

primary processes given above and reactions 5, 6 and 7 as the only secondary reactions which occur, he can show from the percentages of methane, ethane and nitrogen given in Table I that the quantum yield given from pressure increase should be approximately 74% of that calculated from the nitrogen. Experimentally, the last three values of Table II give an average for the pressure method which is 71% of the nitrogen method. The small amount of hydrogen was ignored in this calculation.

**The Photolysis of Azomethane-Acetaldehyde Mixtures.**—Table III shows that under the proper experimental conditions azomethane will photosensitize the decomposition of acetaldehyde. It is probable that this process is initiated by free methyl radicals as indicated in reaction (1). The fact that the percentage of carbon monoxide is not appreciable until the ratio of acetaldehyde to azomethane is of the order of 10 to 1, is an additional indication that free methyls react with azomethane and that the energy of activation of this process is less than that for the aldehyde reaction. Such a conclusion is in accord with the low hydrocarbon to nitrogen ratio discussed above and also explains the failure of Burton, *et al.*,<sup>8</sup> to detect carbon monoxide in a similar experiment with a mixture of azomethane and acetaldehyde since the molecular ratio used by them was approximately 1 to 1. The hydrogen percentages found are somewhat erratic; nevertheless, they lead to the conclusion that this gas comes from the azo-

methane and not from the acetaldehyde. All of these results are consistent with reactions (1) and (2). At the same time it must be recognized that others have presented strong objections to reaction (2) as a room temperature process and it is possible that carbon monoxide was produced by reactions not considered in this discussion.

### Summary

1. The quantum yield of azomethane decomposition by  $\lambda$  3660 Å. at room temperature and in the pressure range 49 to 80 mm., has been found to be unity when calculated on the basis of the number of molecules of free nitrogen formed per quantum absorbed. Quantum yields calculated on the basis of pressure increase in the reaction system averaged 0.75. The nitrogen method is considered more reliable.

2. Analyses of the gaseous photodecomposition products of azomethane gave an average of 1.9% hydrogen, 6.5% methane, 37% ethane and 54% nitrogen. A mechanism is suggested which would account for all gases except the hydrogen.

3. It has been shown by the detection of carbon monoxide that azomethane will photosensitize the decomposition of acetaldehyde when the ratio of acetaldehyde to azomethane is greater than 10 to 1. This is interpreted as meaning that free methyl radicals produced in the photolysis of azomethane will react with either azomethane or acetaldehyde, preferably with the former.

LOS ANGELES, CALIF.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## The Contact Potential of an Iodine Film on Tungsten

BY M. J. COPLEY AND R. W. SPENCE<sup>1</sup>

Monomolecular films of oxygen and of hydrogen on metals have been widely investigated, but little information is available about the properties of halogen films. Van Pragh<sup>2</sup> exposed a platinum surface to iodine vapor, noted its effect on the accommodation coefficient of argon on platinum, and concluded that, at a pressure of 0.027 mm., an iodine film is formed below 1565°K. Glockler and Calvin<sup>3</sup> in their determination

of the electron affinity of iodine from thermionic data taken in the presence of iodine vapor, found no evidence of adsorption of iodine on tungsten at temperatures above 2000°K. with pressures as high as  $10^{-4}$  mm. Hendricks, Phipps and Copley<sup>4</sup> measured the degree of surface ionization taking place when molecular rays of the potassium halides impinged upon a hot tungsten filament. The course of the ionization curves showed that, at temperatures below 1600°K., for the specific rate of arrival ( $4.3 \times 10^{13}$  molecules

(1) Present address: University of Illinois College of Pharmacy, Chicago, Illinois.

(2) Van Pragh, *J. Chem. Soc.*, 798 (1933).

(3) Glockler and Calvin, *J. Chem. Phys.*, **3**, 20 (1935).

(4) Hendricks, Phipps and Copley, *ibid.*, **5**, 868 (1937).

cm.<sup>-2</sup> sec.<sup>-1</sup>) used in their experiments, surfaces were formed having work functions considerably higher than the work function of clean tungsten. They suggested that these high work function surfaces were due to adsorbed films comprised of halogen atoms. In the case of potassium iodide the work function of the WI surface was determined as 5.27 volts.

In order to learn more about the properties of an iodine film on tungsten, its contact potential relative to clean tungsten has been determined. The contact potential method<sup>5-9</sup> of studying adsorbed films on metallic surfaces makes use of the infra-saturation current from a hot filament to the clean and to the coated metal. If A and B are two filaments, A at a constant elevated temperature and B cold, the current between the two filaments is determined by their potential difference. At small positive potentials, within the infra-saturation region, the current varies as the  $3/2$  power of the potential and hence is very sensitive to voltage changes. If the current-volts characteristic of the system is measured with filament B clean, then measured again with filament B coated, and the current in each case plotted against the voltage, the second curve, while parallel to the first, is displaced along the voltage axis. The magnitude of this displacement represents the contact potential difference between the clean and the coated surface.

### Experimental

The apparatus used in making the contact potential measurements is shown in Fig. 1. A and B were aged

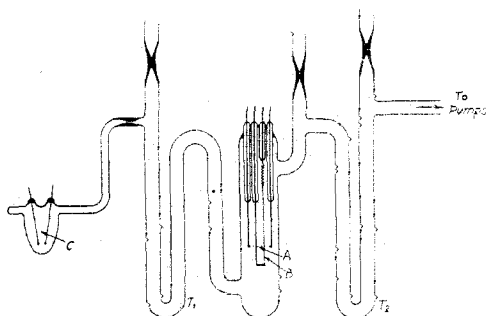


Fig. 1.—Diagram of contact potential cell.

tungsten filaments, 3.4 and 5.6 cm. in length, respectively, and both 0.00767 cm. in diameter, mounted at right angles to one another in a Pyrex glass tube. The vertical fila-

ment was kept taut by a tungsten spring attached to its upper end. No spring was used with the horizontal filament, but when the filament was spot-welded onto the leads, the leads were pinched together slightly to keep it under tension. This arrangement of the filaments<sup>8</sup> ensured that practically all the current measured flowed from a short section at the center of the hot filament to the cold filament; thus the electron source was homogeneous and nearly equipotential.<sup>9</sup> T<sub>1</sub> and T<sub>2</sub> were liquid air traps to freeze out iodine and mercury. The system was evacuated by means of two mercury vapor pumps (not shown in figure) in tandem and was pumped continuously during a run. Carefully purified thalious iodide was used as a source of iodine. It was placed in the electrolytic cell C and after fusion electrolyzed by means of two platinum-tipped tungsten electrodes sealed through the glass wall.

In order to obtain a vacuum sufficiently good to ensure clean surfaces, it was found necessary to give the system a thorough bake-out. This was accomplished by surrounding the entire system, with the exception of the pumps and the electrolytic cell C, by a furnace maintained at 500° for a period of twenty-four to forty-eight hours. Meanwhile the electrolytic cell containing the thalious iodide was hand torched. During this torching the thalious iodide was distilled repeatedly from the cell into the side tube where it was fused and allowed to run back. After such a bake-out, when the filaments had been flashed, the electron emission from the hot filament to the cold filament would usually remain constant for an hour, even without liquid air around the contact potential cell. It was extremely important to have such a high vacuum, since surrounding the contact potential cell with liquid air invariably introduced fluctuations in the galvanometer circuit.

The emission current was measured by the electrical circuit shown in Fig. 2. The currents for heating and flashing

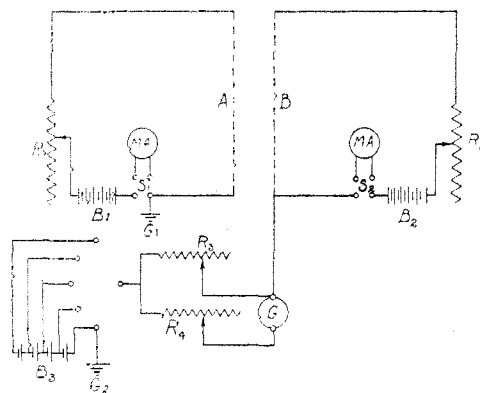


Fig. 2.—Electrical circuit for contact potential measurements.

the filaments were supplied by storage batteries B<sub>1</sub> and B<sub>2</sub>, and were adjusted by the rheostats R<sub>1</sub> and R<sub>2</sub>. The resistance boxes R<sub>3</sub> and R<sub>4</sub> constituted a shunt arrangement for the galvanometer G. Potentials between the two filaments were obtained from the bank of 2-volt storage cells B<sub>3</sub>. The contact potential cell was surrounded by a shield of copper gauze to eliminate anomalous effects.

The apparatus was checked by measuring the contact potential of a WO film relative to clean tungsten. In

(5) Richardson and Robertson, *Phil. Mag.*, **43**, 162 (1922).

(6) Langmuir and Kingdon, *Phys. Rev.*, **34**, 129 (1939).

(7) Reimann, *Phil. Mag.*, **20**, 594 (1935).

(8) Bosworth and Rideal, *Proc. Roy. Soc. (London)*, **A162**, 1 (1937).

(9) Bosworth, *Trans. Faraday Soc.*, **35**, 397 (1939).

making this measurement the filaments were flashed at 2700°K. and readings were taken of the infra-saturation current at voltages ranging from 0 to 8 volts. The emitter filament was kept at 2350°K. and the collector filament at room temperature. After the current-volts characteristic had been measured for the clean collector, air was admitted into the system through a capillary while the collector filament was kept at 1200°K. After the excess air had been removed, the emitter filament was flashed at 2700°K. and then adjusted at 2350°K. and the current-volts characteristic again was measured. The two sets of data when plotted gave curves which were closely parallel; however, the one for the WO surface was shifted along the voltage axis in the positive direction. Several determinations gave values for the contact potential ranging from -1.70 to -1.73 volts, in excellent agreement with the values reported by Reimann<sup>7</sup> and by Bosworth and Rideal.<sup>8</sup>

The procedure for obtaining the W-WI contact potential was identical with that outlined above for determining the W-WO contact potential. To form an iodine film, the thallos iodide was electrolyzed and the iodine caught in liquid air trap T<sub>1</sub>; then it was allowed to vaporize from this trap and come in contact with the filaments. It was found necessary, in order to obtain a film showing a maximum contact potential, to hold the collector filament at an elevated temperature; 1000°K. was finally adopted.

### Results

Figure 3 shows a plot of current versus volts for a typical run. The base curve for the clean tungsten could be duplicated in different runs, even when the vacuum had been broken in the intervening time, if a satisfactory baking-out process was again given to the system. The two curves in every case were very nearly parallel, particularly in the range 4 to 8 volts. The values obtained for the contact potential in twelve separate determinations were, respectively: -0.94, -0.90, -0.88, -0.90, -0.95, -0.93, -0.93, -0.88, -0.95, -0.87, -0.91, and -0.91 with an average value of -0.91 volt.

As stated in a previous paragraph it was necessary to keep the collector filament at 1000 to 1200°K. during the exposure to the iodine vapor. When the collector filament was kept at room temperature during the coating process and the contact potential determined, a value of -0.42 volt was obtained. This difference is presumably due to the formation of a molecular rather than atomic film. Attempts to activate such a molecular film by flashing to 1000°K. or above always gave a value of the contact potential lower than -0.91 volt, indicating some evaporation of the iodine. This behavior of iodine is different from that observed by Reimann<sup>7</sup> for oxygen with tungsten. He found that the value of the W-WO con-

tact potential was the same whether the temperature of the filament during the exposure to oxygen was room temperature or any other temperature for which the film was stable. An attempt was made to obtain more information on this point by admitting air with the collector filament cold; in every case a value in the neighborhood of -0.85 volt instead of -1.70 volts was obtained. It should be pointed out, however, that Reimann formed his WO surfaces with pure oxygen evolved from heated barium peroxide which was present in the contact potential cell.

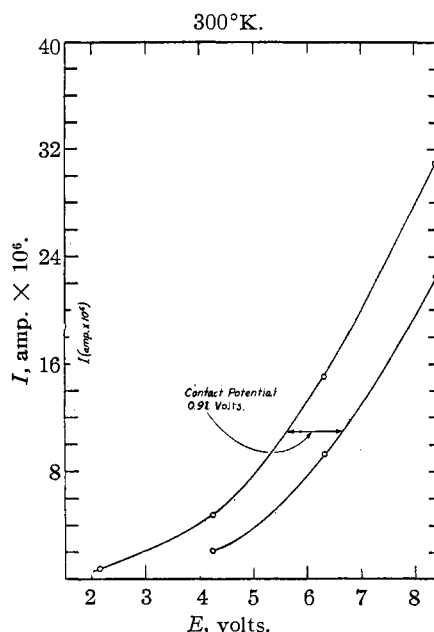


Fig. 3.—Current-volts characteristics of W and of WI surfaces.

If an iodine film was heated to 1250°K. for several minutes between contact potential measurements, the second determination was always low. This indicates that at 1250°K. the rate of evaporation of an iodine film is noticeable. At 1500°K. the rate of evaporation is rapid; however, to remove the last trace of iodine and duplicate the current-volt characteristic of clean tungsten it was necessary to flash to 2000°K.

Eckart<sup>10</sup> has shown that the contact potential difference between two surfaces is

$$V_{12} = \varphi_1 - \varphi_2 \quad (1)$$

where  $\varphi_1$  and  $\varphi_2$  are, respectively, the work function of the clean and coated surfaces. Hence using 4.52 volts for the work function of clean tungsten and 0.91 volt, the average value for

(10) Eckart, *Z. Physik*, **47**, 38 (1928).

$V_{12}$ , we obtain for  $\varphi_2$  a value of 5.43 volts. This value for the work function of a WI surface is in satisfactory agreement with the value 5.27 volts calculated from surface ionization measurements by Hendricks, Phipps and Copley,<sup>4</sup> since their result was obtained by extrapolating data taken over a short temperature range.

The large negative value of the W-WI contact potential suggests that the adsorbed iodine atoms on the surface are highly polarized. Thus on the surface of the coated filament there is an electrical double layer with the negative ends of the dipoles facing out. The dipole moment  $\mu$  of the adsorbed atoms may be estimated by the formula

$$\mu = V_{12}/2\pi\sigma \quad (2)$$

where  $V_{12}$  is the contact potential and  $\sigma$  is the concentration of atoms per cm.<sup>2</sup>. Assuming that the measurements have been made on a complete

monolayer and that the lattice structure is the same as for a cesium film,<sup>11</sup>  $\sigma$  may be taken as  $4.8 \times 10^{14}$  atoms cm.<sup>-2</sup>. Substituting in equation (2) gives a value of 1.0 Debye units for  $\mu$ .

### Summary

Evidence is presented that iodine forms a stable film on tungsten. Above 1250°K. the film evaporates at a noticeable rate, but flashing to 2000°K. is required for its complete and rapid removal.

The contact potential difference at room temperature between a clean tungsten surface and an iodine-coated tungsten surface was found to be -0.91 volt. The magnitude of the dipole moment of the adsorbed atoms in the complete film is estimated as 1.0 Debye unit.

(11) Taylor and Langmuir, *Phys. Rev.*, **44**, 423 (1933).

URBANA, ILLINOIS

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## Activity Coefficients in Concentrated Aqueous Solutions of Strong Electrolytes Described by a Formula Containing the Mean Ionic Diameter as Single Parameter.

### I. Theory and Application to the Alkali Chlorides, Bromides and Iodides<sup>1</sup>

BY PIERRE VAN RYSSELBERGHE AND SYLVAN EISENBERG

#### I. Introduction

If one wishes to represent the activity coefficient of a strong electrolyte by means of a formula valid at all concentrations, from infinite dilution to saturation, it is usually assumed necessary to introduce two parameters: the mean ionic diameter or distance of closest approach between a positive and a negative ion,  $a$ , and a coefficient  $B$  which, multiplied by the first power of the concentration  $C$ , gives a term representing, in a purely empirical manner, the effect of repulsive forces. The corresponding formula is associated with the names of Hückel<sup>2a</sup> and Harned,<sup>2b</sup> and can be written as follows, in the case of one single electrolyte being present

$$\log f_{\pm} = -\frac{z_+z_-\epsilon^2\kappa}{2DkT(1+\kappa a)} + BC \quad (1)$$

in which  $f_{\pm}$  is the mean rational activity coefficient of the ions,  $z_+$  and  $z_-$  are the absolute values

(1) Paper presented at the Meeting of the Pacific Division, American Association for the Advancement of Science, Stanford University, June, 1939.

(2) (a) E. Hückel, *Physik. Z.*, **26**, 93 (1925); (b) H. S. Harned, Chap. XII of Taylor's "Treatise on Physical Chemistry," 2d ed., pp. 797, *et seq.*, D. Van Nostrand and Co., New York, 1931, where earlier references will be found.

of the valences of the positive and of the negative ions,  $\epsilon$  is the elementary charge of positive electricity,  $D$  is the dielectric constant of the solvent,  $k$  is Boltzmann's constant,  $T$  is the absolute temperature,  $\kappa$  is defined by the formula

$$\kappa = \sqrt{\frac{4\pi n\epsilon^2(\nu_+\nu_+^2 + \nu_-\nu_-^2)}{DkT}} \quad (2)$$

in which  $n$  is the number of molecules of salt per cc.,  $\nu_+$  and  $\nu_-$  the numbers of positive and negative ions corresponding to one molecule of salt. The reciprocal of  $\kappa$  is often designated as the *radius of the ionic atmosphere*. The number  $n$  and the concentration  $C$  are connected by the formula

$$C = n \times 1000/N \quad (3)$$

in which  $N$  is Avogadro's number.

For aqueous solutions of uni-univalent electrolytes at 25°, formula (1) can be transformed into the following

$$\log_{10} f_{\pm} = -0.5059 \frac{\sqrt{C}}{1 + \frac{a}{3.042}\sqrt{C}} + BC \quad (4)$$

in which  $a$  is expressed in Ångströms.<sup>3</sup>

(3) The numerical values of the constants used are:  $\epsilon = 4.770 \times 10^{-10}$ ,  $\pi = 3.1416$ ,  $N = 6.064 \times 10^{23}$ ,  $D = 78.54$ ,  $k = 1.371 \times 10^{-16}$ ,  $T = 298.1$ ,  $\log 10 = 2.3026$ .