the temperature coefficients of the following electrodes: H_2, H_2SO_4 (0.1 N) : : Constant Reference, $dE/dT = -0.000,27$; H_2, H_2SO_4 (1.0 N) : : Constant Reference, $dE/dT = -0.000,43$; Constant Reference : : H_2SO_4 (0.1 N), Hg_2SO_4, Hg, $dE/dT = +0.000,28$; Constant Reference : : H_2SO_4 (1.0 N), Hg_2SO_4, Hg, $dE/dT = +0.000,30$. All of the electrodes studied become more electronegative as temperature increases.

3. It has been pointed out that an assumption made in the development of the temperature coefficient of the tenth normal calomel electrode that the e.m.f. of the cell, H_2, HCl (0.1 M) : : H^+ (M), H_2, is proportional to the absolute temperature is not supported by the experiments on sulfuric acid-hydrogen electrodes or by those of Fales and Mudge on the 0.1 M hydrochloric acid hydrogen electrode.

4. The fact that sulfuric acid-hydrogen electrodes become more electronegative as the temperature increases indicates that the activity of the hydrogen ion increases with temperature so rapidly as to offset any increase in potential indicated by an increased value of T in the equation $E = (RT/nF) \log_n (a_{H^+}/a = 1)$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ABSORPTION SPECTRUM AND THE PHOTOCHEMICAL DECOMPOSITION OF ACETONE

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This paper reports a determination of the molal extinction coefficients of gaseous acetone between 3500 Å. and 2000 Å., and rate measurements on the photochemical decomposition of acetone in limited regions of the spectrum. The primary purpose of the work was to determine whether the decomposition is caused by radiation corresponding only to the peak of the curve or if all absorbed energy is effective. The plotting of the absorption curve was a necessary incident. The absorption curves of aqueous and of alcoholic solutions of acetone were known.[1] The curve for gaseous acetone was obtained by the following method.

Oxidized copper gauze screens, of various meshes, were mounted over circular holes (7.5 cm. in diam.) in 15cm. squares of sheet iron. The ratio of the light transmitted by each screen to the total incident light was determined with the aid of a photometer having a bench length of 300 cm. An electric light was mounted at each end, and by adjusting the current in one of them by means of a variable resistance the lamps were made to furnish the same intensity of light. For this adjustment and with no

[1] Bielecki and Henri, *Compt. rend.*, **155**, 456 (1912); **156**, 884 (1913); *Physik. Z.*, **14**, 515 (1913); *Ber.*, **46**, 3570, 3627, 3650 (1913).

screens interposed, the comparison box was placed in the center (150 cm. from either end). With a screen interposed on one side, the comparison box was moved nearer to the light hidden by the screen until the two sides of the field were again equally illuminated. This distance was measured, and by means of the law of inverse squares the absorption of the screen was obtained.

The screens were used in getting the absorption curve of acetone as indicated below. An apparatus was constructed as shown in Fig. 1.

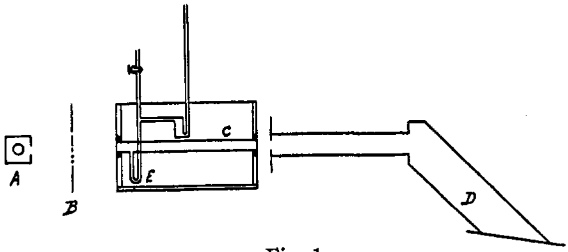

Fig. 1.

The source of light A was enclosed in a box with a small opening. The emerging rays passed through a screen B which absorbed a known amount of light. The light then traversed a long evacuated quartz tube C (59.4 cm. long inside), and its spectrum was photographed in a Hilger quartz spectrograph D. After removing the screen B and introducing pure gaseous acetone into the quartz tube at a pressure indicated by the manometer E, a second photograph was obtained on the same plate. At certain points the two photographs had equal densities and, for these particular wave lengths, we know the acetone absorbed the same proportion of the light that was shut out by the wire screen. As an example we may take a pair of photographs that showed equal densities at positions corresponding to 3110 Å. and 2450 Å. These positions could be located visually within a range of 5 Å. The acetone vapor pressure was 8.1 cm., the temperature 86°, and the screen used absorbed 84.1% of the light falling upon it.

According to Beer's law, $I_T/I_I = 10^{-ecd}$, where I_T is the intensity of light transmitted through a solution of an absorbing substance in a non-absorbing solvent, I_I is the intensity of light incident upon the cell, c is the concentration (moles per liter), d is the thickness of the solution in centimeters, and e is the molal extinction coefficient.

In this case $I_T/I_I = 1 - 0.841 = 0.159 = 10^{-ecd}$, whence $e = 3.72$. Hence, for the wave lengths 3110 Å. and 2450 Å. gaseous acetone has an extinction coefficient of 3.72.

Similar measurements were made with other screens, with combinations of screens, and with acetone vapor under various pressures until sufficient data had been obtained for the construction of the complete absorption curve. The curves for aqueous and alcoholic solutions of acetone and for aqueous α-crotonic acid as measured by Bielecki and Henri,[1] are reproduced in the same cut (Fig. 2) for future reference.

The actual measurements of the molecular absorption (extinction coefficient) of gaseous acetone are summarized in the Table I.

TABLE I

GASEOUS ACETONE

λ	ϵ	λ	ϵ	λ	ϵ
3295	0.153	3125	3.31	2460	3.94
3290	.198	3110	3.72	2450	3.72
3285	.235	3090	3.94	2415	3.31
3270	.392	3070	4.67	2410	2.96
3265	.460	3000	7.03	2400	2.81
3255	.589	2970	8.21	2370	2.36
3230	.93	2920	9.80	2350	1.82
3215	1.24	2820	11.60	2330	1.55
3200	1.55	2720	11.60	2305	1.24
3180	1.82	2600	9.80	2290	0.93
3160	2.36	2540	7.94	2255	.589
3140	2.81	2535	7.03	2240	.460
3135	2.96	2475	4.67	2235	.392

In the second phase of the problem we sought to determine whether the decomposition of acetone is accomplished by light of one frequency only or if all light absorbed is effective. At the suggestion of Dr. G. E. K. Branch this was done by a study of reaction rates as influenced by the use of aqueous solutions of acetone as filters. A very dilute solution of acetone used as a filter between the reaction chamber and the source of light removes completely the radiation corresponding to the peak of the curve (II, Fig. 2) and merely diminishes the intensity of light corresponding to all other frequencies. A more concentrated solution of acetone in the filter cuts off a larger area under the central portion of the curve, but still transmits lower and higher frequencies corresponding to small extinction coefficients.

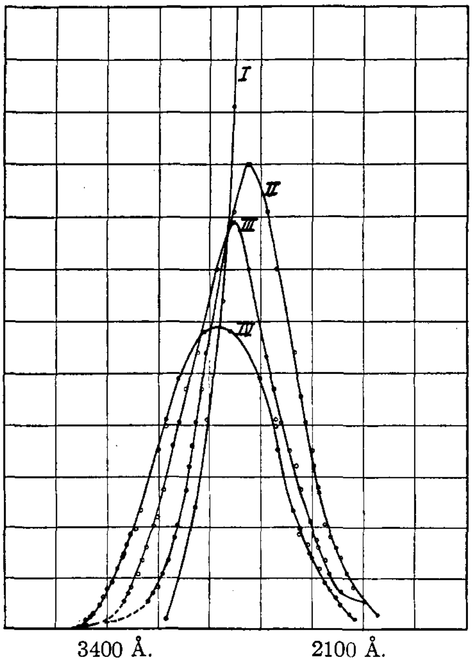

Fig. 2.—*I* = α-crotonic acid; *II* = acetone in water; *III* = acetone in alcohol; *IV* = acetone vapor.

A wooden box, B, (Fig. 3) lined with galvanized iron and filled with water, was used as a thermostat. Heating was accomplished by a 1000-watt submerged coil to which was attached a stirring propeller P. The coil usually required about three hours to bring the bath to boiling, and would then keep the water gently boiling. A quartz tube Q, 59.4 cm. in inside length and 3 cm. in diameter, was used for the reaction chamber. It traversed the entire length of the bath, being fitted to the box at each end with rubber stoppers. The ends of the tube were quartz plates which had been polished on both faces and fused to the tube. A side tube led from the quartz tube to a quartz-to-Pyrex graded joint and a Pyrex glass U-tube. The large quartz tube was carefully cleaned, dried and filled with pure liquid acetone that had been boiled to remove dissolved air. The tube was then placed in the bath and the heat turned on. When the boiling point of acetone was reached (56.6°) vapor displaced the liquid, the latter being forced out through the side tube. When almost all the liquid had been removed, a small amount of mercury was dropped into the side tube to seal the bend and trap the gas remaining in the large quartz tube, and the heating was continued. When the temperature reached 100° the quartz tube was full of acetone vapor at some pressure slightly above atmospheric. Mercury was then dropped in until the inner level reached a mark at H, and by means of a scale attached to the tube C the indicated pressure was read and the barometric pressure was added. The usual pressures were between 75 and 85 cm.

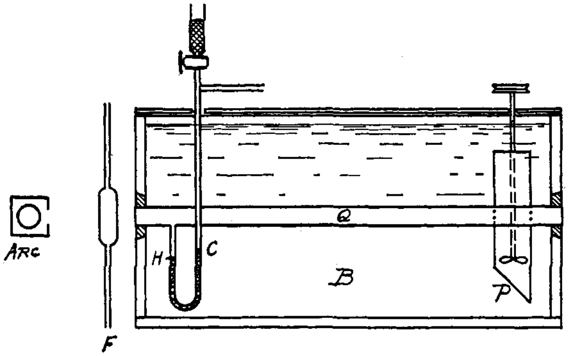

Fig. 3.

After allowing time for the arc to reach a steady state, a shutter in front of the light was opened and the rate of rise of the pressure noted. In each case this was done by keeping the inner mercury level at H by the addition of small quantities of mercury to the outer tube C. The experiments were thus performed at constant volume. A rate measurement was made first with pure water running slowly through the filter cell, F. The shutter was then closed long enough to permit replacement of the water filter by a solution of acetone, and the rate was again measured. It was necessary to keep fresh acetone solution continually running through the filter cell, for otherwise the acetone in it would soon be destroyed by photochemical reactions. The runs were not continued long enough to decompose more than 5% of the vapor. In this way any change in absorption due to a diminution of acetone in the reaction chamber became negligible. The volume of gas, down to the mark H, was 427.0 cc.

Based upon the rate obtained when the reaction chamber was illuminated through a water filter, the results obtained were as follows.

Filter	Water	Acetone	Acetone	Acetone	Acetone	Acetone	Crotonic acid
Concn., *M*	..	0.025	0.05	0.10	0.15	0.25	..
Meas. rate of decompn.	1.00	.68	.54	.45	.39	.30	0.56

These reaction rates are approximately proportional to the fractions of energy transmitted through the filters.

In order to eliminate the higher frequencies and obtain an exposure of acetone vapor to the radiation of longer wave lengths only, we used a solution of α-crotonic acid as a filter. Reference to Fig. 2 shows that such a filter can be used to cut out everything of shorter wave lengths than 2700° Å. The rate of decomposition behind this filter was reduced to 56.3% of the value obtained through a water filter, and this corresponds rather closely to the change in total radiant energy reaching the reaction chamber. In other words, within the boundaries of the absorption curve, energy derived from radiation of any frequency seems to be effective. The question as to whether one quantum of energy in one region is as effective as one quantum in any other region, within the boundaries of the curve, is under investigation.

The conclusions stated above concerning the approximate proportionality between reaction rates and total energy absorbed are based upon estimates of energy distribution in the mercury arc made by Harrison and Forbes[2] under conditions that were not exactly duplicated in our work. We cannot, therefore, use their data as a basis for estimating the relative efficiencies of equal quantities of energy derived from different parts of the spectrum.

Summary

1. The absorption curve of gaseous acetone in the ultraviolet region of the spectrum has been determined.

2. All of the light absorbed is effective in bringing about decomposition.

3. By use of acetone filters it was found that radiation corresponding to the peak of the absorption curve does not possess any special significance with regard to the light which brings about the reaction.

4. By means of crotonic acid filters it was shown that decomposition is not dependent upon the presence of the shorter wave lengths within the absorption region.

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[2] Harrison and Forbes, *J. Optical Soc.*, **10**, 1 (1925).