MEASUREMENTS OF VELOCITY OF THE SYNTHESIS OF HYDROGEN BROMIDE BY CAPACITY CHANGE

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Abstract

Dielectric constant of bromine vapor at 180°C was found to be 1.0128 by comparing the capacity of the condenser containing Br with the capacity when it contained a gas of known dielectric constant. This value is considerably larger than that calculated for diatomic molecules (1.0022), and evidently corresponds to the molecular aggregate $(Br_2)_6$.

Study of the synthesis of HBr, by capacity measurements.—At 18° C in the dark, the reaction takes place slowly if at all, but illumination by a 100 watt lamp for a few minutes produced a considerable change. Blue light was found to be about four times as effective as red. At 58° C the reaction proceeded in the dark, the thermal effect predominating over the photo-chemical.

Null method capacity bridge is described, similar to the regenerative detector, in which the bridge feeds back to the plate circuit.

SINCE any chemical reaction is accompanied by a change in the dielectric constant of the reacting system, the change in the dielectric constant being proportional to the amount of substance transformed, the velocity of the reaction may be found by finding the change in the capacity of the system. This method is, however, only applicable to those reactions in which the conductivity of the reagents is negligible. This method is especially adapted to the measurement of the velocities of photo-chemical reactions, which cannot be measured by the familiar means because of the rapidity of the chemical change. In this paper, the method is applied to the photo-chemical synthesis of H and Br under the influence of light.

DESCRIPTION OF APPARATUS

The apparatus used is shown in Fig. 1. The oscillating system consists of a vacuum tube (106-B Western Electric Co.), two coils L_1 and L_2 coupled together, and two condensers C_1 and C_2 , the values of the coils and condensers being so chosen that the circuit oscillates at a wave-length of about 500 meters. The condenser C_1 is fitted with a variable vernier condenser while the plate-batteries are shunted with a large capacity Cwhich allows the oscillations to travel through it without serious damping.

The bridge consists of four condensers C^1 , C^3 , C^4 and C^5 arranged in the arms of the bridge. The capacity C^1 is connected in parallel with the test condenser C^2 in which is placed the dielectric whose behavior we wish

to ascertain; the capacity C^5 is also connected in parallel with a variable standard condenser C^6 . The mid-points C and D of the bridge are connected through a coil L^1 which is coupled with L_1 and L_2 . The points A and B are connected through a switch S with a coil L^2 which is coupled to the plate circuit by the coil L^3 , L^3 being independent of L_1 and L_2 . In the plate circuit is also connected in series a non-inductively wound variable resistance R which is connected to the potentiometer. The bridge, the oscillating circuit, including with it the coils L_1 , L_2 , L^1 , L^2 and L^3 , and the potentiometer are contained in separate metal boxes which are all earthed. The electric connections between the different systems



Fig. 1. Diagram of apparatus

are run through metal tubes so that all the circuits are screened from external influences. The condenser C^6 and the vernier condenser attached to C_1 can be worked from outside by means of bakelite handle; the switch S is also operated from the outside so as to avoid capacity effects. The condenser C^5 in which is placed the substance whose chemical velocity is to be determined, consists of a small glass tube of about 2 cm diameter and 4 cm long; within this a Pt dish in the shape of a frustrum of a cone, which rests on the walls of the glass container; almost touching it is a perforated Pt disk suspended from the top of the tube by a wire sealed through the glass, which serves as one of the leads. The arrangement is shown in Fig. 2. The tube is tubulated on both sides to allow for the introduction of the reagents.

The whole arrangement is mounted within an asbestos furnace which is used to control the temperature at which the reaction takes place. The coils of the furnace were heated by 120 volt current from storage cells, the current being so constant that it had no effect on the bridge.

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DETERMINATION OF THE CHANGE IN CAPACITY

The tube V is set oscillating, the coils L_1 and L_2 and capacities C_1 and C_2 being so adjusted that the change in plate current with capacity is a maximum. This slope of this curve is a maximum in the neighborhood of the maximum current. The oscillations on the primary circuit are fed through the coil L^1 into the bridge. If the bridge is off balance, A and B will have a difference of potential, so that when the switch S is closed momentarily—the switch is open in the normal position—there will be a current in the circuit containing the inductance L^2 which reacts on the plate circuit through the inductance L^3 . This reaction will make a change in the plate current so that the potentiometer will be thrown off balance and the galvanometer which is used to balance the potentiometer, will be



Fig. 2. Condenser containing reacting gases.

deflected. This action is the same as the regenerative action in detecting circuits and enables us to balance the bridge by a null method which is independent of the steadiness of the oscillator; and the visual method employed has also some advantages over the use of telephones. The bridge is adjusted until the momentary closing of the switch S produces no deflection of the galvanometer. The process is made easier in finding a rough adjustment by noting the difference between the right and left deflections of the galvanometer, which depends on how the bridge is off balance. In order to get an accurate balance the condenser, which is worked from the outside, must always approach the balance from the same side, since the balance obtained from opposite sides disagrees by a small amount. This effect is present in any type of bridge oscillator.

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After the potentiometer has been adjusted roughly, the circuit may be finely adjusted by the vernier C_1 , which allows us to keep the spot of light on the scale if the primary circuit should change slightly.

When the bridge has once been balanced, the bridge should be changed, keeping the capacities C^1 C^3 C^4 and C^5 so that the bridge is always balanced, until the variation of plate current with capacity C^6 is a maximum. In this state the bridge is nearly in resonance with the primary circuit.



Fig. 3. Capacity as a function of time. Effect of illumination with white radiation at 18°C.

The capacity C^6 is next calibrated by placing in C^2 gases whose dielectric constants are known accurately. The calibration may be carried with such gases as hydrogen, oxygen, hydrogen bromide and ammonia, whose dielectric constant as determined experimentally is very nearly the same as the square of the index of refraction.

The bridge is capable of measuring the dielectric constants to five decimal places, a sensitivity which is of the same order of magnitude as that of the most sensitive heterodyne bridges.

THE HYDROGEN AND BROMINE REACTION

The tube containing the Pt condenser was filled with H_2 generated by electrolysis and passed over P_2O_5 before entering the system. Liquid Br_2 was then introduced into the vessel so that the vessel then contained H_2 and Br_2 vapor in equilibrium with a very small amount of liquid bromine at room temperature. The bridge containing the vessel was balanced and readings were taken for several minutes in the dark. The

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light from a 100 watt nitrogen filled lamp was sent through the system through quartz windows in the asbestos furnace. The bridge was kept balanced by changing the capacity C^6 , readings being taken every 20 seconds. After three minutes the light was turned off, and readings taken every half minute for ten or more minutes to see if the reaction proceeded in the dark after being activated by the light.

The results of these investigations are shown in the accompanying graphs for various temperatures and for red and blue light at 18° C. In these graphs the units are so chosen that if the reaction proceeded to completion, the capacity would change by unity. The relative intensity of the radiation transmitted by the red and blue filters was 9/100 for the



Fig. 4. Effect of illumination with red light at 18°C.

blue and 24/100 for red of the total radiation of the lamp. The lamp had been coated with a dye which absorbed the violet and ultraviolet radiation. The spectral region transmitted by the filters extend from 7090A to 5720A and from 4850A to 4375A for the red and blue filters respectively.

The dielectric constant of bromine, measured by this method, was found to be $\kappa = 1.0128$ whereas the calculated constant, assuming the molecule is diatomic, has the following values: (1) by Lorentz's formula $\kappa - 1 = C\rho$, where $\rho = \text{density}$ and C = constant determined by applying the above equation to the liquid state, is $\kappa = 1.0022$; (2) from the index of refraction n = 1.00115, $\kappa = n^2 = 1.0023$. The values of κ calculated from Lorentz's formula and the index of refraction are derived on the assumption that the molecule is diatomic. The value of κ found experimentally is almost six times as large, showing that the molecule of Br

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has an effect six times as large as that of the diatomic Br molecule; i.e., it must have the formula $(Br_2)_6$.

The velocity curves seem to the writer to indicate that the vapor can exist only in the forms $(Br_2)_6$ or Br_2 at the temperature used in the experiment—the first being the natural form for this temperature. If, due to the chemical action, one of the Br atoms in the aggregate unites with a hydrogen atom forming HBr, the aggregate breaks down to the simple molecular form. Since the capacity decreases during the reaction, the HBr must be formed from the complex molecular structure rather than the simple.

The fluctuations in the capacity indicated by the velocity curves are probably due to the change in the molecular aggregate since the effect is quite noticeable in the dark before the reagents are exposed to the



Fig. 5. Effect of illumination with blue light at 18°C.

radiation. The action of the radiation would seem, from the curves, to increase this effect, which would be expected if the reaction tended to break down these complex molecules as we have explained in the previous paragraph.

If we consider the curves for red and blue radiation at 18°C, we see that the chemical reaction is more intense for the blue than for the red radiation, while in the dark before and after illumination no appreciable effect is noticed; i.e., the thermal reaction does not proceed at this temperature. Comparing the curves for white radiation at 18°C and 58°C, i.e. unfittered white light from the lamp, we see that although the effect of the light is predominate in influencing the reaction at 18°C—the dark reaction is not appreciable—the effect at 58° has almost completely

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disappeared and we have only the thermal reaction. Thus the photochemical velocity increases with increasing frequency of the incident light but diminishes with increasing temperature; the photo-chemical change is thus opposite to the effect predicted by the thermal chemical law

$$dx/dt = ce - a/kT = ce - h\nu/kT$$

where dx/dt is the velocity of the thermal reaction, i.e. the reaction in the dark.

This type of apparatus offers a means of measurement for a wide variety of chemical reactions, e.g. the photo-chemical decomposition of



Fig. 6. Capacity as a function of time, at 58°C.

HI, HBr, NH_3 , O_3 and H_2O_2 ; the method is also applicable to reactions in solvents; the writer has used this method to investigate the formation of ethyl acetate at various temperatures in aqueous solution.

Another field which would seem to offer many fruitful results, is the investigation of the degree of aggregation of vapors in contact with the liquid phase.

In conclusion, the writer wishes to express his gratitude to Professor E. P. Adams for suggesting the problem and for his helpful suggestions during the course of the investigation.

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