

$$\Delta H_T = \Delta H_0 + \Delta aT + \frac{\Delta b}{2} T^2 + \Delta cT^{-1} \quad (9)$$

$$\Delta F_T^\circ = \Delta H_0 - \Delta aT \ln T - \frac{\Delta b}{2} T^2 + \frac{\Delta c}{2} T^{-1} + IT \quad (10)$$

Summary

The equation $Q_{273.1}^T = \left[aT + \frac{b}{2} T^2 + cT^{-1} \right]_{273.1}^T$ is suggested for the representation of high temperature thermal data and is shown to be superior to the ordinary power series expression. The suggested equation is readily usable in all thermodynamic calculations, involves no additional labor and may be employed in conjunction with power series expressions, if desired.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

APPARATUS FOR QUANTUM YIELDS OF GAS REACTIONS BY ACTINOMETRY

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RECEIVED MAY 12, 1932

PUBLISHED AUGUST 5, 1932

By proper use of actinometry it is possible to avoid most of the difficulties of radiometric procedures, also the disadvantage that radiometric errors can be estimated only by the original investigator and only before his apparatus is dismantled. When quantum yields are referred to a reproducible standard under identical conditions, systematic errors tend to cancel out. If, later, the given actinometer is restandardized, it is easy to recalculate all quantum yields previously referred to it.

In this Laboratory the quantum yields of uranyl oxalate have been determined within 5% over the range 435 to 254 $m\mu$,¹ also 278 to 208 $m\mu$,² thus providing the basis for an advance in actinometric procedure. We have constructed an apparatus (Figs. 1, 2) for quantitative study of photochemical gas reactions attended by pressure changes. It could easily be modified for studies of gas reactions without pressure change, or of liquid systems.

Light from a vertical mercury vapor lamp O (Fig. 1) was resolved by the conventional train between the quartz condenser, Q_c , and the exit slit, E, cut to fit the image of the spectral line furnishing the monochromatic radiation. A shutter was placed between O and Q_c . A small elliptical quartz lens of short focus, Q_e , lessened the divergence of the issuing beam.

Two quartz cells, each the frustum of a rectangular pyramid, had identical dimensions and a volume approximately 40 cc. All seams were fused. The gas cell, C_g , shown in detail in Fig. 2, had a capillary inlet, I. The acti-

¹ Leighton and Forbes, *THIS JOURNAL*, **52**, 3139 (1930).

² Brackett and Forbes, data to be published.

nometer cell, C_a , had instead a tubulure 4 mm. in internal diameter through which passed a small stirrer propelled by a windmill. Either cell enveloped the light beam diverging from E, just avoiding incidence of light upon the side walls. Each cell was encased in a copper jacket, J, having two rectangular openings, opposite the front and back windows. Copper ribbons

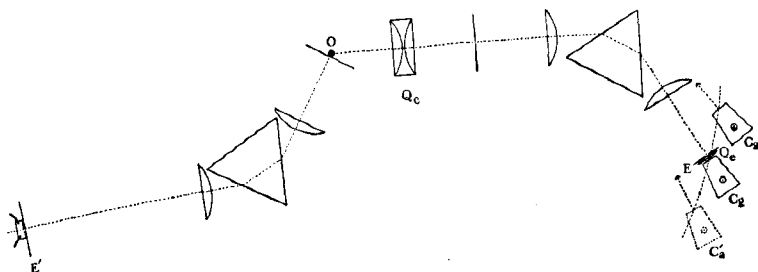


Fig. 1.

10 mm. wide soldered around the edges of these openings and cemented around the ends of the cells made the jackets water-tight. Thermal insulation was provided by cork sheets 6 mm. thick (1 mm. over the front wall). A cork cover insulated the rear window. Water from thermostats was circulated by pumps at a uniform rate through the jackets. The temperature of the issuing water remained constant within $\pm 0.05^\circ$.

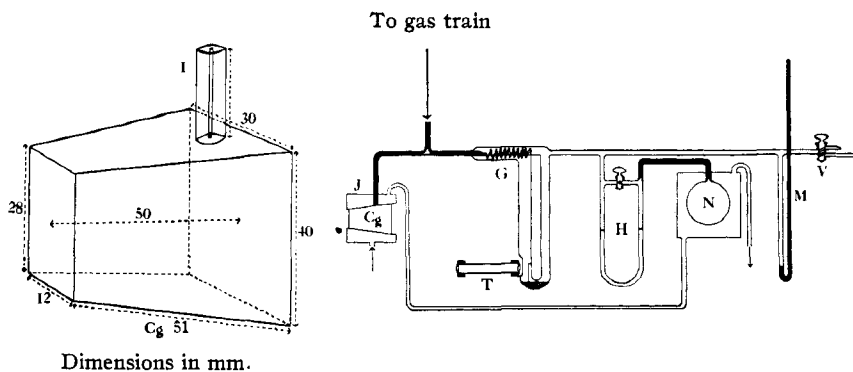


Fig. 2.

The apparatus to the right of O, Fig. 1, permits direct comparison of reaction rate in C_g with that in C_a by exposing the cells alternately behind E for measured times. Frequent shifting would average out lamp fluctuations, but this always is inconvenient, and would be unsuitable if the gas reaction involved induction periods or after effects. Therefore, we added a second monochromator in fixed position to the left of O. Its exit slit E' receives the image of the same spectral line as is incident upon E. By means of the thermopile behind E' and a high-sensitivity galvanometer,

scale deflections *proportional* to the energy flux emerging from either E' or E can be measured frequently during an experiment. Such readings make it possible to separate short-time variations in photochemical reaction rate from simultaneous fluctuations in the lamp.

As C_g must be rigidly mounted, it cannot be removed to allow substitution of C_a . Therefore the train from Q_c to E was solidly mounted upon a horizontal steel plate 3 mm. thick (not shown) which slid freely upon the upper surfaces of three heavy steel bars held parallel to each other. By means of a rigid steel arm suitably bent the plate was pivoted directly under O . To shift radiation from C_g (Fig. 1) to C_a , E was first detached from the plate (all cell windows covered) and the plate swung through the required angle. Next E was attached again to the plate in front of C_a , and the beam accurately centered by means of a screw mechanism operated through a milled head. Exposure of C_a in two positions C_a and C'_a as shown (Fig. 1) made it possible to average out any error due to uneven spatial distribution in the radiation of the lamp.

Pressure changes in C_g were measured in the customary fashion in terms of an artificial atmosphere, using as a null instrument a Bodenstein quartz spiral gage, G , Fig. 2. An offset near the free end of the pointer dipped in triacetin and damped out vibrations. Observing the end of the pointer through the telescope, T , pressure differences of 0.05 mm. of mercury were readily recognized by the excursions of the pointer from the fixed zero point. The gage was connected to the reaction cell by a Pyrex capillary and two graded seals; the combined volume of these was less than five per cent. that of the cell. The Pyrex jacket surrounding the gage communicated with a compensation cell, N , of appropriate volume, thermostated at the same temperature as C_g . All parts of the compensating system not thermostated were wrapped with heavy felt; otherwise drafts produced erratic changes in the apparent pressure within C_g . Differences in pressure between C_g and N could be read from the triacetin manometer H , and total pressures (by cathetometer) from the mercury manometer M .

If the reaction is free from complications, the second monochromator is dispensed with, and C_g and C_a are exposed alternately behind E for measured times Δt_g and Δt_a . Repeating, C_a is exposed on the other side of C_g . While C_a is being exposed, the dark reaction, if any, is studied in C_g . Assume the ratio of total quanta received by C_g and C_a , respectively, equal to $\Sigma \Delta t_g / \Sigma \Delta t_a$, after suitable corrections for difference in the reflections quartz-gas and quartz-water, also for any transmissions exceeding one per cent. Then the quantum yield of the gas reaction $\phi_g = \phi_a \Delta m_g - \Sigma \Delta t_a / \Delta m_a \Sigma \Delta t_g$ where Δm_g and Δm_a equal the moles transformed in C_g and C_a as measured by manometry and titration, respectively.

If the second monochromator is used, galvanometer deflections are frequently recorded during irradiations of C_g and C_a and plotted against the

corresponding times as ordinates. The cell C_a is exposed (using both positions) until the quantity of oxalic acid decomposed is measurable with the degree of precision desired. The area under the curve is divided into strips by ordinates at those times which mark the various stages of the experiments. The area of any strip is proportional to total quanta emerging from either exit slit during the corresponding time interval. Corrections for reflection and transmission are made as stated above. Let A_g be the area of the strip corresponding to a given exposure of C_g , and $(A_a + A'_a)$ the sum of the areas for the two exposures of C_a . Also let $\Sigma(h\nu)_g$ and $\Sigma(h\nu)_a$ be corrected total quanta absorbed, and Δm_g , Δm_a the moles transformed during the same time intervals. Then $\phi_g = \phi_a \Delta m_g \Sigma(h\nu)_a / \Delta m_a \Sigma(h\nu)_g = \phi_a \Delta m_g (A_a + A'_a) / \Delta m_a A_g$.

If the apparatus is carefully handled, the ratio $(A_a + A'_a) / \Delta m_a$ remains constant and reproducible within experimental error, and need not be rechecked for each refilling of the gas cell.

Summary

An apparatus and a method are described whereby the quantum yield of a photochemical gas reaction over any time interval during its progress may be stated in terms of the quantum yield of uranyl oxalate in monochromatic light of the same wave length with a probable error of five per cent.

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A NEW METHOD FOR THE DETERMINATION OF PROPIONIC ACID

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RECEIVED MAY 12, 1932

PUBLISHED AUGUST 5, 1932

There is a need for a suitable method for the quantitative estimation of propionic acid in the presence of formic and acetic acids. This becomes of special importance in connection with the analysis of acids produced by fungi. The fact that oxalic acid is produced by the following method from propionic acid but is not formed from formic and acetic acids under the same circumstances serves as a basis for a new method for the determination of propionic acid.

Method.—To every 5.94 cc. of 0.1 *N* propionic acid, 1.5 g. of anhydrous sodium carbonate, 17.5 cc. of 3.12% potassium permanganate, and 27 cc. of distilled water are added in a 250-cc. Pyrex Erlenmeyer flask. This flask is capped by a small glass beaker and the entire Erlenmeyer covered by a large glass beaker and placed on a steam-bath for four hours. After that time the Erlenmeyer is removed from the steam-bath and 5 cc. of 95% alcohol added to eliminate the excess potassium permanganate. The manganese dioxide is separated by filtering the mixture through an alundum crucible under suction. The alundum crucible is placed in a