
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 75

JUNE 24, 1953

NUMBER 12

THOMAS MIDGLEY, JR.

MAY 18, 1889—NOVEMBER 2, 1944

"Let this epitaph be graven on my tomb in simple style,
'This one did a lot of living in a mighty little while.'"

With these lines Thomas Midgley, Jr., ended his Presidential Address to the American Chemical Society in 1944. He titled that address "Accent on Youth." There, from records of the U. S. Patent Office, he showed that the peak of inventiveness comes at age 35, and that most great inventions have been made between the ages of 25 and 45.

In conformity with that observation, the first of his own major inventions—tetraethyl lead as an antiknock agent—had been made when he was 33, and the last—the fluorine-containing refrigerants—by the time he was 40. It was before he was 30, however, that he had discovered iodine as the first of the chemical antiknock agents, and that he had guided research which yielded the first synthetic high-octane aviation gasoline.

There were four major achievements in which Midgley had a dominant part, all of them in the field of chemistry:

1. Discovery of the chemical antiknock agents.
2. Conception of the possibility of extracting bromine from sea water and guiding the development of a practicable process for it.
3. Development of an altogether new series of refrigerating gases based on fluorine and so non-toxic and non-inflammable as to be invaluable in the fields of refrigeration and air conditioning.
4. Extension of knowledge of the chemistry of the vulcanization of rubber and of the fundamental composition of natural and synthetic rubbers.

Midgley's college training was not, however, in chemistry but in mechanical engineering. His

initial knowledge of the subject thus came only out of his course in high school chemistry, and out of the year of general chemistry and the elementary course in quantitative analysis taken in college by engineering students. But when afterwards he learned that his first love was experimentation, he found that the problems he met which needed solution were mostly chemical. So, as versatility and action were two of his outstanding characteristics, he simply turned chemist.

If it should seem at all surprising that he could do that so effectively, it may be recalled that he learned chemistry just as Michael Faraday got his knowledge of chemistry and physics—by studying the subject himself. But neither Midgley nor Faraday studied chemistry in the abstract. They practiced it in the laboratory all the while, and most intensively. For years Midgley ate chemistry and slept it.

Just as Sir Humphry Davy called Faraday the greatest of all his discoveries, so Charles F. Kettering considered Midgley one of his major discoveries. On Midgley's part, the years of his association with Kettering, whom he affectionately called Boss Ket, were, as he put it, like a story from the Arabian Nights.

Thomas Midgley, Jr., was born in Beaver Falls, Pennsylvania, May 18, 1889. His father, Thomas Midgley, Sr., was a prolific inventor in a variety of fields, notably in that of automobile tires. His mother, Hattie Lena (Emerson) Midgley, was a daughter of James Emerson, inventor of the inserted-tooth saw. When young Midgley was four,

his family moved to Trenton, New Jersey, and two years afterwards to Columbus, Ohio.

Before the Midgley family moved away from Beaver Falls they sold young Midgley's baby bed to the William H. Wilsons, parents of Robert E. Wilson, who lived in Beaver Falls then. Thus as babies Thomas Midgley, Jr., and Robert E. Wilson slept in the same bed, and in later life they became collaborators in research and devoted friends.

In Columbus Midgley attended the public schools until he was partly through high school. One of his friends and playmates then was E. J. Crane, who later was to become the eminent editor of *Chemical Abstracts*.

In high school Midgley played both on the baseball team and the football team. When the spit ball began to be used by baseball pitchers, he and Sanford Brown, one of his teammates, began looking for a substance to give the ball the high degree of slippiness needed for maximum curving effect. Midgley hit upon the idea of using an extract of the inner bark of the slippery elm, a practice which proved so effective that it was later followed extensively by baseball pitchers.

In 1905 he went off to Betts Academy at Stamford, Connecticut, to prepare for college. It was from his chemistry teacher there, Professor H. M. Robert, that he first gained an interest in the periodic table of the elements. That interest continued throughout his life and it later helped to guide him to two of his important discoveries. He told of this in his Perkin Medal Address in 1937, an address which he entitled "From the Periodic Table to Production." There he said that the periodic table had served as a guide in the later and successful phase of what he termed the "fox hunt" which led to tetraethyl lead as an antiknock agent. It served him in the same way also when in the search for a non-toxic refrigerant it pointed to the element fluorine, which, although it seemed so unpromising, proved to be ideally suitable.

After Betts Academy Midgley went to Cornell University where, as before said, he took the course in mechanical engineering. Although in college he made no unusual record, he laid a foundation upon which some years later he built a structure of achievement that gave him a place of eminence in American chemistry.

Upon graduation in 1911, he went to work at the National Cash Register Company, Dayton, Ohio, as a draftsman and designer. After working there a year, he left at the request of his father to assist him in an effort to improve cord tires and tread design. He soon became chief engineer and later superintendent of the small company formed to manufacture the improved tire. But that venture did not prove financially successful and had to be abandoned.

During his year at the National Cash Register Company he had worked in the inventions department formerly headed by Charles F. Kettering. From the then head of that department, W. A. Chryst, he had learned about the developments that had been made there under Kettering's guidance, and as a result had come to the conclusion that research was the thing he himself really wanted to do.

Meanwhile Chryst too had left the National Cash Register Company to become chief engineer of the company which Kettering had established to make starting, lighting and ignition equipment for automobiles, the Dayton Engineering Laboratories Company. So Midgley went there to ask Chryst for a job doing experimental work. It was that day that he met Kettering and that their long and productive association began. Midgley was twenty-seven then, and it was in the fifteen years following that his creative research in the field of chemistry was done.

The first major problem to which Midgley was assigned was investigating knock in the gasoline engine. That annoying racket limits the compression of the gasoline engine and so is a barrier to getting the most out of the fuel. This is because, as cylinder pressure is raised, knock, if present, gets worse and worse, until at last it becomes destructive in its violence.

Midgley's early efforts in this field—in the course of which he made major improvements in engine indicators also—led him to the discovery that iodine is a powerful suppressor of knock. That discovery came about in this wise. Speculating about why kerosine knocked worse than gasoline, as it had been observed to do, he and Kettering surmised that it might be because kerosine did not vaporize and mix with air as readily as gasoline. So they reasoned that if kerosine were colored red it would absorb more radiation and thus evaporate more readily. That theory came to them because they both happened to know that the trailing arbutus, whose leaves are backed with red, grows and blooms in the early spring, even under snow.

Because no red dye was available there at the time, Midgley used iodine to color the kerosine red for the test of the idea he made immediately. And when kerosine made red with iodine was run in the engine, sure enough, the knock was gone completely.

But the color theory was soon demolished by the observation that red dyes had no effect on the knock. Colorless ethyl iodide, though, was effective as an antiknock agent. Evidently the effect was not from color but from the iodine.

Because iodine was not a substance that could be used as an antiknock agent in practice, an intensive effort was made to find something else that would be practicable. In that search a good many other compounds were found which were effective as knock suppressors, but not practical for one reason or another. One of the best of these was ethyl telluride. But the trouble with tellurium ethyl was that it smelled, as Midgley said, like a devilish mixture of garlic and onions. The long search for a practical antiknock agent—guided in its later phases, as has been said, by a special arrangement of the periodic table—led at last to tetraethyl lead.

But soon it was found that when tetraethyl lead was burned in the engine it left solid deposits there, deposits which resulted in serious spark plug erosion and exhaust valve burning. So a long search had to be made for a means of overcoming that difficulty. This led after awhile to the fortunate dis-

covery that the trouble could be corrected by adding an organic bromine compound to the gasoline along with tetraethyl lead.

It was to make possible the application of this solution on the large scale needed that the search for sources of bromine other than brine wells was undertaken. To solve that problem, and to do it from domestic sources, led to the effort which Midgley initiated to develop a process of extracting bromine from sea water, where it is present in the proportion of only about one pound of bromine to ten tons of sea water. That courageous effort yielded a process that proved practical, and so led on to the extraction today, by a still better process, of millions of pounds of bromine each year.

When it became apparent that, if ever air conditioning were to have wide use, a better refrigerant was needed than the noxious or inflammable gases then used in refrigeration, Midgley undertook, at Kettering's instigation, a search for such a compound. Again with the periodic table as a guide, he reached the conclusion that any *new* compound that could have a boiling point properly low to be a refrigerant would have to contain fluorine.

Thus, with characteristic daring and drive, and in the face of warnings about the hazardous nature of fluorine, he and his helpers proceeded to prepare the compound, dichlorodifluoromethane. Contrary to expectation, that compound, known today as Freon, proved to have just the properties needed. It is highly stable, non-inflammable, and altogether without harmful effects on man or animals. Because it has those properties Freon was chosen as the volatile solvent for insect repellents in the aerosol bombs originated in World War II.

But it was only a lucky accident that kept the important discovery from being missed altogether. Of two batches of the compound made from the few small bottles of antimony fluoride available as starting material, the first proved to be completely harmless to the animals on which it was tested. But the second was fatally toxic to them. Investigation then showed that there was an impurity in the second batch of the new compound. And that impurity proved to be phosgene.

But just suppose the second batch of the new compound had been first! In view of the reputation fluorine had, would anyone have suspected that the poisonous effect was due not to the fluorine compound but to an impurity?

Midgley's extensive researches on rubber were undertaken because of a lifelong interest in the subject, an interest which was intensified at the time by high prices and a threatened shortage of rubber. With the help of a few associates, he made extensive studies of the composition of natural and synthetic rubbers and of the chemistry of vulcanization. That work resulted in the publication, mostly in the *Journal of the American Chemical Society*, of a series of about twenty papers. Although nothing of direct commercial character came of it, Midgley considered his long research on the chemistry of rubber as the most scientific of all his endeavors. And from those informed in the field he received generous recognition for it.

Midgley gave eminent service to chemistry

through his contributions to the American Chemical Society in which he was active for twenty-five years. He was a member of the Board of Directors of the Society from 1930 until his death in 1944, and chairman of the Board for the ten years after 1934, as well as president of the Society in 1944.

Concerning his long and unselfish service to the Society, this was said in a resolution by his fellow Directors after his death:

His sound judgment, high ideals, alert energy and kindly human contacts brought success to the American Chemical Society, raising the standards of the whole chemical profession and endearing him to his fellow Directors and to all who served with him. In the truest sense his life represented the best thought, far-reaching vision, and the most practical accomplishments in the field of chemistry of his day and generation.

In respect to recognition for his chemical accomplishments Midgley was particularly fortunate. He received all four of the principal medals for chemical achievement. These, in order of receipt, were the Nichols Medal of the New York Section, American Chemical Society, 1922; the Perkin Medal of the Society of Chemical Industry, 1937; the Priestley Medal of the American Chemical Society, 1941; and the Willard Gibbs Medal of the Chicago Section, American Chemical Society, 1942.

For his pioneering work on engine indicators the Franklin Institute awarded him the Longstreth Medal in 1925. He was elected to membership in the National Academy of Sciences, 1942. He also received the honorary degree, Doctor of Science, from the College of Wooster, 1936, and from The Ohio State University, 1944.

Concerning Midgley's many other accomplishments, space is lacking to do more than mention a few of them. He had a dominant part in producing, during World War I, the first synthetic high-octane aviation gasoline, a mixture of cyclohexane and benzene made by the partial hydrogenation of benzene. He discovered one of the first known catalysts for cracking hydrocarbons to yield aromatic compounds, iron selenide. He investigated engine flames by visual observation, by spectrographic studies and by radiation measurements. He developed the Midgley optical gas engine indicator and the widely used bouncing-pin indicator. He had a major part in organizing the Centennial Celebration of the American Patent System in 1936 and the celebration of the United States Patent Law Sesquicentennial in 1940, and in originating the National Inventors Council in 1940. He was active also in the business side of the industries which came out of his endeavors.

Midgley believed strongly in the worth of scientific societies. Besides the American Chemical Society, in which he had such a vital part, he was a member of several others. Among these were the American Association for the Advancement of Science, the American Institute of Chemical Engineers, and the American Society for Testing Materials. He was a member also of Alpha Chi Sigma, Sigma Xi, Tau Beta Pi and Phi Kappa Phi.

Midgley had the gift of showmanship. This was seen by those who attended the presentations of his papers on the results of his researches. In presenting before the Society his original paper on the discovery of the chemical antiknock agents, for instance, he had the big stage of the Carnegie Music Hall in Pittsburgh full of apparatus. With it he made impressive demonstrations of knock, both in a glass tube and in an engine and of how it could either be increased or stopped altogether by chemical means. So also, in presenting the first paper on the fluorine-containing refrigerants, he demonstrated both their non-toxic and their non-inflammable properties in one breath. He did it by taking his lungs full of the vapor and then exhaling it softly to surround and extinguish the flame of a candle.

Versatile man that he was, Midgley had many interests outside the fields of his researches. He was a careful student of history and an investigator of many things in nature. He had a great fondness for music and poetry, and he often tried his own hand at writing poetry. He played golf too and was far from being a duffer at the game.

Midgley was well and favorably known to everyone by his nickname, Midge. He liked people and he had the ability to mingle with and to enjoy the company of people from every walk of life. As he put it once, "I have always had a fondness for intelligent people." Out of his manifold activities and associations and because of his innate friendliness, he made many friends, and he liked nothing better than to be host to them.

On August 3, 1911, he was married to Miss Carrie

M. Reynolds of Delaware, Ohio. They had two children, Jane (Mrs. Edward Z. Lewis), and Thomas Midgley, 3rd.

In the fall of 1940 just after the meeting of the Society in Detroit Midgley was struck by an acute attack of poliomyelitis. In spite of the care taken during his illness and of all the efforts made afterwards by himself and others, the disease deprived him of the use of his legs and made him a semi-invalid. In typical fashion, he afterwards computed the statistical probabilities of a man of his age catching polio and he expressed the result as "substantially equal to the chances of drawing a certain individual card from a stack of playing cards as high as the Empire State Building." Nevertheless, he said, "It was my tough luck to draw it." But, with the courage and energy characteristic of him, he continued many of his activities in spite of the handicap right up to the time of his death, notably his service to the American Chemical Society.

Midgley died unexpectedly on November 2, 1944, aged 55. At his funeral the minister read from the Bible the familiar verse, "We brought nothing into this world, and it is certain we can carry nothing out." Driving home from the funeral, Kettering made this remark: "It struck me then that in Midge's case it would have been so appropriate to have added 'but we can leave a lot behind for the good of the world.'" And out of a busy, diversified, and creative life Thomas Midgley, Jr., did do that in abundant measure.

T. A. BOYD

PUBLICATIONS OF THOMAS MIDGLEY, JR.

- (1) "High Speed Indicators," *S. A. E. J.*, **6**, 254 (1920).
- (2) "Combustion of Fuels in Internal-combustion Engines," *ibid.*, **7**, 489 (1920).
- (3) With T. A. Boyd, "Application of Chemistry to the Conservation of Motor Fuels," *Ind. Eng. Chem.*, **14**, 849 (1922).
- (4) With T. A. Boyd, "Chemical Control of Gaseous Detonation, with Particular Reference to the Internal-combustion Engine," *ibid.*, **14**, 894 (1922).
- (5) With T. A. Boyd, "Method of Measuring Detonation in Engines," *S. A. E. J.*, **10**, 7 (1922).
- (6) With W. K. Gilkey, "Spectroscopic Investigation of Internal Combustion," *ibid.*, **10**, 218 (1922).
- (7) "Molecular Movements during Combustion in Closed Systems," *ibid.*, **10**, 357 (1922).
- (8) With T. A. Boyd, "Detonation Characteristics of Some Blended Motor Fuels," *ibid.*, **10**, 451 (1922).
- (9) With T. A. Boyd, "Detonation Characteristics of Blends of Aromatic and Paraffin Hydrocarbons," *Ind. Eng. Chem.*, **14**, 589 (1922).
- (10) With C. A. Hochwalt and G. Calingaert, "A New Metalloorganic Compound—Diplumbic Hexaethyl," *THIS JOURNAL*, **45**, 1821 (1923).
- (11) "Some Fundamental Relations among the Elements and Compounds as Regards the Suppression of Gaseous Detonation," *Ind. Eng. Chem.*, **15**, 421 (1923).
- (12) With Robert Janeway, "Pressure-Volume-Quantity Indicator Card," *S. A. E. J.*, **12**, 105 (1923).
- (13) With Robert Janeway, "Laws Governing Gaseous Detonation," *ibid.*, **12**, 367 (1923).
- (14) "Progress of Antiknock Fuels," *A. P. I. Bull.*, **4**, 141 (1923).
- (15) With C. A. Hochwalt, "Ferrous Selenide as a Contact Catalyst for Cracking," *Ind. Eng. Chem.*, **16**, 365 (1924).
- (16) With H. H. McCarty, "Radiation Characteristics of the Internal-combustion Engine," *S. A. E. J.*, **14**, 182 (1924).
- (17) "Tetraethyl Lead Poison Hazards," *Ind. Eng. Chem.*, **17**, 827 (1925).
- (18) "How We Found Ethyl Gas," *Motor*, **43**, 92 (1925).
- (19) With Albert L. Henne, "Natural and Synthetic Rubber. I. Products of the Destructive Distillation of Natural Rubber," *THIS JOURNAL*, **51**, 1215 (1929).
- (20) With Albert L. Henne, "Natural and Synthetic Rubber. II. Reduction of Isoprene by Sodium-Ammonia," *ibid.*, **51**, 1293 (1929).
- (21) With Albert L. Henne, "Natural and Synthetic Rubber. III. Dimethyloctadiene," *ibid.*, **51**, 1294 (1929).
- (22) With Albert L. Henne, "Convenient Method for Preparing Sodium-Potassium Alloys," *Ind. Eng. Chem., Anal. Ed.*, **1**, 75 (1929).
- (23) With Thomas and Hochwalt Laboratories, "Coated Spiral Fractionating Columns," *ibid.*, **1**, 86 (1929).
- (24) With Albert L. Henne, "Natural and Synthetic Rubber. IV. 4-Methyl-4-octene by Isoprene Ethylation," *THIS JOURNAL*, **52**, 2075 (1930).
- (25) With Albert L. Henne, "Natural and Synthetic Rubber. V. Tetramethyl-octadiene," *ibid.*, **52**, 2077 (1930).
- (26) With A. L. Henne, "Organic Fluorides as Refrigerants," *Ind. Eng. Chem.*, **22**, 542 (1930).
- (27) With Albert L. Henne, "Natural and Synthetic Rubber. VI. The Pyrolysis of Natural Rubber in the Presence of Metallic Oxides," *THIS JOURNAL*, **53**, 203 (1931).

- (28) With Albert L. Henne and Mary W. Renoll, "Natural and Synthetic Rubber. VII. Fractional Precipitation of Natural Rubber," *ibid.*, **53**, 2733 (1931).
- (29) With A. F. Shepard and A. L. Henne, "Physical Properties of the Normal Paraffin Hydrocarbons, Pentane to Dodecane," *ibid.*, **53**, 1948 (1931).
- (30) With A. L. Henne and A. F. Shepard, "Natural and Synthetic Rubber. VIII. Products of the Destructive Distillation of Sodium Rubber," *ibid.*, **54**, 381 (1932).
- (31) With Albert L. Henne and Alvin F. Shepard, "Natural and Synthetic Rubber. IX. The Products of Destructive Distillation of Ebonite," *ibid.*, **54**, 2953 (1932).
- (32) With Albert L. Henne and Mary W. Renoll, "Natural and Synthetic Rubber. X. Constituents of the Rubber Hydrocarbon," *ibid.*, **54**, 3381 (1932).
- (33) With Albert L. Henne and Mary W. Renoll, "Natural and Synthetic Rubber. XI. Constituents of the Milled Rubber Hydrocarbon," *ibid.*, **54**, 3381 (1932).
- (34) With Albert L. Henne, "The Separation and Identification of Sol Rubber Hydrocarbons," *J. Phys. Chem.*, **36**, 2880 (1932).
- (35) With A. L. Henne, "Decomposition of Dichlorodifluoromethane by Flames," *Ind. Eng. Chem.*, **24**, 641 (1932).
- (36) With Albert L. Henne and Alvin F. Shepard, "Natural and Synthetic Rubber. XII. Reversible Vulcanization by Organometallic Derivatives," *THIS JOURNAL*, **56**, 1156 (1934).
- (37) With Albert L. Henne, Alvin F. Shepard and Mary W. Renoll, "Natural and Synthetic Rubber. XIII. The Molecular Weight of Sol Rubber," *ibid.*, **56**, 1325 (1934).
- (38) With Albert L. Henne and A. F. Shepard, "Natural and Synthetic Rubber. XIV. A Structural Formula for Ebonite," *ibid.*, **56**, 1326 (1934).
- (39) With A. F. Shepard and A. L. Henne, "The Preparation of Thiophene and its Homologs from 1,3-Diolefins and Sulfur," *ibid.*, **56**, 1355 (1934).
- (40) With A. L. Henne, A. F. Shepard and Mary W. Renoll, "Natural and Synthetic Rubber. XV. Oxygen in Rubber," *ibid.*, **57**, 2318 (1935).
- (41) "Synthetic Weather," *Ind. Eng. Chem.*, **27**, 1005 (1935).
- (42) "Chemistry in the Next Century," *ibid.*, **27**, 494 (1935).
- (43) With Albert L. Henne, "Reactivity and Influence of Fluorine in Aliphatic Compounds," *THIS JOURNAL*, **58**, 882 (1936).
- (44) With Albert L. Henne, "Mercuric Fluoride, A New Fluorinating Agent," *ibid.*, **58**, 884 (1936).
- (45) With Albert L. Henne and Henry M. Leicester, "Natural and Synthetic Rubber. XVI. The Structure of Polystyrene," *ibid.*, **58**, 1961 (1936).
- (46) "From the Periodic Table to Production," *Ind. Eng. Chem.*, **29**, 241 (1937).
- (47) With Albert L. Henne, "Natural and Synthetic Rubber. XVII. The Separation of Sol Rubber and Gel Rubber," *THIS JOURNAL*, **59**, 706 (1937).
- (48) With Albert L. Henne and Mary W. Renoll, "Natural and Synthetic Rubber. XVIII. The Protein from Natural Rubber and its Amino Acid Constituents," *ibid.*, **59**, 2501 (1937).
- (49) With Mary W. Renoll and Albert L. Henne, "Determination of Carbon and Hydrogen Content by Combustion," *Ind. Eng. Chem., Anal. Ed.*, **9**, 566 (1937).
- (50) "Man-made Molecules," *Ind. Eng. Chem.*, **30**, 120 (1937).
- (51) "Problem + Research + Capital = Progress," *ibid.*, **31**, 504 (1939).
- (52) "Employer-Employee Legal Relationships," *Chem. Eng. News*, **17**, 273 (1939).
- (53) "Remarks in Acceptance of the Priestley Medal," *ibid.*, **19**, 1021 (1941).
- (54) "Critical Examination of Some Concepts in Rubber Chemistry," *Ind. Eng. Chem.*, **34**, 891 (1942).
- (55) "A Message from Our President (Editorial)," *ibid.*, **36**, 1 (1944).
- (56) "Accent on Youth," *Chem. Eng. News*, **19**, 1646 (1944).
- (57) "The Future of Industrial Research—the Chemist's View," *ibid.*, **22**, 1756 (1944).

[CONTRIBUTION NO. 34 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

Thiacyclobutane: Heat Capacity, Heats of Transition, Fusion and Vaporization, Vapor Pressure, Entropy, Heat of Formation and Thermodynamic Functions¹

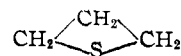
BY D. W. SCOTT, H. L. FINKE, W. N. HUBBARD, J. P. MCCULLOUGH, C. KATZ, M. E. GROSS, J. F. MESSERLY, R. E. PENNINGTON AND GUY WADDINGTON

RECEIVED JANUARY 16, 1953

Detailed studies were made of the thermodynamic properties of thiacyclobutane. The properties determined experimentally included: heat capacity of the solid and the liquid between 12 and 321°K., transition temperature (176.7°K.), heat of transition (159.8 cal. mole⁻¹), triple point (199.91°K.), heat of fusion (1971 cal. mole⁻¹), vapor pressure between 48 and 132° [log₁₀ *p* = 7.01667 - 1321.331/(*t* + 224.513) (*p* in mm. and *t* in °C.)], heat of vaporization (8234 cal. mole⁻¹ at 327.53°K.), heat capacity of the vapor (*C_p*^o = 20.7 cal. deg.⁻¹ mole⁻¹ at 377.20°K.), entropy of the liquid (44.72 and 47.32 cal. deg.⁻¹ mole⁻¹ at 298.16 and 327.53°K., respectively), entropy of the vapor (*S*^o = 68.17 and 69.75 cal. deg.⁻¹ mole⁻¹ at 298.16 and 327.53°K., respectively) and heat of formation [for the reaction: 3C(graphite) + 3H₂(g) + S(rhombic) = C₂H₄S(l), Δ*H*_{298.16}^o = 6.20 kcal. mole⁻¹]. The functions -(*F*^o - *H*_{298.16}^o)/*T*, (*H*^o - *H*_{298.16}^o)/*T*, *H*^o - *H*_{298.16}^o, *S*^o and *C_p*^o were computed by the methods of statistical mechanics for selected temperatures up to 1000°K. Values of the standard heat, standard free energy and common logarithm of the equilibrium constant of formation were obtained for the same temperatures. Spectroscopic and calorimetric data were shown to favor a planar-ring structure of C_{2v} symmetry for the thiacyclobutane molecule.

The cyclic sulfides constitute one of the classes of organic sulfur compounds that are included in the thermodynamic research program of A.P.I. Research Project 48A. Recent publications from this Laboratory have reported the results of thermodynamic studies of two compounds of this class, the three-membered ring compound, thiacyclo-

propane² and the five-membered ring compound, thiacyclopentane.³ The present paper reports the results of a thermodynamic study of a third cyclic sulfide, the four-membered ring compound, thiacyclobutane (trimethylene sulfide),



(1) This investigation was part of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurements of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

(2) G. B. Guthrie, Jr., D. W. Scott and Guy Waddington, *THIS JOURNAL*, **74**, 2795 (1952).

(3) W. N. Hubbard, H. L. Finke, D. W. Scott, J. P. McCullough, C. Katz, M. E. Gross, J. F. Messerly, R. E. Pennington and G. Waddington, *ibid.*, **74**, 6025 (1952).