

## THE TWENTY-TWO MOST FREQUENTLY CITED APL PUBLICATIONS

During World War II, not a single article was submitted by the APL staff for publication in technical journals. Instead, essential information exchanges were documented by means of more than 1700 technical reports, all neatly listed in a most illuminating final report when the Proximity Fuze Program was formally transferred from the Office of Scientific Research and Development to the Navy's Bureau of Ordnance in 1944.

Return to more conventional ways of reporting the results of technical work had to await the end of the war. A high-altitude research program (under James Van Allen) begun in 1946 and using captured V-2 rockets and U.S.-built Aerobee rockets as instrument carriers led to a series of interesting publications.<sup>1</sup>

A year earlier, as a flood of mass-produced proximity fuzes was introduced into the Navy and Army, APL embarked on a wide-ranging R&D effort to develop guided missiles as a means of defending Navy ships from attack at a distance beyond the reach of artillery shells. This program had a policy of accompanying the exploration of new and difficult areas of technology (such as controlled flight at supersonic speeds and the development of unconventional ramjet power plants) with research programs that would provide a foundation of understanding to the needed engineering approaches. The policy was carried out in two ways: An in-house Research Center was established in 1947 to deal with topics largely related to the work in the development activities, and a group of associate contractors was assembled to do research that would influence the development effort.

In the four decades since the first APL journal article was published,<sup>2</sup> several thousand papers appeared in technical journals, particularly after APL programs expanded into a variety of technical areas beyond the guided missile effort. They provide a fascinating picture of shifting concerns at APL.

How can one judge the impact of these articles? Quantitative assessments are difficult. However, one criterion of "success" can be quantified, namely, the

impact an article had on other authors in selecting it as a useful reference citation in their own publications. Novelty, clarity, and significant insights will be evaluated by potential citers. If these criteria are met to the satisfaction of a large number of people, the article will be cited frequently.

An analysis of the citation frequency of several million articles published during the past two decades showed<sup>3</sup> that less than one-third of 1 percent of them will be cited by others more than 100 times. In fact, most will not be cited even twice.

The APL publications were evaluated on the basis of their citation frequency. A paper was considered "frequently cited" if it received more than 150 citations in 25 years since its publication, more than 120 citations in 15 years, or more than 50 citations in 5 years. Twenty-one articles and one book surpassed these numbers (Table 1). Most fell into three distinctive categories: combustion, free radical physics and chemistry, and space physics.

In this and subsequent issues of the *Johns Hopkins APL Technical Digest*, the authors of many of these articles describe informally and from their personal perspectives what led them to the studies and what consequences developed. Each contribution expresses the author's impressions and evaluations. In their totality, they furnish a commentary on research areas where APL has made substantial contributions.

### REFERENCES

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- <sup>2</sup> E. A. Bonney, "Aerodynamic Characteristics of Rectangular Wings at Supersonic Speeds," *J. Aeronaut. Sci.* 14, 110 (1947).
- <sup>3</sup> E. Garfield, "Uses and Misuses of Citation Frequency," *Current Contents* 16 (43), 3-9 (October 28, 1985).

ACKNOWLEDGMENT—The assistance of the Reference Library staff of the Milton S. Eisenhower Library at The Johns Hopkins University is gratefully acknowledged. They provided the source material on citation frequency as listed in the *Science Citation Indexes*, published by the Institute for Scientific Information, Philadelphia.

**Table 1**—Frequently cited articles by APL authors  
[numbers of citations/years since publication]

- 1948  
R. A. Alpher, H. Bethe, and G. Gamow, "The Origin of Chemical Elements," *Phys. Rev.* **73**, 803 (1948).
- 1958  
C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, "Electron Spin Resonance of Atomic and Molecular Free Radicals Trapped at Liquid Helium Temperature," *Phys. Rev.* **112**, 1168 (1958). [187/23]
- 1960  
F. J. Adrian, "Matrix Effects on the Electron Spin Resonance Spectra of Trapped Hydrogen Atoms," *J. Chem. Phys.* **32**, 972 (1960). [158/25]
- 1961  
F. J. Adrian, E. L. Cochran, and V. A. Bowers, "ESR Spectrum and Structure of the Formyl Radical," *J. Chem. Phys.* **36**, 1661 (1961). [168/20]  
L. Monchick and E. A. Mason, "Transport Properties of Polar Gases," *J. Chem. Phys.* **35**, 1676 (1961). [272/19]
- 1962  
E. L. Cochran, F. J. Adrian, and V. A. Bowers, "ESR Study of Ethynyl and Vinyl Free Radicals," *J. Chem. Phys.* **40**, 213 (1962). [152/20]  
S. N. Foner and R. L. Hudson, "Mass Spectrometry of the HO<sub>2</sub> Free Radical," *J. Chem. Phys.* **36**, 2681 (1962). [197/20]  
E. A. Mason and L. Monchick, "Heat Conductivity of Polyatomic and Polar Gases," *J. Chem. Phys.* **36**, 1622 (1962). [237/18]
- 1964  
A. A. Westenberg and N. deHaas, "Quantitative Measurement of Gas Phase O and N Atom Concentrations by ESR," *J. Chem. Phys.* **40**, 3087 (1964). [134/15]
- 1965  
R. M. Fristrom and A. A. Westenberg, *Flame Structure*, McGraw-Hill (1965). [283/15]  
D. J. Williams and G. D. Mead, "Nightside Magnetosphere Configuration as Obtained from Trapped Electrons at 1100 Kilometers," *J. Geophys. Res.* **70**, 3017 (1965). [181/15]
- 1967  
A. A. Westenberg and N. deHaas, "Atom-Molecule Kinetics at High Temperature Using ESR Detection. Technique and Results for O+H<sub>2</sub>, O+CH<sub>4</sub>, and O+C<sub>2</sub>H<sub>6</sub>," *J. Chem. Phys.* **46**, 490 (1967). [131/15]
- 1969  
A. A. Westenberg and N. deHaas, "Atom-Molecule Kinetics Using ESR Detection V. Results for O+OCS, O+CS<sub>2</sub>, O+NO<sub>2</sub> and H+C<sub>2</sub>H<sub>4</sub>," *J. Chem. Phys.* **50**, 707 (1969). [102/10]
- 1974  
A. J. Zmuda and J. C. Armstrong, "The Diurnal Flow Pattern of Field-Aligned Currents," *J. Geophys. Res.* **79**, 4611 (1974). [147/10]
- 1975  
L. W. Hunter, "On Infinite Order Sudden Approximations for an Arbitrary Potential Energy," *J. Chem. Phys.* **62**, 2855 (1975). [94/9]
- 1976  
T. Iijima and T. A. Potemra, "The Amplitude Distribution of Field-Aligned Currents at Northern High Latitudes Observed by Triad," *J. Geophys. Res.* **81**, 2165 (1976). [119/5]  
T. Iijima and T. A. Potemra, "Field-Aligned Currents in the Dayside Cusp Observed by Triad," *J. Geophys. Res.* **81**, 5971 (1976). [63/5]  
M. Sugiura and T. A. Potemra, "Net Field-Aligned Currents Observed by Triad," *J. Geophys. Res.* **81**, 2185 (1976). [60/5]
- 1977  
L. C. Aamodt, J. C. Murphy, and J. G. Parker, "Size Consideration in the Design of Cells for Photoacoustic Spectroscopy," *J. Appl. Phys.* **48**, 927 (1977). [59/4]
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T. Iijima and T. A. Potemra, "Large-Scale Characteristics of Field-Aligned Currents Associated with Substorms," *J. Geophys. Res.* **83**, 599 (1978). [94/5]
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S. M. Krimigis et al., "Low-Energy Charged Particle Environment at Jupiter: A First Look," *Science* **204**, 998 (1979). [74/5]  
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## IN THE BEGINNING . . . .

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R. A. Alpher, H. Bethe, and G. Gamow, "The Origin of Chemical Elements," *Phys. Rev.* **73**, 803 (1948).

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In the early spring of 1948, a Letter to the Editor, entitled "The Origin of Chemical Elements," was submitted for publication in *Physical Review*. It provided a very brief summary of the principal results of my doctoral thesis, for which George Gamow of George Washington University (GWU) was advisor. I had pursued evening studies at GWU while having been employed first with the Department of Terrestrial Magnetism of the Carnegie Institution of Washington; next with the Navy; and then, from 1944, with the Applied Physics Laboratory. After World War II, Gamow served as a consultant at APL while he was a member of the GWU faculty. The name of Hans Bethe as coauthor was added by Gamow strictly for fun. The submitted manuscript showed "in absentia" after Bethe's name, but the qualifier was removed in the actual publication. It is very likely that the choice by *Physical Review* of an April 1 publication date was no accident. At Gamow's invitation, Bethe served on my thesis defense committee at GWU.

The Letter to the Editor, which soon became identified in the literature as the " $\alpha\beta\gamma$ " theory, has seen continuing interest and frequent citation because it was the first attempt at describing nucleosynthesis that had a measure of success and because it provided some credibility to the idea that the universe had evolved from a hot dense early state. It should be pointed out that the contemporary view is that prestellar nucleosynthesis was limited to the lightest elements, with all other elements being produced in stellar interiors. The experiment between the calculated abundance of primordial helium and the observed cosmic abundance is particularly noteworthy.

The motivation for the thesis was the increasing awareness in the late '30s and early '40s that the relative abundance distribution of the chemical elements was a universal property, a "cosmological observable," that demanded understanding. Scientists at the time sought this understanding in a variety of models, a number of which suggested that the abundance distribution reflected a thermal equilibrium that had been frozen in. No single set of physical conditions was found that could do the job; conditions that seemed to yield light elements gave no heavy elements. The situation was characterized as a "heavy element catastrophe."

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With that dilemma at hand, Gamow proposed in 1942 and again in 1946 that the relative abundance distribution reflected the quenching of a rapid sequence of nonequilibrium reactions that went on in a hot prestellar state of the expanding universe, a notion that was the starting point for my thesis work. An important ingredient for the quantitative embodiment of these notions was the appearance in 1947 of a collection of measurements by D. J. Hughes of Brookhaven National Laboratory across the periodic table of cross sections for neutron-capture reactions at energies of approximately 1 megaelectronvolt. The inverse correlation of capture cross section with relative abundance was almost too good to be true. Moreover, much of the needed insights into the concepts of relativistic cosmology were available in the literature.

The conceptual model underlying the calculations described in the Letter to the Editor was an expanding, cooling, homogeneous cosmology, a universe of radiation with a trace of matter present, primarily as neutrons. Protons formed from neutron decay, followed by a sequence of  $(n, \gamma)$  reactions, with intervening  $\beta$  decay to stabilize the resultant nuclei. The abundances rapidly grew up to the observed distribution, and then the reactions quenched as the supply of neutrons diminished and as cooling and dilution reduced reaction rates. All of this occurred within a few minutes after a temporal singularity in the model—an event now termed the "Big Bang." The actuality of the calculations described in the letter and in a subsequent lengthier publication of the thesis (*Phys. Rev.* **74**, 1557 (1948)) was that the expansion was not considered explicitly; that is, it was assumed that the element-building reactions proceeded rapidly compared to the characteristic time of the expansion. In sum, the model was a static one.

The results were exciting in that the heavy element catastrophe was obviated, and one had for the first time a model of the universe with physical content. There were many problems with the early model, problems that we were the first to recognize. Nevertheless, in their principal features, a Letter to the Editor in 1946 by Gamow (*Phys. Rev.* **70**, 572 (1946)), the 1948  $\alpha\beta\gamma$  letter, and a series of subsequent papers with Robert Herman (see below) were the beginnings of what is now called the standard or canonical model of the universe.

The 1948 *Physical Review* paper marked the beginning of a period of intellectual activity on cosmological problems for me, for several colleagues at APL, and for Gamow that proceeded at an intense level for over five years and that has proceeded sporadically since then. In retrospect, it is interesting to recall that, for the most part, the cosmological work at APL was done

### The Origin of Chemical Elements

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AS pointed out by one of us,<sup>1</sup> various nuclear species must have originated not as the result of an equilibrium corresponding to a certain temperature and density, but rather as a consequence of a continuous building-up process arrested by a rapid expansion and cooling of the primordial matter. According to this picture, we must imagine the early stage of matter as a highly compressed neutron gas (overheated neutral nuclear fluid) which started decaying into protons and electrons when the gas pressure fell down as the result of universal expansion. The radiative capture of the still remaining neutrons by the newly formed protons must have led first to the formation of deuterium nuclei, and the subsequent neutron captures resulted in the building up of heavier and heavier nuclei. It must be remembered that, due to the comparatively short

time allowed for this process,<sup>1</sup> the building up of heavier nuclei must have proceeded just above the upper fringe of the stable elements (short-lived Fermi elements), and the present frequency distribution of various atomic species was attained only somewhat later as the result of adjustment of their electric charges by  $\beta$ -decay.

Thus the observed slope of the abundance curve must not be related to the temperature of the original neutron gas, but rather to the time period permitted by the expansion process. Also, the individual abundances of various nuclear species must depend not so much on their intrinsic stabilities (mass defects) as on the values of their neutron capture cross sections. The equations governing such a building-up process apparently can be written in the form:

$$\frac{dn_i}{dt} = f(t)(\sigma_{i-1}n_{i-1} - \sigma_i n_i) \quad i = 1, 2, \dots, 238, \quad (1)$$

where  $n_i$  and  $\sigma_i$  are the relative numbers and capture cross sections for the nuclei of atomic weight  $i$ , and where  $f(t)$  is a factor characterizing the decrease of the density with time.

We may remark at first that the building-up process was apparently completed when the temperature of the neutron gas was still rather high, since otherwise the observed abundances would have been strongly affected by the resonances in the region of the slow neutrons. According to Hughes,<sup>2</sup> the neutron capture cross sections of various elements (for neutron energies of about 1 Mev) increase exponentially with atomic number halfway up the periodic system, remaining approximately constant for heavier elements.

Using these cross sections, one finds by integrating Eqs. (1) as shown in Fig. 1 that the relative abundances of various nuclear species decrease rapidly for the lighter elements and remain approximately constant for the elements heavier than silver. In order to fit the calculated curve with the observed abundances<sup>3</sup> it is necessary to assume the integral of  $\rho_n dt$  during the building-up period is equal to  $5 \times 10^4$  g sec./cm<sup>2</sup>.

On the other hand, according to the relativistic theory of the expanding universe<sup>4</sup> the density dependence on time is given by  $\rho \approx 10^8/t^2$ . Since the integral of this expression diverges at  $t=0$ , it is necessary to assume that the building-

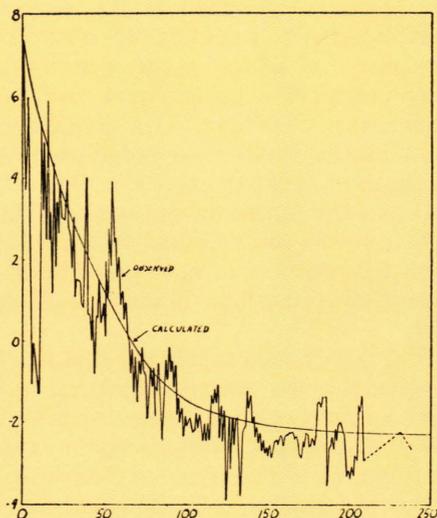


FIG. 1.  
Log of relative abundance  
v.s.  
Atomic weight

by the participants primarily as an avocational activity. APL provided secretarial, computing, and drafting services. In particular, during the year prior to the 1948 publication, I found it exciting and profitable to discuss my work with Robert Herman of APL (now at the University of Texas), a most unusual physicist who is a creative polymath. As soon as my formal requirements at GWU were completed, Herman and I began to explore a number of questions in depth, occasionally being joined by Gamow and, for a final and gratifying piece of work, by James W. Follin, Jr., who is still at APL. I would like to highlight several of the many papers produced during this five-year interval.

I mentioned above that my thesis calculations, as reported in the  $\alpha\beta\gamma$  letter, had been for a static situation—reaction rates much more rapid than the expansion time scale. Even before the Letter to the Editor was published, Herman and I considered the universal expansion explicitly in calculating element-building reactions. The work was published in *Physical Review* **74**, 1737 (1948) and in *Reviews of Modern Physics* **22**, 153 (1950).

In one particularly exciting piece of research, Herman and I examined the matter/radiation relativistic model in detail and realized that we could use the physical conditions derived for nucleosynthesis at early times to extrapolate to present-day conditions. All one needed was an estimate of the contemporary density of matter in the universe. This led us to propose that the universe should now be filled with a radiation background at about 5 K representing radiation from the early universe that had expanded and cooled (red shift-

ed) (see *Nature* **162**, 774 (1948) and *Phys. Rev.* **75**, 1089 (1949)). It was very satisfying to have the theoretical prediction that was made in 1948 confirmed with observations in 1965 by A. A. Penzias and R. W. Wilson of the Bell Laboratories, for which they received the Nobel Prize in 1978. The existence of this cosmic background radiation and the prediction of light element abundances (principally helium) by the model are taken today as very strong evidence for the validity of the canonical Big Bang model.

The other research I want to highlight is a detailed study of the physics of the early universe, a study in which Herman and I were joined by Follin (*Phys. Rev.* **92**, 1347 (1953)). The methodology developed in that paper is still used today in nucleosynthesis calculations and studies of elementary particle reactions in the early universe. In his book, *The First Three Minutes* (Basic Books, New York (1977)), Nobel Laureate Steven Weinberg characterized the Alpher-Follin-Herman paper as “the first thoroughly modern analysis of the early history of the universe.” The principal thrust of that paper was to develop the initial conditions for the period of nucleosynthesis in the early universe in as detailed a manner as possible, given the contemporary knowledge of the physics of elementary particles. Currently, there is much activity among elementary particle theorists and cosmologists to develop a theoretical picture based on unified field theories of an even earlier epoch of the universe that would lead to the conditions described in our 1953 paper and in later improved calculations of nucleosynthesis without any ad hoc assumptions.

## CHEMISTRY AND TRANSPORT PROPERTIES COMBINED

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R. M. Fristrom and A. A. Westenberg, *Flame Structure*, McGraw-Hill, New York (1965).

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The book, *Flame Structure*, was an outgrowth of our studies on the structure of laminar flames. This, in turn, was a small part of APL's Bumblebee Propulsion Program that was aimed at understanding the combustion, aerodynamics, and general behavior of ramjet engines. A prototype of the ramjet had been successfully flown in 1948, but there was an urgent

need for a more scientific interpretation of its basic elements. Combustion was one of the outstanding enigmas. Mankind has used fire for half a million years, but scientific understanding had been the product of only the past few decades.

To address the ramjet propulsion problem, William H. Avery gathered an active research team at APL and included many outstanding external collaborators. He and Robert W. Hart had produced a simplified analysis of ramjet combustion that John P. Longwell and Malcolm E. Weiss at Esso developed into a test method. At the academic end of the spectrum, the program supported the classic treatise, “Molecular Theory of Gases and Liquids,” by Joseph E. Hirschfelder, Charles F. Curtiss, and Robert B. Bird and their group

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# FLAME STRUCTURE

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## The Physical Interpretation of Flame Structure Data 309

tube expansion ratio  $A$  through the flame, which is shown in Fig. XIII-10. The velocity profile was then determined from the continuity relation  $\rho v A = \rho_0 v_0$ , using the density derived from the temperature and molecular-weight profiles (the latter obtained from the concentration profiles to be discussed) and the equation of state. The small circled points on the velocity profile of Fig. XIII-10 were obtained this way, while the large circles are

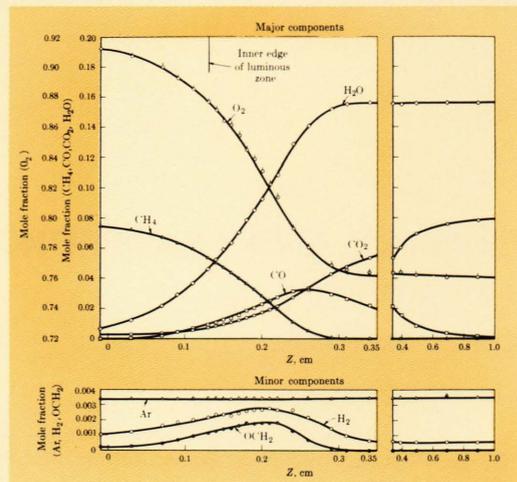


Fig. XIII-11 Concentration profiles in 0.1-atm methane-oxygen flame [4]. Same flame as Fig. XIII-9.

independent check points obtained directly by the repetitive-flash particle track method.

The concentration profiles for the stable species illustrated in Fig. XIII-11 were obtained by sampling and mass spectrometer analysis, as discussed in Chap. IX. The five major and two minor flame constituents are given (argon was also present as a slight impurity in the oxygen). One of the attractive features of this flame was its relative simplicity in regard to the number of species present.

at the University of Wisconsin. APL developed the engineering design for surface-to-air ramjet-powered missiles that have protected the Navy for many decades.

In the small, fundamental enclave headed by Arthur Westenberg, we attacked the scientific understanding of combustion, combining the analysis of Hirschfelder with the extensions to transport gas processes by Edward A. Mason of the University of Maryland and Louis Monchick. Experimentally, Westenberg and Ronald Walker tackled diffusion coefficients and later, with Newman deHaas, added coefficients of thermal conductivity. Meanwhile, with the advice and mass spectrometer of Samuel N. Foner and Richard L. Hudson, Rochelle Prescott began flame sampling while we worked out methods for measuring detailed velocities and temperatures in the reaction zone of premixed flames. With the dexterity and skill of Conrad Grunfelder and the help of our many friends at APL, we developed a complete library of methods for the experimental description of the structure of such laminar flames. The mathematical analysis was ably handled by Stanley Favin.

At that time, the problem was considered so formidable that we had some initial difficulty in publishing our revolutionary results. However, as the consistency of the analysis was recognized, the techniques became standard, and we received several prizes for our work (the Silver Medal of the Combustion Institute and the Hillebrand Award of the Chemical Society of Washington). Encouraged by this recognition, we decided that, if the work were to have lasting impact, it would have to be collected and summarized.

This was the genesis of the book. As with most authors, we had delusions of grandeur and set out to rewrite the entire field of combustion. But when managerial commitments took away our main collaborator, Walter G. Berl, we decided on the more modest goal of a critical quantitative discussion of the mea-

surement and interpretation for flame structure data. Writing covered several years, although, as is true of most books, the major effort came in the last eight months. Within two years, the Soviets had translated and published an edition in Russian without notifying us. (In those days, the USSR did not subscribe to the Geneva copyright convention.)

The book has stood the test of time well beyond our fondest hopes. Our timing was fortunate. The book remains a standard reference, even though the field was less than a decade old when it was written and has remained an active area in research in the following years.

Nonetheless, time passes and two developments have made the coverage somewhat out of date. The first was molecular-beam-inlet mass spectrometry, which opened up the direct measurement of radical concentrations. The second, in the past decade, was the use of laser methods that made possible in situ measurements that have removed many of the doubts about probing and flame disturbance by the insertion of sampling devices. With some exceptions (certain trace radicals), the earlier results have been confirmed, but a new era has definitely begun.

These developments have prompted me to revise and expand the original book. The contents are still useful, but the book has been out of print for 15 years; I still get periodic requests for copies.

Since Westenberg's early retirement (much lamented by his friends at APL though welcomed by his wife and his new friends in Vermont), the task of revision has fallen to me, and I am beginning the first draft of the last chapter of a revised book with its enlarged title *Flame Structure and Processes*. It remains to be seen if the timing and coverage will revitalize this "light classic," as one kind friend described the original, but one would hope that the timing will invite continued interest in the problem.

## MEASUREMENTS OF RATES OF ELEMENTARY REACTIONS

ARTHUR A. WESTENBERG

A. A. Westenberg and N. deHaas, "Quantitative Measurement of Gas Phase O and N Atom Concentrations by ESR," *J. Chem. Phys.* **40**, 3087 (1964).

A. A. Westenberg and N. deHaas, "Atom-Molecule Kinetics at High Temperature Using ESR Detection. Technique and Results for  $O + H_2$ ,  $O + CH_4$ , and  $O + C_2H_6$ ," *J. Chem. Phys.* **46**, 490 (1967).

A. A. Westenberg and N. deHaas, "Atom-Molecule Kinetics Using ESR Detection V. Results for  $O + OCS$ ,  $O + CS_2$ ,  $O + NO_2$ , and  $H + C_2H_4$ ," *J. Chem. Phys.* **50**, 707 (1969).

During the 1950s and 1960s, APL was an internationally recognized center for research in combustion, an activity that ranged from fundamental studies of "simple" flames, through engineering research of various types, to attacks on practical problems in jet engines, rockets, fires, etc. My own interests tended generally toward fundamental flame research, and, by the early 1960s, it had become apparent that the major obstacle to further understanding of flames and their propagation was the nearly total lack of reliable data on the identity and rates of the various chemical reactions involved. It was this state of affairs that led directly to our exploitation of electron spin resonance (ESR) spectroscopy in the chemical kinetic research described in the above frequently cited papers and a number of other publications.

Up to that time, most attempts at handling the kinetic aspects of flame chemistry had fallen back on the egregiously inadequate subterfuge of lumping all the many chemical events into one empirical "overall" reaction, which had little or no connection to what was actually happening. In reality, there was a (usually) large number of elementary reaction steps (e.g.,  $O + H_2 \rightarrow OH + H$ ) involving simple atoms or the unstable fragments of molecules known as free radicals (e.g., OH). Thus it was evident that accurate data on these reactions were essential to a solid understanding of the whole complex process and that a good method was required for monitoring and measuring the concentration of unstable atoms and radicals in the gas phase. This is a different problem than simply *detecting* these species, most of which had already been found and identified by a variety of means—usually spectroscopic. But their reliable concentration measurement on both a relative and absolute basis under controlled conditions useful for reaction rate studies had simply not been accomplished, except in a few special cases.

In pondering the situation around 1960 and stimulated by a provocative paper<sup>1</sup> suggesting the use of the stable paramagnetic gas  $O_2$  as a calibration material for some free atoms (also paramagnetic), it seemed to me that ESR spectroscopy might be a potent tool for

kinetic studies. The ESR spectra of many atoms and a few radicals had been studied in the gas phase and were well known, although I had no prior personal experience in the field and no equipment. The latter is complex and quite cumbersome (including a large, delicate electromagnet, much electronic gadgetry, etc.), and we were fortunate enough to find the funds (not from the APL research budget, by the way) for the purchase of a good commercial ESR spectrometer, thereby avoiding the horrendous task of building our own device and greatly facilitating our entry into the research. The advice of others at APL with much ESR experience, notably Edward Cochran and Frank Adrian, was also most helpful.

The first priority was to prove to ourselves (and others) that we could make precise and accurate measurements of gas phase atom and radical concentrations by this method. After setting up the appropriate auxiliary apparatus for generating the atoms, getting them into the heart of the detection system (a resonant microwave cavity), and so on, we spent a year or so just learning to handle the equipment and practicing the technique. Then the crucial phase was to compare results with some other independent (and reliable) method. The method chosen—so-called gas phase titration—was probably the best available at the time, but it was itself essentially untested by independent means. The first paper cited above describes the theory and practice of the ESR technique and its successful comparison with this independent method for O and N atoms, which also established the validity of the latter method, of course. Clearly, the paper was of considerable interest to the scientific community. Incidentally, it is amusing (although it wasn't at the time) to note that the paper was at first rejected by the editor on the grounds that one of the referees (obviously ill-chosen!) thought it unsuitable for that journal. Happily, after a little rebuttal from us, the editor changed his mind.

With the validity of the basic ESR technique established, we proceeded to exploit it as vigorously as possible in a variety of kinetic applications. Since one of the most important aspects of the rate of an elementary chemical reaction is its dependence on temperature, it was of great importance to be able to use ESR in a well-defined system (i.e., free of competing reactions, wall effects, etc.) over a wide temperature range. The second cited paper describes how this was accomplished by using the ESR detector in conjunction with a steady-state, fast-flow system (thus converting time to a distance variable) that could be cooled or heated over a range of approximately 200 to 1000 K. This was really the first time such definitive rate measurements over a wide range had been reported, and it aroused much interest from both combustion researchers and those

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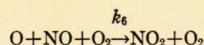
## Quantitative Measurements of Gas Phase O and N Atom Concentrations by ESR\*

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(Received 12 December 1963)

The general theory relating the measured integrated intensities of ESR absorption lines to the concentrations of odd electron species in the gas phase is reviewed and discussed in some detail. It is then applied in the form required for determining the absolute concentrations of O, N, and H atoms using O<sub>2</sub> as a calibrating gas as first suggested by Krongelb and Strandberg. Experimental data are presented which verify the theoretical predictions of the intensities of various O<sub>2</sub> lines. The determination of absolute O and N concentrations by ESR is shown to be a reliable experimental technique by comparison with the independent results of titration with NO<sub>2</sub> and NO, respectively. Agreement of the two techniques strongly supports the validity of both. The O-NO<sub>2</sub> titration curves enable a value for the rate constant of



to be evaluated at 300°K as  $2.9 \times 10^{16} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$  in agreement with other reported values.

## INTRODUCTION

THE use of electron spin resonance (ESR) absorption spectroscopy for the quantitative measurement of odd electron species in the gas phase is only beginning to be exploited. The first studies of such spectra were carried out by Beringer and Castle on the stable paramagnetic gases oxygen,<sup>1</sup> nitric oxide,<sup>2</sup> and nitrogen dioxide.<sup>3</sup> These were soon followed by similar studies on the chemically reactive gaseous atoms hydrogen,<sup>4</sup> oxygen,<sup>5</sup> and nitrogen<sup>6</sup> produced in a discharge flow system. Since then several other atoms and free radicals have been detected in the gas phase by the ESR technique including iodine,<sup>7</sup> fluorine,<sup>8</sup> chlorine,<sup>9</sup> bromine,<sup>10</sup> hydroxyl,<sup>11</sup> difluoramino (NF<sub>2</sub>),<sup>12</sup> and sulfur monoxide (SO).<sup>13</sup> Thus the possibilities for performing many interesting and important chemical kinetic (or other) studies in gases using ESR detection are obvious. The technique is extremely sensitive, allows essentially unambiguous identification with little interference, has considerable generality (as shown by the above partial listing of detectable species), and possesses the advantage of any spectroscopic method of not perturbing the system.

The quantitative analytical aspects of the technique are, of course, more difficult and have received less attention. The only feasible way to make reliable spectroscopic measurements of concentration on an absolute basis is to use some known calibrating substance or device as a reference, so that the problem is actually changed to that of relative concentration measurement. For gas-phase ESR work, the usual solid calibration standards such as diphenylpicrylhydrazyl are unsatisfactory because of differences in the cavity filling factor between gas sample and solid standard. The real basis for successful quantitative measurements of gas-phase species was provided by Krongelb and Strandberg in a very useful paper<sup>14</sup> which described the use of gaseous O<sub>2</sub> as a calibrating material. This fills the resonant cavity in exactly the same way as the radicals being measured (providing radical concentration gradients are negligible).

With any new technique it is highly desirable to be able to compare it with results from another independent method—preferably one that is well-established. In the case of gaseous radical measurement it cannot be said without reservation that any of the methods in use are well-established, nor have there been many attempts to make intercomparisons. The subject has been reviewed recently.<sup>15</sup> As far as the specific problem of comparing ESR data on atom concentration with data from other methods is concerned, Shaw used both diphenylpicrylhydrazyl<sup>16</sup> and a mechanical rotating calibrator<sup>17</sup> as a reference for the ESR determination of absolute H-atom concentrations. Comparisons were made with data from a calorimeter probe detector. Hildebrandt, Barth, and Booth<sup>18</sup> made an attempt to

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<sup>1</sup> R. Beringer and J. G. Castle, Jr., *Phys. Rev.* **75**, 1963 (1949); **81**, 82 (1951).

<sup>2</sup> R. Beringer and J. G. Castle, Jr., *Phys. Rev.* **76**, 868 (1949); **78**, 581 (1950).

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<sup>8</sup> H. E. Radford, V. W. Hughes, and V. Beltran-Lopez, *Phys. Rev.* **123**, 153 (1961).

<sup>9</sup> V. Beltran-Lopez and H. G. Robinson, *Phys. Rev.* **123**, 161 (1961).

<sup>10</sup> N. Vanderkooi and J. S. MacKenzie, *Advan. Chem. Ser.* **36**, 98 (1962).

<sup>11</sup> H. E. Radford, *Phys. Rev.* **122**, 114 (1961).

<sup>12</sup> L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *J. Chem. Phys.* **35**, 1481 (1961).

<sup>13</sup> C. C. McDonald, *J. Chem. Phys.* **39**, 2587 (1963).

<sup>14</sup> S. Krongelb and M. W. P. Strandberg, *J. Chem. Phys.* **31**, 1196 (1959).

<sup>15</sup> K. R. Jennings, *Quart. Rev.* **15**, 237 (1961).

<sup>16</sup> T. M. Shaw, *J. Chem. Phys.* **31**, 1142 (1959).

<sup>17</sup> T. M. Shaw and C. Milazzo, *Gen. Elec. Microwave Lab. Rept. TIS-R60ELM-178* (1960).

<sup>18</sup> A. F. Hildebrandt, C. A. Barth, and F. B. Booth, *Physical Chemistry in Aerodynamics and Space Flight* (Pergamon Press Ltd., London, 1961), p. 194.

involved in the study of basic chemical kinetics. That paper was followed by a number of others on various reactions, of which the third paper cited above was one.

Part of the popularity of this work may also have been because, by about 1970, the study of atmospheric chemistry began to be very active. This was stimulated by the growing awareness of pollution problems (Los Angeles-type smog being of prime concern), soon followed by possible stratospheric ozone depletion (first by the anticipated proliferation of supersonic aircraft and later by the widespread use of Freon® refrigerants and spray-can propellants). Understanding of these global problems relies heavily on detailed knowledge of elementary reaction rates of the type we were measuring. As an example, one of our earliest studies was of the reaction  $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ , which had always been thought to be a very slow reaction; we showed conclusively that it was about 1000 times faster than previously reported. This was a very important result because it indicated that the reaction could be the main route for conversion of CO to  $\text{CO}_2$  in the atmosphere as well as in flames. Our papers<sup>2,3</sup> on the reaction have been widely noted.

One of my favorite papers in the series and probably the most important from the viewpoint of fun-

damental chemical kinetic theory was our study<sup>4</sup> of the reactions  $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$  and  $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ . They represent the simplest of all atom-molecule reactions, and accurate data on their rates are vital to the theory of reaction rates. Thus, our results attracted considerable attention from theoreticians, and they have been woven deeply into the fabric of their work.

The study of chemical kinetics has now become even more detailed and elaborate, and newer techniques (mostly spectroscopic applications of lasers) have superseded ESR work in gases. We "skimmed the cream" nearly a quarter century ago, but time keeps marching on.

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## EXPLORATIONS INTO THE KINETIC THEORY OF GASES

LOUIS MONCHICK

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L. Monchick and E. A. Mason, "Transport Properties of Polar Gases," *J. Chem. Phys.* **35**, 1676-1697 (1961).

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By the late 1950s, the transport properties of non-polar gases seemed well in hand, but polar gases were a different story. The permanent dipoles made the intermolecular forces strongly dependent on the relative orientations of the molecules so that a collision trajectory was extremely difficult to compute. Although the basic kinetic theory existed, the collision dynamics was far too complicated for the computers of the day. Incidentally, it is *still* too complicated, in that a full calculation is difficult enough to be infeasible in practice, although not impossible. The obvious trick of first averaging over orientations to produce an effective spherical interaction threw the baby out with the bathwater.

The trick that did work, described in the above cited paper, grew out of earlier independent studies of gas properties at very high temperatures, a subject of great

interest then at APL. Monchick had just calculated the collision integrals for an exponential repulsion potential, and Mason, at the University of Maryland, had just worked on the kinetic theory for dissociated gases, where multiple interactions that depend on the relative orientations of the electron spins occur between valence-unsaturated atoms. The latter problem had shown that the correct procedure was to calculate collision integrals for each spin orientation and then average the integrals over all possible orientations. The result suggested a feasible approximation for polar molecules: first calculate the collision integrals for fixed relative orientation, and then average. Presumably, in each collision only the orientation around the distance of closest approach would dominate.

Thus our collaboration was born: "How hard would it be to calculate the collision integrals for a polar Stockmayer potential with fixed orientation?" "Not quite like duck soup, but close to it." There was no reason for the collaboration other than mutual interest and the fun of attacking a long-standing problem. We never had any official institutional connection and were not even especially close geographically. But the

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## Heat Conductivity of Polyatomic and Polar Gases\*

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The formal kinetic theory of Wang Chang and Uhlenbeck and of Taxman has been used to derive explicit expressions for the heat conductivity of polyatomic and polar gases. By systematic inclusion of terms involving inelastic collisions the usual modified Eucken expression is derived as a first approximation, and as a second approximation an expression involving the relaxation times for various internal degrees of freedom (as well as the viscosity, diffusion coefficients, and heat capacity). For polar gases a second effect is often important in that a resonant exchange of rotational energy is possible.

The comparison of experimental results with those calculated using empirical values of relaxation times is generally satisfactory, and most of the previously noted anomalies in the ratio  $f = \lambda M / \eta C_V$  are accounted for quantitatively.

## I. INTRODUCTION

THE rigorous Chapman-Enskog kinetic theory of gases, although strictly applicable only to the noble gases, gives a good account of the viscosity and diffusion properties of simple nonpolar polyatomic gases.<sup>1</sup> Recently these results have been extended to polar gases.<sup>2</sup> However, the heat conductivity of polyatomic gases, nonpolar as well as polar, is not described satisfactorily by the classical kinetic theory. The reason is that the classical theory takes account only of elastic collisions and so ignores the internal degrees of freedom of the molecules, which transport an appreciable quantity of energy. Various attempts to patch up the classical theory, taking into account the transport of internal energy, have been made, which are essentially variations on a suggestion originally made by Eucken.<sup>3</sup> In the classical theory, the ratio  $\lambda M / \eta$  is proportional to the heat capacity

$$\lambda M / \eta = f C_V, \quad (1)$$

where  $\lambda$  is the heat conductivity,  $M$  the molecular weight,  $\eta$  the viscosity,  $C_V$  the molar heat capacity at constant volume, and  $f$  is a pure number almost exactly equal to  $\frac{5}{2}$ . Eucken's suggestion was that this be generalized by writing it as a sum of contributions from the translational and various internal degrees of freedom,

$$\lambda M / \eta = f_{tr} C_{V\ tr} + f_{int} C_{V\ int}, \quad (2)$$

where  $C_{V\ tr} = \frac{3}{2} R$  is the translational heat capacity, and  $C_{V\ int} = C_V - C_{V\ tr}$  is the internal heat capacity. By analogy with noble gases  $f_{tr}$  was assigned a value

of  $\frac{5}{2}$ , and by simple mean free path arguments  $f_{int}$  was assigned a value of 1. This leads to the well-known expression for what has since been known as the Eucken factor,

$$\lambda M / \eta C_V = f, \quad (3)$$

$$f_{\text{Eucken}} = 1 + \frac{2}{3} (R / C_V), \quad (4)$$

which was found to give very reasonable agreement with experiment for many nonpolar polyatomic gases near 0°C.<sup>4</sup>

As more experimental results became available over a range of temperatures, however, it became clear that the simple Eucken expression had definite deficiencies. If values of  $f_{int}$  are calculated from experimental results, assigning the value  $\frac{5}{2}$  to  $f_{tr}$ , it is apparent that  $f_{int}$  is temperature dependent, ranging from 0.7 to 1.3 over the range 80° to 380°K for a number of nonpolar gases.<sup>5</sup> Thus, the value of 1 for  $f_{int}$  may often be nearly correct in an average sense, but fails to give the correct temperature dependence. For polar gases, the observed values of  $f$  are often appreciably lower than the Eucken value,<sup>6</sup> i.e., the heat conductivities of polar gases are anomalously low.

Although the Eucken correction has no rigorous theoretical basis, it appears to contain a good deal of physical truth. Its most obvious fault lies in having set  $f_{int} = 1$ . It has been suggested that the transport of internal energy occurs by a diffusion mechanism,<sup>7,8</sup> which leads to the modification

$$f_{int} = \rho D / \eta, \quad (5)$$

where  $\rho$  is the gas density and  $D$  the self-diffusion coefficient. Recently a more rigorous derivation has been

\* This work was supported in part by the U. S. Navy and in part by the National Aeronautics and Space Administration.

<sup>1</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954). Hereafter referred to as MTGL.

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<sup>6</sup> R. G. Vines and L. A. Bennett, *J. Chem. Phys.* **22**, 360 (1954).

<sup>7</sup> CC pp. 238-240; see also MTGL pp. 499-501.

<sup>8</sup> K. Schäfer, *Z. physik. Chem.* **B53**, 149 (1943).

paper was the first result of a collaboration that lasted over 10 years and resulted in 18 more journal articles (in which our names appeared in idiosyncratic order).

Why has this work held up so well for 25 years? We suspect for the following reasons: (a) success in correlating a wealth of experimental data; (b) physical attractiveness and mathematical tractability of the model; (c) lack of anything better (“The game may be crooked, but it’s the only game in town.”); and (d) recent improved justification for its premises—it is the classical limit of the currently popular “infinite-order-sudden” approximation of quantum scattering theory.

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In the first of a series of 19 papers published by us (Mason, now at Brown University, was then at the University of Maryland, and Monchick had joined APL several years previously), the problem of calculating the viscosity of polar gases had been successfully attacked, ignoring the internal structure of the gas molecules. Phenomenological theories of heat conduction existed at the time (one worked out by A. Eucken and one by J. O. Hirschfelder), but they disagreed with each other, with experiment, and with a kinetic theory that had been worked out by C. S. Wang Chang and G. E. Uhlenbeck. Encouraged by their success in predicting the viscosity of polar gases and having nothing

better to do at the time, we blithely decided to enquire why the phenomenological and kinetic theories disagreed. Rather quickly, several errors were found in the kinetic theory; when they were corrected, the following results were deduced: (a) the asymptotic limit of rare inelastic collisions led to Hirschfelder’s phenomenological theory; (b) the total heat flux consisted of fluxes of internal and kinetic energy that were not independent but were related by relaxation of internal energy into kinetic energy and vice versa; (c) the rate of these relaxation effects was rather well described by a theory of rotational relaxation developed by John G. Parker of APL’s Milton S. Eisenhower Research Center; and (d) the rate of transport of rotational energy in a polar gas was rather less than the rate of diffusion of the polar molecules themselves. The differences between those two rates were due to a resonant exchange of rotational energy facilitated by polar forces; it was as if a packet of rotational energy carried by a molecule in one direction was suddenly stolen and carried off by another molecule traveling in the opposite direction. This, it turned out, was adequately calculated by a rather simple semiclassical scattering approximation.

The resulting approximation explained all the experimental “anomalies” and has become the standard heat conductivity formula for polyatomic and polar gases. The seemingly idle question had led to “the biggest game in town.” Together and separately, we subsequently explored extensions to thermal diffusion, mixtures, thermal transpiration, quantum effects, and ionized gases.