specimen gave no depression. Monobromobarbituric acid was obtained from each of the salts by a procedure similar to that employed by Biltz and Hamburger[5] with the ammonium salt. Yields of 30–50% of pure 5-bromobarbituric acid were obtained; m. p. 215–216°;[7] Br calcd., 38.61; found, 38.90. The loss is due to the solubility of the sodium salt and the instability of 5-bromobarbituric acid in aqueous solution.[7]

The products obtained by Nightingale and Schaefer have thus been demonstrated to be alkyl ammonium 5-bromobarbiturates. The "dark tarry oils" which they obtained with dibromobarbituric acid and aromatic amines were formed in a similar bromination process; such experiments have been reported previously in the literature. Dibromobarbituric acid and aniline give monobromobarbituric acid and p-bromoaniline,[8] while with dimethylaniline monobromobarbituric acid and p-bromodimethyl-aniline are obtained.[9]

[7] Bock, Ber., 55, 3401 (1922).
[8] Conrad and Reinbach, ibid., 35, 522 (1902).
[9] Gupta and Thorpe, J. Chem. Soc., 121, 1898 (1922).

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CESIUM FILMS ON TUNGSTEN

Sir:

When cesium atoms strike a tungsten filament at high temperature (filament surrounded by negatively charged cylinder), every atom is ionized. At lower temperature the number of adsorbed atoms (adatoms) per unit area (σ) can be measured by flashing the filament and allowing the evaporated atoms to strike a second parallel filament from which they evaporate as ions. The potentials of the two filaments are so chosen that no ions escape from the first but all escape from the second. A galvanometer ballistic kick gives a quantitative determination of σ.

Dr. J. Bradshaw Taylor has developed this method for measuring the rates of evaporation of atoms (ν_a), ions (ν_p) and electrons (ν_e) as functions of σ and T. The following conclusions are drawn.

The tungsten surface, after considerable heating at 2800°K., is homogeneous, except that a small fraction (0.0050) can hold adatoms more firmly than the rest. With rising pressure, and a filament at 1100–1200°K., the first atoms are adsorbed on this active surface, which becomes saturated before 0.5% of the remaining surface is occupied. The active spots are separate spaces holding one atom each from which the heat of evaporation is 80 Kg. cal. per g. atom. The following refers to the homogeneous surface.

With low filament temperatures and high pressures, σ reaches a limit σ_1 = 3.563×10^{14} atoms per sq. cm. of true surface (34% greater than apparent surface) corresponding to a monatomic film with one Cs atom for four tungsten atoms. The electron emission at constant T reaches a maximum at $\Theta = \sigma/\sigma_1 = 0.67$.

From the data on ν_a, by Gibbs' adsorption equation, the spreading force F (dynes. cm.$^{-1}$) can be calculated and the two-dimensional equation of state is $F = \sigma_1 kT\Theta/(1 - \Theta) + F'$. Using the virial of the force f acting at a distance r between adatoms: $F' = 0.25\ \sigma\Sigma(rf)$. The forces are strong repulsove forces varying as r^{-4}. The adatoms constitute dipoles, whose moment M decreases as Θ increases by the depolarizing force of neighboring adatoms. It is deduced theoretically (without adjustable parameters) that

$$F' = 3.338\ M^2\sigma^{5/2} + 1.531 \times 10^{-5}\ M^{4/3}T^{1/3}I\sigma^2$$

I being an integral which decreases from 0.893 to 0 as Θ increases from 0 to 1. From experimental values of F it is found that $M = 16.3 \times 10^{-18}$ at $\Theta = 0$, this coefficient decreasing to 9.8 at $\Theta = 0.3$ and 7.6 at $\Theta = 0.6$. The contact potential $V = 2\pi\sigma M$ can thus be calculated from ν_a, agreeing with direct measurements and with values calculated from

$$\ln \nu_e = 63.44 - (11606/T)(4.760 - V)$$

V being in volts.

The experimental values of ν_a give

$$\ln[\nu_a(1 - \Theta)/\Theta] - 1/(1 - \Theta) = A - B/T$$

where

$$A = 61 + 4.8\ \Theta - 2.4\ \Theta^2$$

and

$$B = 32380/(1 + 0.714\ \Theta)$$

The thermodynamic relation

$$\ln(2\nu_p) = \ln \nu_a + (11606/T)(V_w - V_i - V)$$

gives ν_p (in agreement with experiment), where $V_i = 3.874$ volts (ionizing potential of Cs) and $V_w = 4.622$ (work function for W).

From these equations ν_a, ν_e, ν_p and V are calculable, as functions of T and Θ (up to 0.65), from a curve giving $M(\Theta)$ and from V_i, V_w and the heat of evaporation of adatoms from a bare tungsten surface, 63.5 Kg. cal. per g. atom (2.757 volts).

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