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Great advances are currently being made in the experimental study of gas phase chemical kinetics, and the exploitation of electron spin resonance spectroscopy (ESR) in this field has proved to be very fruitful. These advances are the result of solutions to several problems which have hindered the classical methods of studying kinetics. The use of well-defined flow reactors and the availability and use of new and powerful free radical detecting instruments are cited as prime reasons for this progress. This article briefly reviews some of the shortcomings of the classical methods in studying kinetics; it describes some of the results of the ESR experimental technique and considers some of its future applications.

APPLICATIONS of **E S R** to the CHEMICAL KINETICS of GASES

It is no exaggeration to say that the experimental study of chemical kinetics is undergoing a period of revolutionary change. Chemical kinetics is concerned with the *rates* of chemical reactions, i.e., the speed with which reactants are converted to products. Consider the simple case where a species A reacts with B to form some unspecified product or products. A chemist would write this process as follows:

$$A + B \rightarrow Products .$$
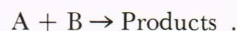
At any time during the reaction the rate is given by the time derivative of the concentration* of either reactant. It is a fundamental fact of kinetics that the rate of such an elementary reaction is proportional to the concentrations of the reactants, so that one may write

$$\frac{d(A)}{dt} = \frac{d(B)}{dt} = -k(A)(B) \qquad (1)$$

where concentrations are denoted by parentheses

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* The term "concentration" means the quantity of a substance per unit volume in any convenient units. The chemist commonly uses gram moles per cubic centimeter.

and the negative sign means that (A) and (B) decrease with time, i.e., they are consumed in the reaction. The proportionality constant k is called the *specific rate constant* or just the rate constant, the term "constant" being something of a misnomer since k is usually a strong function of temperature. Thus the primary objective of a chemical kinetic experiment is the determination of the rate constant and its temperature dependence for a given reaction, assuming the reaction is known in the first place.

The classical methods of studying kinetics usually involved mixing the reactants at time zero and then either sampling the reacting mixture at later times, or stopping the reaction (often by sudden cooling) and analyzing the mixture at a series of times, so that the progress of the reaction could be followed. This is satisfactory when the reaction is a very simple one, but the difficulty is that most reactions are not simple but actually involve several consecutive and simultaneous chemical events. This is particularly true for gas phase reactions (the exclusive concern of this article) which practically always involve free radicals—highly reactive fragments of the more common stable molecules. The

classical studies were usually restricted in their measurement techniques to quite long reaction times and to the analysis only of the stable reactants and final products so that, despite much cunning detective work and many shrewd approximations, there often remained considerable doubt as to the true reaction being measured and the results were often inaccurate. The upshot was that it became something of a cliché to refer to agreement within an order of magnitude between separate investigations as being "pretty good for kinetics."

The great strides that are presently being made in experimental gas kinetics are due to two reasons: (1) the use of well-defined systems in which the chemistry is simplified to the point where the reaction of interest is isolated, or nearly isolated, and (2) the availability and exploitation of new and powerful instruments, particularly those for detecting and measuring free radicals. Both of these are often incorporated in an experimental attack on a specific problem. One might mention the great success of flash photolysis coupled with kinetic spectroscopy, whereby a short, intense flash of light results in the extremely rapid dissociation of a molecular species into free radicals whose subsequent fate, or some product species, is then followed in time by appropriate high-speed spectroscopy. Another very active approach involves use of the shock tube, where the dissociation is produced by the rapid increase in temperatures across a shock wave and the reaction is monitored by various spectroscopic or thermal means.

One disadvantage common to both of the foregoing methods is the fact that they are transient techniques and, since gas phase radical reactions are typically quite fast (reaction times of a few milliseconds), this can lead to practical difficulties in accomplishing the necessary measurements. Another problem is that of free radical detection, most of the available techniques being useful only for a particular radical and/or suffering from uncertainties as to calibration. The remainder of this article is devoted to a discussion of some of the research at the Applied Physics Laboratory which has aimed at surmounting the above problems by the development of steady state techniques with some generality for the absolute measurement of elementary radical-molecule rate constants.

Electron Spin Resonance for Gas Phase Radical Detection

The technique which has proved to be a very powerful tool for the detection and measurement of free atoms and radicals in kinetic studies is electron spin resonance (ESR). It has the great advantage of considerable generality for this purpose, since a common characteristic of all free radicals is that they have one or more "free" or unpaired electrons, i.e., electrons that are not being used to form chemical bonds. This means that the radical will have a magnetic moment due to the spin of this electron, so that it can interact with an external magnetic field. In the simplest possible case, that of a ground state hydrogen atom which has one electron with spin quantum number $s = \pm\frac{1}{2}$, the effect of an externally applied magnetic field H is to split the energy levels of the atom into two (neglecting the effects of nuclear spin), corresponding to $s = +\frac{1}{2}$ and $s = -\frac{1}{2}$. This is the simple Zeeman effect. Electromagnetic radiation of the proper frequency ν can then be absorbed by the atoms in causing transitions between these two levels. Since the splitting is a direct function of the field strength H, the basic relation for the absorbed radiation energy is simply $h\nu \propto H$, where h is Planck's constant. An ESR spectrometer operates on this principle. The sample to be measured is contained in a microwave cavity constructed to be resonant at some convenient fixed frequency (commonly about 10,000 Mc/s, which is the X-band radar frequency). An external DC magnetic field is then varied slowly until its magnitude is such that the above resonant absorption condition is fulfilled. With a microwave frequency of 10,000 Mc/s, most radicals show an absorption spectrum in the field range of 3000-8000 gauss. Appropriate electronic instrumentation allows the absorption to be detected and displayed, the details being available in standard references.[1]

The first such spectrum of a gas phase molecule (actually a stable "free radical") to be observed in this way was that of nitric oxide by Beringer and Castle,[2] and Beringer and Rawson[3] first detected free hydrogen atoms soon after this. Since then many other spectra have been observed and analyzed, so that the list of important gaseous species measurable by the ESR technique now includes the atoms H, O, N, P, S, and all of the halogens, the free radicals OH, SO, SH, SN, ClO, BrO, and NF_2, and the stable molecules O_2, NO, and NO_2. In addition, it is possible to detect truly free electrons, i.e., electrons that are unattached to any other species, although this is a classical phenomenon caused by cyclotron resonance of the

[1] See, for example, D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworths, London, 1958.

[2] R. Beringer and J. G. Castle, Jr., "Magnetic Resonance Absorption in Nitric Oxide," Phys. Rev., **78**, 1950, 581–586.

[3] R. Beringer and E. B. Rawson, "Electron Spin Gyromagnetic Ratio in Atomic Hydrogen," Phys. Rev., **87**, 1952, 228.
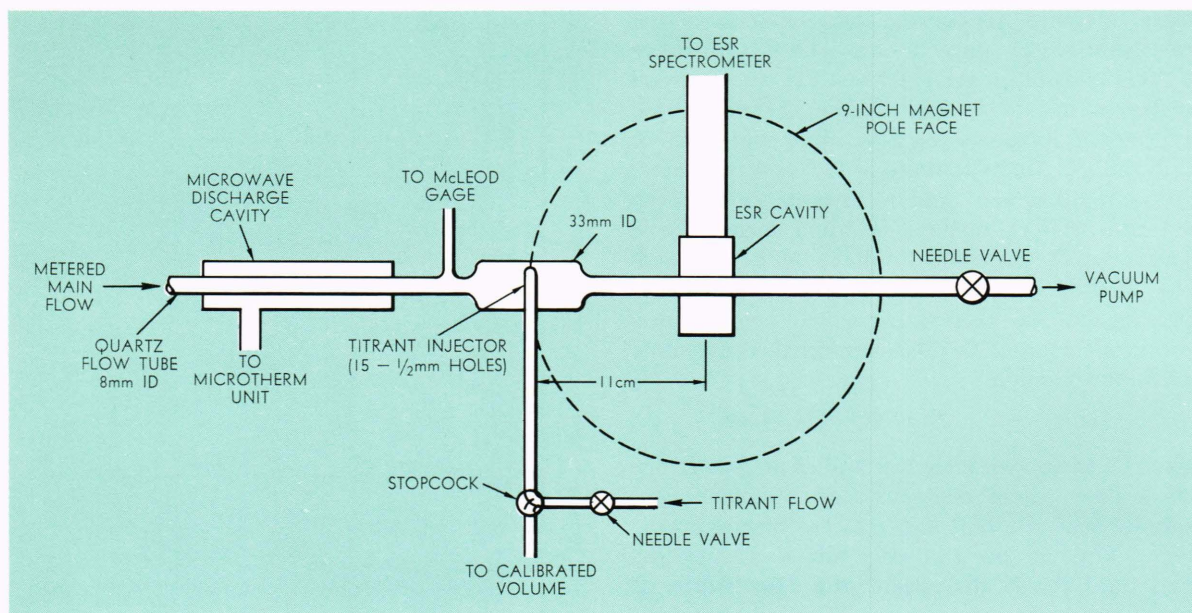
Fig. 1—Diagram of flow apparatus for ESR-titration comparison.

electrons which has nothing to do with electron spin. Up to the present time no radical species containing three or more atoms (other than NF_2 and the stable NO_2) has been detected in the gas phase by ESR, although several of these such as HO_2, CH_3, and NH_2 have been observed frozen out at low temperatures and would be of great interest in gas kinetic studies. The reason for the difficulty in detecting such gaseous polyatomic radicals presumably lies in the coupling between the electron spin and rotational motion that tends to make their spectra very complex and easily smeared out into weak, broad lines. If the species has a strong electric dipole moment there is sometimes the hope of seeing transitions of the electric dipole type that are stronger than the magnetic dipole type. It is not completely clear that the failure to observe polyatomic radicals has been due only to their inherently weak spectra or partly due to ineffective means of generating them. The atomic spectra are all quite simple, while those of the diatomic species tend to be more complex because of various coupling effects of the electron spin and rotational motion as mentioned. Nevertheless, the details have been worked out and the spectrum of a given species is usually easily recognizable and unambiguous, so there is no difficulty about identification. Furthermore, for use in monitoring the concentration of a given species, one line of the spectrum is all that is necessary, and any complexities are usually unimportant.

Besides its versatility and relative simplicity, the ESR technique also has the virtue of good sensitivity. The practical lower limit of detectability for simple species such as hydrogen atoms is roughly 10^{12} per cm^3, which corresponds to about 0.003% atoms at a total pressure of one millimeter at room temperature. Concentrations which can be measured accurately are, of course, a factor of perhaps ten higher than this, but even so the excellent sensitivity of the method is apparent.

The accuracy of ESR radical concentration measurements on an absolute basis requires special comment. Many useful experiments require only relative concentrations that are easily obtained, since with suitable caution about the influence of certain instrumental variables the spectrometer signal will be strictly proportional to the free radical concentration. The determination of absolute concentrations from the signal intensity and the known instrumental parameters of the spectrometer is rarely, if ever, practical. There are too many instrumental variables (crystal sensitivity, amplifier gain, microwave power, etc.) which are difficult to assess to permit the direct approach. Instead one almost always resorts to the alternative of calibrating with a known reference substance, thus converting an absolute measurement to a relative one. In the case of ESR spectrometry, the key to this problem was pointed out by Krongelb and Strandberg,[4] who suggested the use of O_2 as a

[4] S. Krongelb and M. W. P. Strandberg, "Use of Paramagnetic-Resonance Techniques in the Study of Atomic Oxygen Recombinations," *J. Chem. Phys.*, **31**, 1959, 1196–1210.

stable reference gas for the determination of the concentrations of simple atoms. The first objective of APL research in this field was the experimental testing of this idea.[5] The theoretical expressions relating the intensities of ESR absorption lines of H, N, and O atoms to those of O_2 were evaluated. Then attention was paid to the question of the best independent method of atom measurement against which the ESR result could be checked. The method chosen was a so-called gas phase titration that has been rather widely used recently for certain atoms. To illustrate, in the case of N atoms, the reaction

$$[1] \qquad N + NO \rightarrow N_2 + O$$

is known to be extremely fast and clean cut. If one has a flow system containing an unknown concentration of N atoms and a means of monitoring them, NO can be gradually added at metered rates until the N disappears just downstream of the NO injection point. At this "titration endpoint" the NO flow rate is equal to the N flow rate, so that the N concentration can be evaluated from the NO and total flow rates.

The apparatus set up for this experiment is shown in Fig. 1; N_2 gas flowed from left to right at linear velocities of several hundred centimeters per second (slower in the expanded injector section) and pressures of about one millimeter. In passing through the microwave discharge cavity the N_2 was dissociated to N atoms to a small extent. Then, NO could be metered through the injector and the N atoms monitored at the ESR cavity, the ESR being used simply as a qualitative detector in this application. The titration curves of atom signal height versus NO flow rate obtained in this way are typified by those shown in Fig. 2. The N signal decreases linearly with increasing NO as predicted, and since reaction [1] requires the generation of one O atom for each N atom consumed, the O signal increases linearly to the endpoint as shown. Beyond the endpoint the reaction of O with the excess NO present causes the O signal to decrease slowly. Before each such titration, the absolute N atom concentration with no NO flowing was independently determined by ESR by comparing its integrated signal intensity with that of pure O_2 when the latter was introduced to the flow tube at a known pressure. The results of several such ESR-titration checks are given in Table I(a). The two entirely independent methods agree within about 10%, which is very strong evidence for the validity of both.

[5] A. A. Westenberg and N. deHaas, "Quantitative Measurements of Gas Phase O and N Atom Concentrations by ESR," *J. Chem. Phys.*, **40**, 1964 3087–3098.
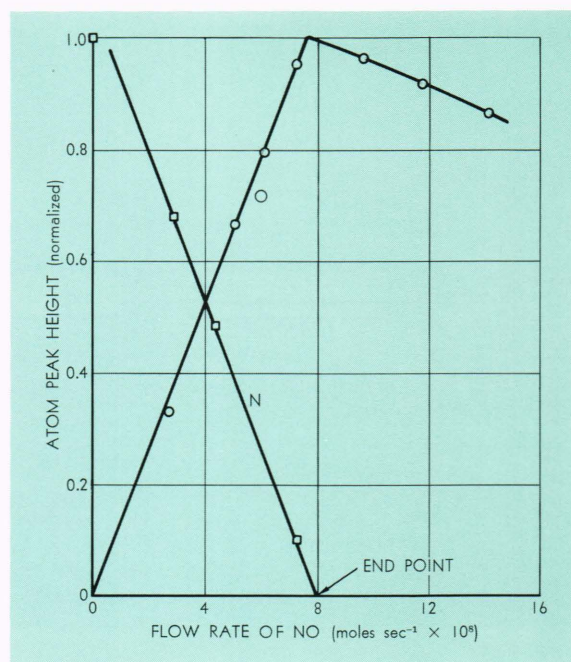
Fig. 2—Disappearance of N atoms and appearance of O atoms during titration of N with NO. Pressure = 1.0 mm, initial N concentration = 0.52%.

A similar series of experiments was carried out on the determination of O atoms in O-O_2 mixtures. Here the mixture contained its own O_2 standard and O/O_2 ratios could be determined directly by ESR without a separate filling with O_2. For the titration check the fast reaction

$$[2] \qquad O + NO_2 \rightarrow NO + O_2$$
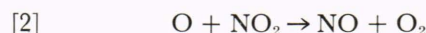
was used. The comparison is given in Table I(b)

TABLE I

COMPARISON OF ABSOLUTE ATOM CONCENTRATIONS DETERMINED BY ESR USING O_2 AS REFERENCE GAS WITH INDEPENDENT TITRATION RESULTS. (A) N ATOMS, NO TITRATION. (B) O ATOMS, NO_2 TITRATION.

Pressure (mm)	N mole fraction ($\times 10^2$)	
	(ESR)	(Titration)
(a)		
1.04	0.456	0.413
0.66	0.407	0.456
0.54	0.674	0.623
0.41	0.876	0.964
	O mole fraction ($\times 10^2$)	
(b)		
0.58	13.6	14.6
0.87	16.7	16.7
1.33	6.27	7.62
1.33	3.08	3.19
0.75	3.46	3.56

and again verifies the excellent reliability of the absolute ESR measurements.

The use of O_2 as a reference gas is valid only for those species (usually simple atoms) that exhibit magnetic dipole transitions, i.e., the coupling with the incident microwave radiation is by way of its oscillating magnetic field. For certain important diatomic radicals (of which OH and SO are examples) the transitions are of the type in which the electric dipole moment of the radical interacts with the incident microwave electric field. Since the microwave electric field vector has a different geometric orientation in the cavity than its magnetic component, O_2 cannot be used as a standard. Fortunately, however, NO can be used as a stable reference since it also exhibits electric dipole transitions. The theoretical relations for determining OH[6] and OD[7] in this way have been worked out. The measurement of free electrons also requires the use of NO as reference. An ESR cavity capable of detecting both magnetic and electric dipole transitions can be readily constructed.[8]

Applications to the Kinetics of the OH Radical

The reactions of the hydroxyl radical OH are of considerable intrinsic interest and are important in many combustion systems. They have been particularly difficult to measure, however, and practically all of the early work is now known to be in error. The main reason for this (aside from inadequate detection methods) was that the source of OH was usually an electric discharge in water vapor, which has proved to be too ill-defined for kinetic studies. Most of the OH is generated outside the discharge by complex reactions which tend to obscure the reaction being measured. Meaningful research in this area requires a reliable OH source and a good detection system. The ultraviolet absorption spectrum of OH has frequently been used in its detection and it is extremely sensitive, but as an absolute method it suffers from the lack of a good calibration procedure. Thus some of the first applications of ESR to kinetics which were performed at APL centered around its use for OH detection.

[6] A. A. Westenberg, "Intensity Relations for Determining Gas-Phase OH, Cl, Br, I, and Free-Electron Concentrations by Quantitative ESR," *J. Chem. Phys.*, **43**, 1965, 1544–1549.

[7] A. A. Westenberg and W. E. Wilson, "ESR Intensity Relations and Some Gas-Phase Chemical Kinetics of the OD Radical," *J. Chem. Phys.*, **45**, 1966, 338.

[8] A. A. Westenberg and N. deHaas, "Quantitative ESR Measurements of Gas-Phase H and OH Concentrations in the N-NO_2 Reaction," *J. Chem. Phys.*, **43**, 1965, 1550–1556.

A nearly ideal source of OH for kinetic studies is afforded by adding NO_2 to a flow of H atoms. This gives OH from the reaction

$$[3] \qquad H + NO_2 \rightarrow NO + OH$$

which is one of the fastest elementary reactions known, even at room temperature, and is a form of titration reaction. For steady state operation the fast flow system shown in Fig. 3 was constructed. It was similar to the apparatus in Fig. 1 except that two injectors were provided on a flow tube of uniform cross section, so that the linear velocity—and hence reaction time—could be ac-
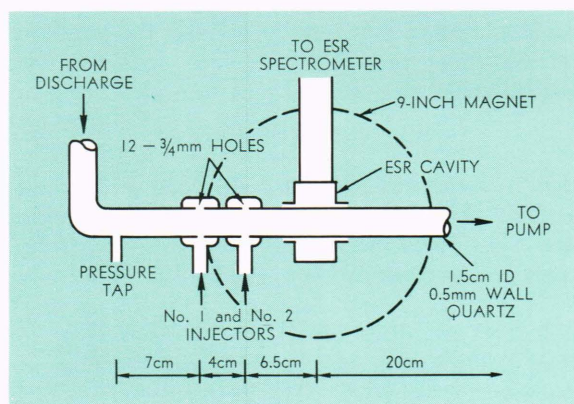

Fig. 3—Diagram of flow apparatus for OH kinetic studies.

curately known. The apparatus was also arranged so that the ESR cavity could be moved to various positions along the flow tube. Linear flow velocities in the range of 3000-5000 cm/sec at about one millimeter pressure could be attained in this system. Dissociation of H_2 (either in an inert carrier gas or pure) was accomplished far upstream by a microwave discharge. This stream containing a few percent of H atoms then passed Injector No. 1 where NO_2 was metered in at a rate just sufficient to consume all of the H according to reaction [3]. This occurred so rapidly that reaction was complete in a distance of a centimeter or so and a very well-defined OH source was provided. Starting with a little H_2, heavily diluted in inert argon or helium, which was completely dissociated to H in the discharge, and with NO_2 added in an amount equivalent to the H, the resultant flow contained nothing but OH and NO in the inert carrier gas.

Downstream of the OH source at Injector No. 1, the OH starts to decay because of the reaction[9]

[9] F. Kaufman and F. P. Del Greco, "Fast Reactions of OH Radicals," *Ninth Symposium on Combustion*, Academic Press, New York, 1963, 659–668.

[4] $$OH + OH \rightarrow H_2O + O$$
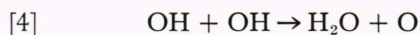
which is fairly fast and must be accounted for in any OH kinetic measurement, since it is always occurring. Loss of OH on the walls is negligible in such a system. The O from reaction [4] is consumed as soon as formed by the very fast reaction

[5] $$O + OH \rightarrow O_2 + H$$
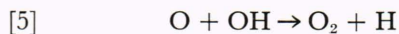
so that the net decay rate of OH may be written as

$$- \frac{d(OH)}{dt} = 3k_4 \, (OH)^2 \qquad (2)$$

where k_4 is the rate constant of reaction [4]. Letting $y = (OH)_0 / (OH)$, where $(OH)_0$ is the absolute concentration at some reference position, and converting time to distance z by means of the flow velocity v, Eq. (2) may be integrated to give

$$y = 1 + 3k_4 \, (OH)_0 \, z / v \qquad (3)$$

Thus by measuring both the decay of OH along the flow tube and $(OH)_0$ by means of ESR (using pure NO as a calibration standard for the latter), a plot of y vs z should be linear with a slope equal to $3k_4 \, (OH)_0 / v$, from which k_4 can be determined. Such plots for three different flow conditions are illustrated in Fig. 4, and they bear out the behavior predicted by Eq. (3). Many experiments of this type have enabled the rather precise value of k_4 given in Table II to be obtained.[10]

TABLE II

SUMMARY OF RATE CONSTANTS FOR VARIOUS OH RE-ACTIONS MEASURED BY THE ESR TECHNIQUE IN A FAST FLOW SYSTEM AT $300°$K.

	Reaction	k ($cm^3 \, mole^{-1} \, sec^{-1}$)
[4]	$OH + OH \rightarrow H_2O + O$	$1.55 \pm 0.12 \times 10^{12}$
[6]	$H_2 + OH \rightarrow H_2O + H$	$3.9 \pm 0.2 \times 10^9$
[7]	$CO + OH \rightarrow CO_2 + H$	$1.15 \pm 0.05 \times 10^{11}$
[8]	$CH_4 + OH \rightarrow H_2O + CH_3$	$6.5 \pm 1.5 \times 10^9$
[4D]	$OD + OD \rightarrow D_2O + O$	$0.95 \pm 0.10 \times 10^{12}$
[7D]	$CO + OD \rightarrow CO_2 + D$	$3.30 \pm 0.10 \times 10^{10}$

Once the value of k_4 was known it was possible to measure the rate constants of other OH reactions. For example, suppose H_2 is admitted through Injector No. 2 (Fig. 3) at a steady rate such that its concentration is always much greater than that of OH. The concentration of H_2 will then be constant along the flow tube since the
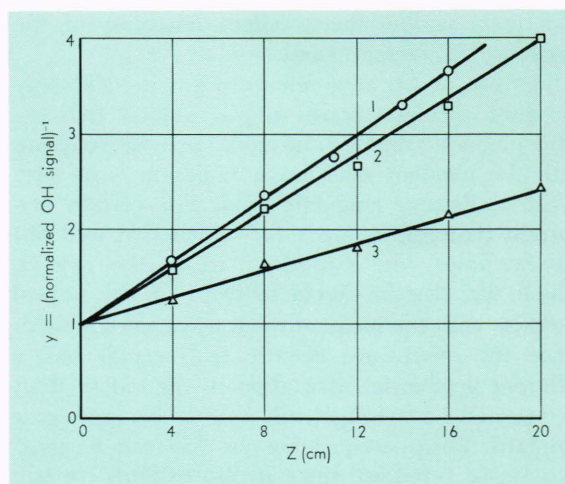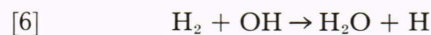

Fig. 4—Plots showing second-order decay of OH. Curve 1: $v = 3370$ cm sec^{-1}, $(OH)_0 = 1.22 \times 10^{-10}$ mole cm^{-3}. Curve 2: $v = 3050$ cm sec^{-1}, $(OH)_0 = 1.06 \times 10^{-10}$ mole cm^{-3}. Curve 3: $v = 4870$ cm sec^{-1}, $(OH)_0 = 0.72 \times 10^{-10}$ mole cm^{-3}.

amount used up by OH will be negligible. When H_2 is present the reaction

[6] $$H_2 + OH \rightarrow H_2O + H$$

takes place simultaneously with reactions [4] and [5]. The OH decay equation must then be written

$$- \frac{d(OH)}{dt} = 3k_4 \, (OH)^2 + k_6 (H_2) \, (OH) \quad (4)$$

which can be integrated with (H_2) constant and put in a form suitable for determining k_6. When CO is added instead of H_2 an exactly analogous procedure may be used to measure the rate constant k_7 for

[7] $$CO + OH \rightarrow CO_2 + H$$
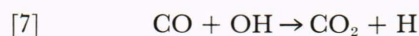
Examples of the OH decay curves observed when H_2 or CO were present are given in Fig. 5. The additional OH loss mechanism means that the simple linear behavior of Eq. (3) demonstrated in Fig. 4 is no longer obeyed. The greater curvature of the CO plot in Fig. 5 compared to the H_2 plot (even though there was more H_2 present than CO) is a direct indication that $k_7 > k_6$. Results of this work are given in Table II, along with similar data on the reaction[11]

[8] $$CH_4 + OH \rightarrow H_2O + CH_3$$

Measurements were also carried out of the rate constants for the reactions analogous to reactions

[10] G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, "Studies of Hydroxyl Radical Kinetics by Quantitative ESR," *J. Chem. Phys.*, **44**, 1966, 2877–2884.

[11] W. E. Wilson and A. A. Westenberg, "Study of the Reaction of Hydroxyl Radical with Methane by Quantitative ESR," *Eleventh Symposium on Combustion* (To be published).
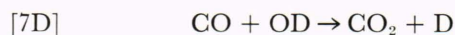
[4] and [7] in which the deuterated hydroxyl radical OD was used.[7] This was prepared in the same way as the OH, i.e., D_2 was dissociated and NO_2 was added to give OD according to

[3D] $D + NO_2 \rightarrow NO + OD$.

As described previously, the rate constant k_{4D} for

[4D] $OD + OD \rightarrow D_2O + O$

was determined first. Then CO was added and k_{7D} for

[7D] $CO + OD \rightarrow CO_2 + D$

was measured. These results are also given in Table II. The ratios $k_4/k_{4D} = 1.6$ and $k_7/k_{7D} = 3.5$ are interesting examples of the effect of isotopic substitution on rate constants, and afford opportunity for informative application of reaction rate theory. The lighter isotopic species OH shows the larger rate constants as expected.

Reactions [6], [7], and [8] are all important as common flame reactions. The precise measurements at room temperature described above are of particular value because they provide good anchor points in the determination of the temperature-dependence of these rate constants. These low temperature data may be combined with other data obtained by various means at higher temperatures to evaluate the parameters A and E (the activation energy) in the so-called Arrhenius relation (after its originator) usually used to express the rate constant as a function of temperature, i.e.,

$$k = A \exp\left(-E/RT\right), \qquad (5)$$

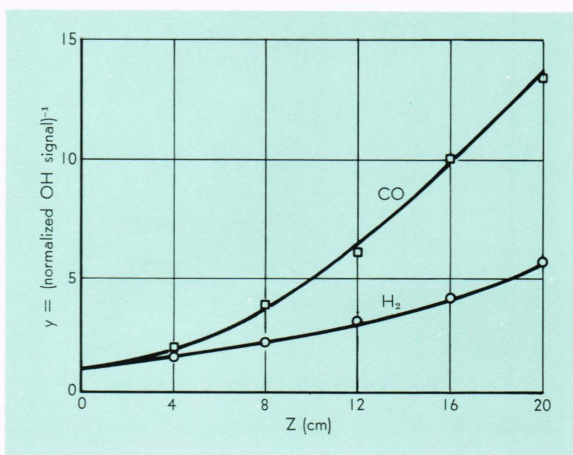where R is the ideal gas constant. These parameters for reactions [6], [7], and [8] are summarized in Table III. The room temperature value for k_7 obtained by the ESR technique has been especially important in establishing the true Arrhenius parameters for reaction [7], since earlier studies had predicted values of k_7 nearly a factor of 10^{-3} smaller than that listed in Table II. This caused previous estimates of the activation energy E_7 to be much too high, an error which had led to much confusion in flame kinetics.

TABLE III

PARAMETERS A AND E IN THE ARRHENIUS EXPRESSION K = A EXP $\left(-E/RT\right)$ FOR VARIOUS OH REACTIONS DETERMINED FROM ROOM TEMPERATURE ESR MEASUREMENTS AND OTHER DATA OBTAINED AT HIGH TEMPERATURES.

Reaction	A $(cm^3\ mole^{-1}\ sec^{-1})$	E $(kcal/\ mole)$
[6] $H_2 + OH \rightarrow H_2O + H$	2.3×10^{13}	5.2
[7] $CO + OH \rightarrow CO_2 + H$	3.1×10^{11}	0.6
[8] $CH_4 + OH \rightarrow H_2O + CH_3$	2.9×10^{13}	5.0

The Future

All of the kinetic results obtained with the ESR technique discussed in the previous section have been confined to room temperature. The reason is that all of the work so far has depended upon moving the ESR cavity itself to monitor radical concentrations at various reaction times, and the difficulties of doing this on a flow tube which is either heated or cooled are formidable. For this reason efforts are currently underway at APL which are directed at the development of a heated fast flow system in which the detecting cavity is located at a fixed point outside the hot region, i.e., at a point maintained at room temperature. The reaction time would then be varied by means of a movable injector inside the heated section through which one reactant could be introduced to an atom-containing stream. Under certain conditions such a technique is feasible, and initial results have been promising indeed, so that significant data on a wide variety of atom-molecule reactions should be forthcoming. Many other interesting applications of the ESR technique are conceivable, both in the quantitative measurement of kinetic constants and as a qualitative tool for radical detection which should be of great value in unraveling the details of reaction mechanisms. Thus future research in this field promises to be very active and fruitful.

Fig. 5—Decay of OH in presence of (separately) added CO and H_2. Flows were similar in the two cases, but $(H_2) > (CO)$.