calculated to the formation of ammonium azide, as was done in the present work, the quantum yield becomes 3.7 ± 0.5, which is to be compared with the experimental value of 3.6 for the photosensitized decomposition.

One is led to the conclusion that the mechanism of the mercury photosensitized decomposition is probably identical with that of the photochemical decomposition. One may write, therefore, as a possible mechanism[5]

$$\begin{array}{rcll} h\nu + Hg & = & Hg^* & (1) \\ Hg^* + HN_3 & = & Hg + N_2 + HN & (2) \\ HN + HN_3 & = & H_2 + 2N_2 & (3) \\ HN + HN_3 & = & N_2 + N_2H_2 & (4) \\ N_2H_2 + HN_3 & = & N_2 + NH_3 & (5) \\ NH_3 + HN_3 & = & NH_4N_3 \text{ (solid)} & (6) \end{array}$$

with 18% of the hydrogen azide molecules reacting according to equations (2) and (3) and 82% according to equations (2), (4), (5) and (6).

Summary

The mercury photosensitized decomposition of gaseous hydrogen azide by monochromatic radiation of wave length 2537 Å. has been investigated over the pressure range 0.3 to 20 mm. The final products of the decomposition were found to be ammonia and nitrogen with ammonium azide and hydrogen as intermediate products during the earlier stages of the decomposition. The quantum yield for the initial stage of the decomposition was found to approach the value 2.86 molecules of hydrogen azide decomposed per quantum absorbed when calculated to the formation of ammonia or 3.6 when calculated to the formation of ammonium azide. It is shown that the photosensitized decomposition closely parallels the photochemical decomposition described by previous investigators.

PASADENA, CALIF. RECEIVED NOVEMBER 13, 1934

NOTES

The Iodimetric Determination of Copper[1]

BY JOHN R. CALDWELL

It is desirable to have a general method for reducing absorption by analytical precipitates in cases where the usual expedients are impracticable. It has been found that the presence of certain protective colloids, and of some organic compounds such as nitrobenzene, exerts a profound influence upon the physical nature of analytical precipitates. When used under appropriate conditions, these agents may have a twofold function, they not only bring about rapid flocculation and settling of the precipitate, but also alter the nature of its surface so that the adsorptive capacity and further reactivity are greatly reduced. This property of protective colloids is of general application and has been employed with considerable success in several standard analytical procedures. Among these are included modifications of the Volhard chloride titration[2] and the iodimetric determination of copper. The latter will be discussed in detail.

In the iodimetric determination of copper, blue iodo-starch is carried down by precipitated cuprous iodide and renders the end-point indistinct. At least two attempts have been made to remedy this condition[3,4] but both have certain disadvantages. It was found that a solution of white shellac in alcohol would alter the nature of the surface of the precipitate and reduce adsorption of blue iodo-starch color.

Experimental.—Standard sodium thiosulfate solution was added until most of the iodine was consumed. At this point, 0.5 to 1.0 ml. of 4% alcoholic solution of white shellac was added. This solution was put in slowly from a medicine dropper while swirling the contents of the flask. The precipitate was allowed to settle for twenty to thirty seconds, and the titration completed. Instead of a dark blue solid suspended in a turbid solution, there was a heavy cream-colored precipitate which settled out in a few seconds leaving a clear, blue supernatant liquid that contained practically all of the iodo-starch color.

Results.—Samples of electrolytic copper ranging from 0.05 to 0.31 g. were titrated according to the above procedure. In a series of twelve determinations, the sum of plus and minus errors was +0.0001 g., showing that no systematic error was introduced. Two copper ores were

---

(1) Presented before the division of Colloid Chemistry at the 88th meeting of the American Chemical Society, Cleveland, Ohio, September 10–14, 1934.

(2) J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, 7, 38 (1935).

(3) A. H. Low, "Tech. Methods of Ore Anal.," John Wiley and Sons, 1922, 9th ed., p. 79.

(4) E. H. Smith, *Chemist Analyst* **18**, 6 (1929).

analyzed by the short ammonium fluoride method[5] and satisfactory agreement with analyses by other methods obtained.

The shellac has a two-fold function: it causes the precipitated cuprous iodide to flocculate rapidly and settle out as heavy curds, and it also deactivates the surface so that further adsorption is reduced. In the ore analyses referred to above, iron is present as a colloidal complex and may inhibit to some extent the action of the shellac, but in any case the end-point is greatly improved.

[5] Park, *Ind. Eng. Chem., Anal. Ed.*, **3**, 77 (1931)

DEPARTMENT OF CHEMISTRY
OHIO STATE UNIVERSITY
COLUMBUS, OHIO
RECEIVED JULY 26, 1934

A Note on the Calculation of Heat of Reaction from Values of the Equilibrium Constant at Two Temperatures

BY T. B. DOUGLAS AND H. D. CROCKFORD

The relation of the mass action constant to temperature is given by the equation

$$d \ln K = \Delta H \, dT/RT^2 \qquad (1)$$

If ΔH is a linear function of the temperature according to the equation

$$\Delta H = a + bT \qquad (2)$$

elimination of ΔH from (1) and integration lead to the equations

$$R \ln (K_2/K_1) = a[(1/T_1) - (1/T_2)] + b \ln (T_2/T_1) \qquad (3)$$

$$\frac{RT_1T_2 \ln (K_1/K_2)}{T_2 - T_1} = a + b\frac{T_1T_2}{T_2 - T_1} \ln (T_2/T_1) \qquad (4)$$

If now a temperature T_0 is defined by the equation

$$T_0 = \frac{T_1T_2}{T_2 - T_1} \ln (T_2/T_1) \qquad (5)$$

the right-hand member of (4) is ΔH_0, the value of ΔH for the temperature T_0. The resulting equation

$$\Delta H_0 = RT_1T_2 \ln (K_1/K_2)/(T_2 - T_1) \qquad (6)$$

is the same as is usually obtained from (1) by the use of the assumption that ΔH is independent of the temperature.

We have shown therefore that, when ΔH is a linear function of the temperature, (6) can still be used to calculate ΔH from two values of K and the two corresponding temperatures. The calculation does not require knowledge of the constants a and b and the ΔH thus calculated is for one particular temperature T_0, which is calculated by (5) without knowledge of a or b.

The authors recently published a paper[1] on the ionization constants of certain sulfur derivatives of phenylacetic acid at 0 and 25°. ΔH was calculated by equation (6) for these two temperatures. More exactly the ΔH values obtained are not average but are specifically for 12.1° as determined by substituting 0 and 25° in (5).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, N. C.
RECEIVED AUGUST 21, 1934

[1] Crockford and Douglas, THIS JOURNAL, **56**, 1472 (1934).

Influence of Thermal Diffusion in Certain Equilibrium Measurements

BY E. D. EASTMAN AND SAMUEL RUBEN

Emmett and Shultz[1] find the Deville method of equilibrium measurement to be subject to large errors attributable to thermal diffusion in the gas phase. They account in this way for discrepancies of long standing in various metal–metal oxide reduction equilibria involving hydrogen and water vapor, and between direct and indirect values of the water gas equilibrium.

This factor was considered by Eastman and Evans[2] in their work by the Deville method in the iron–oxygen–hydrogen system. There were, however, several considerations which led them to believe it might be disregarded. Thus, the tube in which the temperature gradient occurred was of large diameter and was placed horizontally in the hope of securing rapid convection. The speed of attainment of equilibrium was taken as an indication that mixing in the gas phase was in fact rapid, and that in consequence no sort of Soret equilibrium was likely to be important. Moreover, it was believed that had a Soret effect been present, especially if only partially established and varying in completeness with the temperature, it would have been manifested in the plots of log K *vs.* $1/T$ as a divergence from linearity. In the Fe–FeO systems first investigated no such divergence was present. In the later experiments with $FeO–Fe_3O_4$ mixtures (at higher total pressures) there was some divergence which we now think might be ascribed to differing thermal diffusion effects in different parts of the temperature and pressure ranges. In view of these facts it has seemed desirable to look for Soret effects in blank experiments with apparatus duplicating the essential features of that employed by Eastman and Evans.

[1] Emmett and Shultz, THIS JOURNAL, **55**, 1376 (1933).

[2] Eastman and Evans, *ibid.*, **46**, 888 (1924).