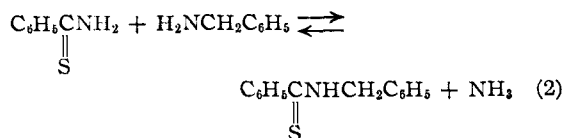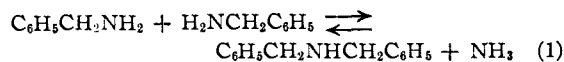of styrene, such cleavage has not been observed with other amines, e. g., morpholine, where the yield of phenylthioacetmorpholide is very good, and consequently this mode of formation is not considered probable. An alternative mode of formation is by oxidation (replacement of two hydrogens by sulfur) of part of the benzylamine used.[5]

It was found that by heating equimolecular portions of benzylamine and sulfur a 91% yield of N-benzylthiobenzamide was obtained. Wallach[6] reported that the reaction of benzylamine with sulfur in a sealed tube at 180° gave thiobenzamide. The discrepancy between our results and those of Wallach may be explained by the fact that ammonia was given off copiously from our reaction. Any reaction in which ammonia is one of the products would be favored in an open reaction vessel where the ammonia could escape and would be suppressed in a sealed tube where it would remain at the site of the reaction. Two such possible reactions which would lead to our product would be

$$C_6H_5CH_2NH_2 + H_2NCH_2C_6H_5 \rightleftharpoons$$
$$C_6H_5CH_2NHCH_2C_6H_5 + NH_3 \quad (1)$$

$$C_6H_5\overset{\|}{\underset{S}{C}}NH_2 + H_2NCH_2C_6H_5 \rightleftharpoons$$
$$C_6H_5\overset{\|}{\underset{S}{C}}NHCH_2C_6H_5 + NH_3 \quad (2)$$

It was also found that heating an equimolecular mixture of benzylamine and morpholine with sulfur gives thiobenzmorpholide, presumably by the same route as the benzylamine–sulfur reaction.

Acknowledgment.—The author wishes to acknowledge the helpful criticisms of Dr. John A. King in the preparation of this manuscript.

Experimental[7,8]

Reaction of Benzylamine with Sulfur.—A mixture of benzylamine (21.4 g., 0.20 mole) and sulfur (8.0 g., 0.25 mole) was heated at reflux for forty-five minutes. Evolution of ammonia was noticed almost immediately after heating was begun. The cooled reaction mixture was treated with Skellysolve "C" (100 ml.) and then filtered. The solid material weighed 19.5 g. (91%) and melted at 81–83°. After crystallization from Skellysolve "C" (250 ml.) it melted at 84–85°.

Anal. Calcd. for $C_{14}H_{13}NS$: N, 6.16; S, 14.10. Found: N, 5.85; S, 14.10.

There was no depression in melting point when this compound was mixed with the material reported to be N-benzylphenylthioacetamide[2] but now known to be N-benzylthiobenzamide.

Hydrolysis of above Reaction Product.—The compound melting at 84–85° (2.0 g.) was refluxed for one hour with 65% (by weight) sulfuric acid (30 ml.). The hydrolysis mixture was cooled and extracted with two 30-ml. portions of ether. The combined ether extracts were extracted with 25 ml. of 10% sodium hydroxide solution and the caustic extract was acidified with dilute hydrochloric

(5) For discussion of this type of oxidation see McMillan and King, submitted for publication in THIS JOURNAL.

(6) Wallach, *Ann.*, **259**, 300 (1890).

(7) Melting points uncorrected.

(8) Analyses performed under the direction of Mr. M. E. Auerbach.

acid. The acidified solution was extracted with two 30-ml. portions of ether; the ether solution was dried over anhydrous sodium sulfate and the ether was removed under vacuum. The residue was crystallized from water giving white crystals (0.4 g.) melting at 120–121°, undepressed when mixed with an authentic sample of benzoic acid.

The hydrolysis mixture was made alkaline with 10% sodium hydroxide solution and then extracted with three 100-ml. portions of ether. The ether was dried over anhydrous potassium carbonate and the ether was removed under vacuum. The residue was treated with saturated alcoholic picric acid solution and gave a picrate which after crystallization from alcohol melted at 193–195°, undepressed when mixed with an authentic sample of benzylamine picrate.[9]

Reaction of Benzylamine, Morpholine and Sulfur.—A mixture of benzylamine (10.7 g., 0.10 mole), morpholine (8.7 g., 0.10 mole) and sulfur (6.4 g., 0.20 mole) was heated at 160° for one hour. The cooled reaction mixture was taken up in 150 ml. of boiling alcohol and then chilled. The solid that formed weighed 8.4 g. (40.6%) and melted at 137–138°, undepressed when mixed with an authentic sample of thiobenzmorpholide.[5]

(9) Moureu and Lazennec, *Bull. soc. chim.*, [3] **35**, 1183 (1906).

STERLING–WINTHROP RESEARCH INSTITUTE
RENSSELAER, NEW YORK   RECEIVED APRIL 16, 1947

Diffusion Coefficient of Nitroglycerin in Rocket Powder and in Cellulose Acetate[1]

BY S. S. PENNER[2] AND S. SHERMAN[3]

Double base rocket powders, consisting of approximately 60% nitrocellulose, 40% nitroglycerin and some minor components, constitute one type of widely used rocket propellant. These powders burn easily over their entire exposed surface. In order to restrict burning to a preferred direction and thereby lengthen the total burning time it is necessary to cover a portion of the powder surface with a strongly bonded inert material such as cellulose acetate. These wrappings of cellulose acetate, though initially almost noncombustible, lose their protective action in the course of time because of the diffusion of nitroglycerin into the cellulose acetate. By determining the nitroglycerin concentration as a function of the distance from the cellulose acetate–powder interface at a given time, it is possible to ascertain the average diffusion coefficient of nitroglycerin in cellulose acetate and in powder. Knowledge of the maximum allowable nitroglycerin concentration in the cellulose acetate permits calculation of maximum safe storage times at all temperatures for which diffusion coefficients are available.

A complete experimental study was not carried through. In view of the limited experimental

data available for calculation of the diffusion coefficient, an approximate treatment was employed which is strictly applicable only if the cellulose acetate and the powder have identical physical properties as regards the diffusion of nitroglycerin. The theoretical treatment of diffusion through a composite cylinder for the boundary values of interest in connection with the present study has been reported elsewhere.[4]

More extensive experimental investigations along the lines discussed in this report were carried out independently by B. H. Sage[5] and, at a later date, by J. J. Donovan.[5]
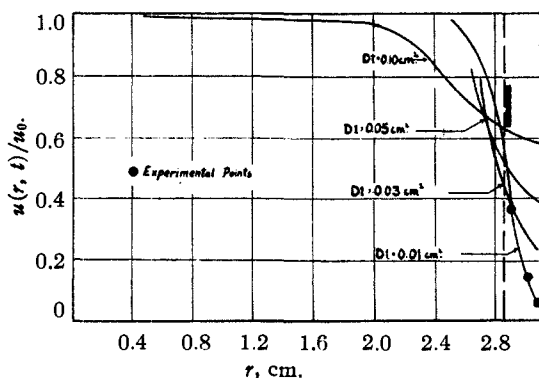

Fig. 1.—Comparison between experimental and calculated data.

Theoretical Treatment.—Consider an infinite cylinder of radius b surrounded by a cylindrical shell of thickness $c - b$. The initial concentration of diffusing material is U_0 in the cylinder and zero in the shell. From these data the boundary value problem may be formulated as follows[6]

$$\partial u/\partial t = D[\partial^2 u/\partial r^2 + (1/r)(\partial u/\partial r)], \; 0 \leqslant r < c, t > 0 \tag{1}$$

$$u(r,0) = U_0, 0 \leqslant r < b \tag{2}$$
$$u(r,0) = 0, b < r < c \tag{3}$$
$$\partial u(c - 0,t)/\partial r = 0 \tag{4}$$

Here $u(r,t)$ represents the concentration of diffusing material at any point at any time, D is the coefficient of diffusion, r is the radial distance from the axis of the cylinder, and t represents the time. Condition (4) arises from the assumption that no nitroglycerin is lost through the outer boundary of the cellulose acetate wrapping. The general solution of the problem specified by equations (1) to (4) may be written as[7]

$$u(r,t)/U_0 = b^2/c^2 +$$

$$(2b/c^2) \sum_{j=1}^{\infty} J_1(\lambda_j b) J_0(\lambda_j r) e^{-D\lambda_j^2 t}/\lambda_j [J_0(\lambda_j c)]^2 \tag{5}$$

where the positive eigen values λ_j satisfy the condition

(4) Penner and Sherman, *J. Chem. Phys.*, **15**, 569 (1947).

(5) Unpublished data in classified OSRD reports.

(6) For application of the Laplacian in cylindrical coördinates see Churchill, "Fourier Series and Boundary Value Problems," McGraw-Hill Book Co., New York, N. Y., 1941.

(7) For methods of solution of boundary value problems see ref. 1; also Byerly, "Fourier Series and Spherical Harmonics," Ginn and Co., London, 1893.

$$J_1(\lambda_j c) = 0$$

and J_0 and J_1 represent, respectively, Bessel functions of order zero and order one of the first kind.

Calculation of Diffusion Coefficient.—The particular grain of wrapped powder for which analyses for nitroglycerin were available consisted of a long cylindrical powder stick 2.858 cm. in radius, wrapped with cellulose acetate 0.228 cm. thick. The powder grain was stored for a period of two months at an average temperature close to room temperature. At the end of this time it was sectioned and nitroglycerin analyses were carried out according to U. S. Army Specification R11B. The material to be analyzed is extracted with ether. The ether in the extract is then replaced by glacial acetic acid. Finally, the nitroglycerin is reduced with ferrous chloride and the concentration of ferric ion determined with titanous chloride.

By use of equation (5) it is possible to calculate the ratio $u(r,t)/U_0$ as a function of r for various values of the parameter Dt. The results of this calculation are represented in Fig. 1. Since the storage time was two months or 1440 hours, D in sq. cm. per hour is 1/1440 of the value of Dt for which theoretical and experimental results agree. Reference to Fig. 1 indicates that a satisfactory value for Dt is 0.01 sq. cm. so that D is 7×10^{-6} sq. cm. per hour.

The theoretical curve for $Dt = 0.01$ sq. cm. lies considerably below the experimental points closest to the cellulose acetate–powder interface. This discrepancy may probably be ascribed to contamination during sectioning of the sample closest to the interface with some powder, thereby causing abnormally large values of the nitroglycerin concentration and also impairing the reproducibility of the results.

The curves for different values of Dt show that the theoretical curve is quite sensitive to the value chosen for Dt. In view of the close agreement between experimental and calculated curves for $Dt = 0.01$ sq. cm., it follows that the calculated value for the average diffusion coefficient in powder and cellulose acetate is of the correct order of magnitude.

The boundary value problem specified by equations (1) to (4) may be simplified for the particular powder grain used for the present study. Thus, the composite cylinder may be approximated by a powder slab of thickness b in contact with a slab of cellulose acetate of thickness $c - b$. The composite slab treatment leads to the same value for Dt as the cylindrical treatment given here. Equally good results are obtained if the powder is considered to be a semi-infinite solid. However, it is not permissible to represent the relatively thin cellulose acetate coating by a semi-infinite solid.