068 ,, |
| 10 | 462 | 6.230 ,, | 3.170 ,, | 4.520 ,, |
| 20 | 492 | 12.460 | 6.340 ,, | 9.040 ,, |

Table XIV.

| Time (mins.) | Intensity of light (cal/cm²/sec) | P (atm) | | | |
|---|---|---|---|---|---|
| | | w. l.=430 $\mu\mu$ | w. l.=492 $\mu\mu$ | w. l.=550 $\mu\mu$ | w. l.=640 $\mu\mu$ |
| 0 | 0.004055 | 0 | 0 | 0 | 0 |
| 1 | 0.004055 | $0.292 \times 10^{-26}$ | $0.452 \times 10^{-26}$ | $0.405 \times 10^{-26}$ | $0.250 \times 10^{-26}$ |
| 2 | 0.004055 | 0.584 ,, | 0.904 ,, | 0.810 ,, | 0.500 ,, |
| 3 | 0.004055 | 0.876 ,, | 1.356 ,, | 1.215 ,, | 0.750 ,, |
| 4 | 0.004055 | 1.168 ,, | 1.808 ,, | 1.620 ,, | 1.000 ,, |
| 5 | 0.004055 | 1.460 ,, | 2.260 ,, | 2.025 ,, | 1.250 ,, |
| 6 | 0.004055 | 1.752 ,, | 2.712 ,, | 2.430 ,, | 1.500 ,, |
| 7 | 0.004055 | 2.044 ,, | 3.164 ,, | 2.835 ,, | 1.750 ,, |
| 8 | 0.004055 | 2.336 ,, | 3.616 ,, | 3.240 ,, | 2.000 ,, |
| 9 | 0.004055 | 2.628 ,, | 4.068 ,, | 3.645 ,, | 2.250 ,, |
| 10 | 0.004055 | 2.920 ,, | 4.520 ,, | 4.050 ,, | 2.500 ,, |
| 20 | 0.004055 | 5.840 ,, | 9.040 ,, | 8.100 ,, | 5.000 ,, |

greater becomes the reaction velocity and it reaches a maximum for a particular wave length.

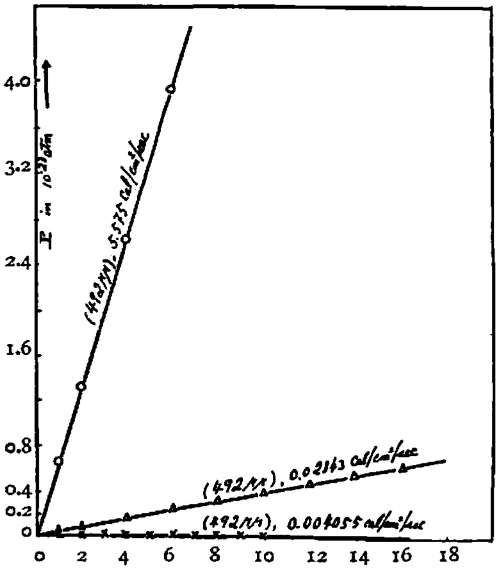


Fig. 10

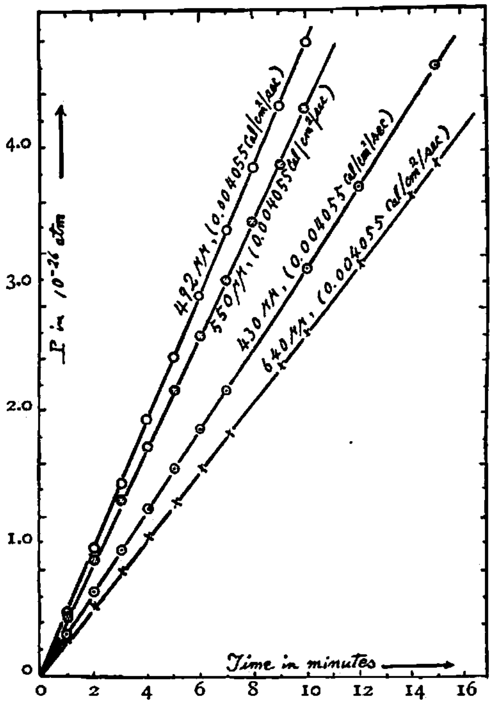


Fig. 11

6) Examination of the Absolute Value of Equilibrium Hydrogen Pressure of the Cell.

The equilibrium pressure of the copper oxide electrode was measured by Nernst's formula as copper electrode, and $4\,CuO \rightleftarrows 2\,Cu_2O + O_2$ was proposed as the mechanism of the photo-cell used. From this reaction mechanism, the author tried to confirm theoretical consideration of the reaction velocity from the standpoint of the ordinary reaction kinetics, and found that the theoretical consideration agreed quite well with the experimental as already mentioned.

Whether the ordinary reaction kinetics is applicable to the experiments carried out in such a degree of the pressure of hydrogen as $10^{-26}$ atm is a question, but further investigation will solve it[6]. There is, however, no question about the applicability from the formal view-point of the reaction kinetics.

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[6] According to the kinetical theory of gas, the number of the molecules colliding with 1 cm² of the surface area for 1 minute is given by

$$n = 1^2 \times v \times n_0,$$

## II) Thermodynamical Consideration.

In order to make clear the thermodynamical property of the cell used, the following measurements were made: (i) the calculation of $\Delta F$ and $\Delta H$ in the light and the dark of a reversible reaction system, $Cu_2O+\frac{1}{2}O_2=2\,CuO$, (ii) that of equilibrium constant $K$ of the same system, and (iii) that of the entropy of $CuO$.

### 1) $\Delta F$ and $\Delta H$ in the Light and the Dark of a Heterogeneous System, $Cu_2O+\frac{1}{2}O_2=2\,CuO$.

From E. M. F. (=0.8424,[7]) of $\mathrm{Cu}\,|\,\mathrm{Cu_2O},\ \mathrm{CuO}\,\frac{\mathrm{N}}{10}\,\mathrm{NaOH}\,|\,\mathrm{H_2}$ at 25°±0.02°C., we have

$$2\,CuO+H_2=Cu_2O+H_2O$$

$$(\Delta F)^{D}_{298}=-2\times 23{,}074\times 0.8424=-38{,}875\ cal. \tag{2.1}$$

$$\begin{aligned}(\Delta H)^{D}_{298}&=-2\times 23{,}074\times(0.000507\times 298.1+0.8424)\\&=-45830\ cal.\end{aligned} \tag{2.2}$$

In the case of the formation of water,

$$H_2+\frac{1}{2}O_2=H_2O$$

$$(\Delta F)^{D}_{298}=-56560^{8)} \tag{2.3}$$

$$(\Delta H)^{D}_{298}=-68270^{9)} \tag*{(2.3)}$$

Hence,

$$Cu_2O+\frac{1}{2}O_2=2\,CuO$$

$$(\Delta F)^{D}_{298}=-17620\ cal. \tag{2.5}$$

$$(\Delta H)^{D}_{298}=-22440\ cal. \tag{2.6}$$

There is no experimental result appropriate to compare with this value: the heat of formation of $Cu_2O+\frac{1}{2}O_2=2\,CuO$ is -35,000 cal according to Dulong,[10] and

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where $v$ is the velocity of a molecule (cm/sec) and $n$ the number of the molecules in 1 c.c.
At 298°K.,

$$v=4.10^4$$

At $0.292\times 10^{-26}$ atm,

$$\begin{aligned}n_0&=3\times 10^{19}\times 0.292\times 10^{-26}\\&=8.76\times 10^{-8}\\ \therefore\quad n&=4\times 10^{4}\times 8.76\times 10^{-8}\\&=3.5\times 10^{-3}\end{aligned}$$

[7] S. Horiba and N. Hayami, *loc. cit.*

[8] Lewis; *Thermodynamics*, 465.

[9] Lewis; *Ibid.* 477.

[10] Dulong; *Compt. rend.* 7, 87 (1848).

-36,200 cal. according to Andrews[11], which differ more or less from the value obtained.

Similary, $(\Delta F)^R_{298}$ and $(\Delta H)^R_{298}$ of some intensities of light were calculated. The values obtained are given in Table XV and Fig. XII. It is apparent from the figure that the relation between both $\Delta F$ and $\Delta H$ and the intensity of light is linear.

Table XV.

The Influence of Intensity of Light on ΔF and ΔH at 25°C.

| Intensity of light (cal/cm²/sec) | E. M. F. of Cell [A] (volts) obs. | $E_a$ $Cu \mid Cu_2O,\ CuO\ \frac{N}{10} NaOH \mid H_2$ (volts) calc. | $(\Delta F)_{298}$ (calc.) | $(\Delta H)_{298}$ (calc.) | $\Delta S = \frac{\Delta H - \Delta F}{T}$ $Cu_2O + \frac{1}{2}O_2 = 2CuO$ |
|---|---|---|---|---|---|
| 0 | 0.2323 | 0.8424 | —17620 | —22440 | —15.20 |
| 0.002318 | 0.2298 | 0.8449 | —17565 | —22350 | —16.12 |
| 0.004055 | 0.2282 | 0.8465 | —17496 | —22270 | —16.05 |
| 0.00813 | 0.2233 | 0.8514 | —17170 | —22124 | —16.63 |
| 0.02843 | 0.2174 | 0.8573 | —17039 | —21820 | —16.05 |
| 0.1042 | 0.2087 | 0.8660 | —16596 | —21400 | —16.15 |
| 5.575 | 0.1848 | 0.8899 | —15493 | —20420 | —16.54 |
| 14.100 | 0.1628 | 0.9119 | —14478 | —19520 | —16.93 |

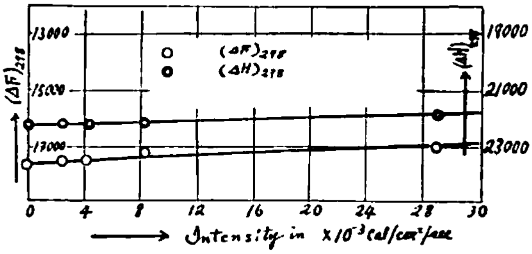

Fig. 12

The influence of intensity of light on ΔF and ΔH at 25°C.

2) Equilibrium Constant.

In order to measure the equilibrium voltage of the cell, $Cu \mid Cu_2O,\ CuO\ \frac{N}{10} HaOH \mid H_2$, the equilibrium constant of $4\,CuO \rightleftarrows 2Cu_2O + O_2$ was measured, using the following equation:

$$\Delta F = -RTlnKp_{O_2} \qquad \text{(i)}$$

$$log\, K_{P_{O_2}} = -\frac{(-\Delta H)}{4.57 \times 298.1} + \Sigma n\ 1.75\ log\ T + \Sigma nC \qquad \text{(ii)}$$

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[11] Andrews; *Phil. Mag.*, (3), 32, 321 (1848).

$$E_\alpha = E_\beta + \frac{0.059}{4} log\ P_{O_2}\ ; \qquad ln\ P_{O_2} = ln\ K_{P_{O_2}}. \qquad \text{(iii)}$$

For example, the case in the dark is as follows:

$$4\ CuO \rightleftarrows 2\ Cu_2O + O_2$$

$$(\Delta F)^{0}_{298} = 2 \times 17620 = 35,240\ cal.$$

$$\Delta F = -RTlnK_{P1}$$

$$log\ K_{P1} = \frac{-2 \times 17620}{2.303 \times 1.988 \times 298.1} = -25.82,$$

$$K_{P1} = P_{O2} = 1.814 \times 10^{-26} atm.$$

From equation (ii),

$$log\ K_{P_{O2}} = -\frac{2 \times 22440}{4.571 \times 298.1} + 1.75\ log\ 298.1 + 2.8 = -25.72$$

$$\therefore\ K_{P2} = 1.905 \times 10^{-26} atm.$$

And from equation (iii),

$$log\ P_{O2} = \frac{4 \times (0.8424 - 1.226)}{0.059} = -26.00$$

$$\therefore\ P_{O2} = 10.0 \times 10^{-26} atm.$$

Similary, the equilibrium constants in the case of different intensities of light can be obtained. Those values are in good agreement as given in Table XVI and Fig. XIII.

Table XVI.

Equilibrium Constant and Intensity of Light.

| Number of Expt. | $J_{abs}$ (cal/cm²/sec.) | $S_{CuO}$ (calc. from Table) | $P_{O2}$ $E_\alpha = E_\beta + \frac{0.059}{4} \log P_{O_2}$) | $K_{P_{O2}}$ $(-\Delta F = RTlnK_{P1})$ | $K_{P_{O_2}}$ (Nernst's Formula) |
|---|---|---|---|---|---|
| 1 | 0.00 | 15.18 | $1.000 \times 10^{-26}$ | $1.814 \times 10^{-26}$ | $1.905 \times 10^{-26}$ |
| 2 | 0.002318 | 14.73 | 1.514 " | 1.405 " | 2.042 " |
| 3 | 0.004055 | 14.76 | 1.862 " | 2.399 " | 2.692 " |
| 4 | 0.00813 | 14.47 | 3.981 " | 6.918 " | 4.266 " |
| 5 | 0.02843 | 14.76 | $1.000 \times 10^{-25}$ | $1.047 \times 10^{-25}$ | $1.349 \times 10^{-25}$ |
| 6 | 0.1042 | 14.71 | 3.981 " | 5.012 " | 4.266 " |
| 7 | 5.575 | 14.51 | $1.622 \times 10^{-23}$ | $1.995 \times 10^{-23}$ | $1.349 \times 10^{-23}$ |
| 8 | 14.100 | 14.32 | $5.012 \times 10^{-22}$ | $6.206 \times 10^{-22}$ | $3.020 \times 10^{-22}$ |

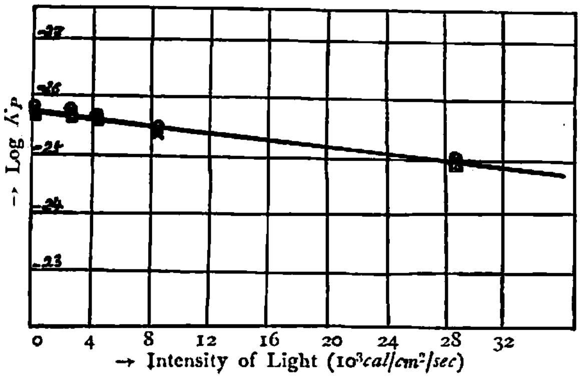

Fig. XIII

Equilibrium Constant (at 25°C.)

○ Log $P_{O_2}$

× Log $K_{P_1}$

● Log $K_{P_2}$

### 3) Entropy.

In the dark,

$$Cu_2O+\frac{1}{2}O_2=2\ CuO$$

$$(\varDelta F)^{D}_{298}=-17{,}620\ cal: \qquad (\varDelta H)^{D}_{278}=-2244\ cal$$

$$\therefore\quad \varDelta S=\frac{\varDelta H-\varDelta F}{F}-15.20 \text{ (Entropy Unit).}$$

Accordingly, the value of $S_{CuO}$ will be as follows:

$$-15.20=S_{CuO}-S_{\frac{1}{2}O_2}-S_{Cu_2O}$$

$=2\ S_{CuO}=24.1$[12]$-21.46$

$$\therefore\quad S_{CuO}=15.18 \text{ (Entropy Unit).}$$

Table XVI gives the values in the light.

$S_{CuO}$ was calculated in another way. From the temperature coefficient of the voltage of the $\mathrm{Cu}\big|\mathrm{Cu_2O},\ \mathrm{CuO}\frac{\mathrm{N}}{10}\mathrm{NaOH},\ \mathrm{HgO}\big|\mathrm{Hg}$ cell ($=0.00017$ volt[13]) and from the following equation:

$$\varDelta S=-\frac{d(\varDelta F)}{dt}nF\frac{dE}{dT}$$

we have

$$Cu+HgO=CuO+Hg$$

$$\varDelta S=nF\frac{dE}{dt}$$

$$=2\times 23{,}074\times 0.000170=7.84 \text{ (Entropy Unit).}$$

And from the value, $S_{Cu}=818,$[14] $S_{HgO}=16.11,$[15] and $S_{Hg}=17.8$[16],

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12) Lewis; *Thermodynamics*, 452 (Calculated from sp. ht.)

13) S. Horiba and N. Hayami, *loc. cit.*

14) Lewis; *ibid.*, 464.

15) $S_{HgO}$ was obtained thus:

$$H_g+\tfrac{1}{2}O_2=H_gO \qquad (\Delta F)^{D}_{298}=-13{,}804\ cal.$$

$$(\Delta H)^{D}_{298}=-21{,}489\ cal.$$

$$\therefore\quad \Delta S=\frac{-21489+13804}{298.1}=-25.79. \text{ (Entropy Unit).}$$

Hence,

$-25.79=S_{HgO}-17.8$[1]$-24.1.$

$$\therefore\quad S_{HgO}=16.11 \text{ (Entropy Unit.)}$$

This value coincides with $S_{HgO}=16.3$[2] (Gunther), $S_{HgO}=16.2$

1) Lewis; *Thermodynamics*, 495.

2) Lewis; *ibid.*

16) Lewis; *Thermodynamics*, 465.

$$S_{CuO}=7.84+8.18+16.11-17.8$$
$$=\mathbf{14.33}\ \text{(Entropy Unit).}$$

It is observed that this value agrees, on the whole, with those obtained from $\Delta F$ and $\Delta H$.

## Summary.

1) A heterogeneous electrode, Cu $\big|$ Cu$_2$O, CuO$\frac{N}{10}$NaOH, which was in equilibrium in the dark has been assumed to be a kind of reversible reaction system and the chemical kinetics of reactions in the dark and in the light has proved to be applicable to such a heterogeneous system. The velocity equation of the reaction system at any wave length and intensity of light is given by

$$\frac{d(\Delta P)}{dt}=k_1\cdot J_{abs}-k_d'\,[O_2],$$

and it has been ascertained that the velocity formula of the reaction in the dark satisfies the reaction of the first order:

$$-\frac{d(\Delta P')}{dt}=k_d'\,[O_2].$$

and the formula of the photochemical reaction, excluding the reaction in the dark, satisfies that of the zero order:

$$\frac{dP}{dt}k_1\cdot J_{abs}=k_1'.$$

2) On the other hand, making thermodynamical research on the said reaction system, the equilibrium constants in the light and the dark have been calculated from the formulae and they have proved to be in good agreement. Further thermodynamical constants have been calculated. Hence the entropy in the case of the formation of $CuO$, which has been proved to agree fairly well with the theoretical value. Thus, it has been experimentally demonstrated that the Becquerel effect of copper oxide electrode in alkali solution is brought about according to the photochemical reversible reaction of a heterogeneous system:

$$4\,CuO \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} 2\,Cu_2O+O_2$$

The author takes this opportunity to express his deep gratitude to Professor S. Horiba for his continued guidance.

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