with both nitrogen–air and argon–air. As can be seen from Table I, however, there are compositions on the rich and lean sides corresponding to the same flame temperature. For such mixtures with the same flame temperature a thermal theory would predict the same values for the burning velocity ratio. It is true that the reaction rates for CH_4 and CD_4 mixtures will be somewhat different even though the activation energies are comparable. Thus, in using the Semenov equation to predict the burning velocity ratio the quantity $\left(\int_0^{T_f} w_{CH_4}\,dT/\int_0^{T_f} w_{CD_4}\,dT\right)^{1/2}$ will have a temperature independent factor different from unity. Although at a particular composition this factor may account for the observed burning velocity ratio, the Semenov equation still predicts that this ratio is the same for mixtures with the same flame temperature. Thus, a purely thermal theory does not account for the observed increase in the burning velocity ratio as the initial concentration of fuel increases.

The burning velocity ratios predicted by the Tanford–Pease theory are dependent on the values taken for activation energies and diffusion coefficients. There is also an uncertainty in the effect of isotopic substitution upon the rates of the reactions of the fuel with active species.[10] Thus, it would be difficult to form valid conclusions from a comparison of the experimental burning velocity ratios with those predicted by the Tanford–Pease equation. Nevertheless, it is significant that the ratios of flame speeds for light to heavy methane increase progressively in going from lean to rich mixtures, for this is the direction in which hydrogen and deuterium atom concentrations become more important relative to hydroxyl or oxygen.

In conclusion it is believed that the above analysis of the experimental burning velocities of CH_4 and CD_4 presents evidence in favor of a diffusion mechanism. The Tanford–Pease equation is in much better agreement with the experimental values for the mixtures with argon–air than the Semenov bimolecular equation. In addition it has been pointed out that it is unlikely that a thermal theory can explain the observed effect of composition on the ratio of the burning velocities of corresponding CH_4 and CD_4 mixtures.

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A Method for Analyzing Pressure–Time Curves of Gas Phase Reactions

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Two methods are given for deriving from an assumed reaction paradigm expressions for the time derivatives of the total pressure in terms of rate constants and stoichiometric constants or functions. Experimentally determined initial values for these derivatives can be obtained and their behavior compared with the behavior of these derived expressions.

The rate at which a substance undergoes a chemical reaction in the gas phase is frequently obtained by measuring the total pressure in the system as a function of time. Conventional treatment of such data is limited to an evaluation of the initial pressure, the initial rate of pressure increase and the time required for a given percentage increase in the total pressure. No method has been available for obtaining useful information from the shape of the pressure–time curve. The purpose of this paper is the presentation of such a method.

Evaluation of the Time Derivatives of the Pressure.—Since a numerical value for at least the first and second time derivatives of the pressure is required, it is necessary to obtain an analytical rather than a graphical representation of the data. This can be accomplished by using the data to obtain an equation of the form

$$P_T = a_0 + a_1t + a_2t^2 + a_3t^3 + \ldots \qquad (1)$$

Fortunately, the ingenious abbreviated least-squares treatment of Baily[1] and Cox and Matuschak[2] is ideally suited to this purpose. Because of the nature of the experiment, it is easy to meet the sole requirement of this abbreviated method, *i.e.*, that the values of the independent variable (time) form an arithmetic progression. Using this procedure, evaluation of the four coefficients in a cubic equation can be accomplished in about 15 minutes with an automatic calculator.

From eq. 1, it follows that

$$a_0 = P_0 \qquad (2)$$

$$a_1 = (dP_T/dt)_{t=0} \qquad (3)$$

$$2a_2 = (d^2P_T/dt^2)_{t=0} \qquad (4)$$

$$6a_3 = (d^3P_T/dt^3)_{t=0} \qquad (5)$$

where P_0 is the initial pressure and P_T is the total pressure at time, t. Higher derivatives can, of course, be evaluated; however, the possibility of obtaining directly interpretable quantitative information from anything higher than the second derivative is remote except in the case of very simple reactions. In such cases the information so obtained is of the same nature as that obtained from the second derivative but is inherently less accurate. However, though lacking in accuracy, the numerical value of the third derivative can frequently be used to obtain information whose magnitude or sign may be of assistance in understanding more complex reactions. Regardless of whether the treatment is limited to an evaluation of the first and second derivatives or extended to include an evaluation of the third, it has been found that precision is greatly improved if the data are taken over a time range sufficiently large to require one

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(1) J. L. Baily, *Ann. Math. Statistics*, **2**, 355 (1931).

(2) C. J. Cox and M. C. Matuschak, *J. Phys. Chem.*, **45**, 362 (1941).

more term in equation 1 than needed to evaluate the highest derivative for which a value is desired. Thus, in order to obtain values for the first and second derivatives, equation 1 will be a cubic.

Having evaluated the first and second time derivatives, it now becomes necessary to find a suitable paradigm for the reaction through which physical significance can be attached to these derivatives. Calculation of a rate constant from the values of $(\mathrm{d}P_\mathrm{T}/\mathrm{d}t)_{t=0}$ is easily accomplished through a knowledge of the order. Since attaching physical significance to the numerical value of the second derivative can only be done by fitting a reaction paradigm to the data (a process of trial and error), the method for doing this is best illustrated by an example.

Gas Phase Decomposition.—For any gas phase reaction followed experimentally by measuring the total pressure, it is tacitly assumed that the rate of increase in the total pressure is proportional to some power of the pressure of the reactant, P_x.

$$\mathrm{d}P_\mathrm{T}/\mathrm{d}t = k_\mathrm{T}P_\mathrm{x}^n \tag{6}$$

For a decomposition where the relative concentrations of the products do not change during the course of the reaction, the decrease in pressure of the reactant is proportional to the increase in total pressure.

$$P_0 - P_\mathrm{x} = \alpha_0(P_\mathrm{T} - P_0) \tag{7}$$

Solving this expression for P_x and substituting in eq. 6, the rate equation becomes

$$\mathrm{d}P_\mathrm{T}/\mathrm{d}t = k_\mathrm{T}[P_0 - \alpha_0(P_\mathrm{T} - P_0)]^n \tag{8}$$

Higher time derivatives of the pressure are obtained from equation 8 by repeated differentiation.

$$\mathrm{d}^2P_\mathrm{T}/\mathrm{d}t^2 = nk_\mathrm{T}[P_0 - \alpha_0(P_\mathrm{T} - P_0)]^{n-1}(-\alpha_0\mathrm{d}P_\mathrm{T}/\mathrm{d}t) \tag{9}$$

$$\mathrm{d}^3P_\mathrm{T}/\mathrm{d}t^3 = n(n-1)k_\mathrm{T}[P_0 - \alpha_0(P_\mathrm{T} - P_0)]^{n-2}(-\alpha_0\mathrm{d}P_\mathrm{T}/\mathrm{d}t)^2 + nk_\mathrm{T}[P_0 - \alpha_0(P_\mathrm{T} - P_0)]^{n-1}(-\alpha_0\mathrm{d}^2P_\mathrm{T}/\mathrm{d}t^2) \tag{10}$$

Expressions for the initial values of these derivatives can be evaluated easily since, when $t = 0$, $P_\mathrm{T} = P_0$.

$$(\mathrm{d}P_\mathrm{T}/\mathrm{d}t)_{t=0} = k_\mathrm{T}P_0^n = a_1 \tag{11}$$

$$(\mathrm{d}^2P_\mathrm{T}/\mathrm{d}t^2)_{t=0} = -n\alpha_0k_\mathrm{T}^2P_0^{2n-1} = 2a_2 \tag{12}$$

$$(\mathrm{d}^3P_\mathrm{T}/\mathrm{d}t^3)_{t=0} = n(2n-1)\alpha_0^2k_\mathrm{T}^3P_0^{3n-2} = 6a_3 \tag{13}$$

Or, in general

$$(\mathrm{d}^pP_\mathrm{T}/\mathrm{d}t^p)_{t=0} = \alpha_0^{p-1}k_\mathrm{T}^pP_0^{pn-p+1}\prod_{x=1}^{p-1}(xn - x - 1) = p!a_\mathrm{p} \tag{14}$$

Essentially the same results are obtained for the first two derivatives if the products change during the course of the reaction, provided this change does not result from a reaction between the reactant and one of its products. Under these circumstances, α_0 must be replaced by some function of time, $\alpha(t)$. Since the exact nature of this function does not need to be known it is represented as a series expansion in t.

$$\alpha(t) = \alpha_0 + \alpha_1t + \alpha_2t^2 + \alpha_3t^3 + \cdots \tag{15}$$

Equation 8 then becomes

$$\mathrm{d}P_\mathrm{T}/\mathrm{d}t = k_\mathrm{T}[P_0 - \alpha(t)(P_\mathrm{T} - P_0)]^n \tag{16}$$

The second and third derivatives are then, respectively

$$\mathrm{d}^2P_\mathrm{T}/\mathrm{d}t^2 = -nk_\mathrm{T}[P_0 - \alpha(t)(P_\mathrm{T} - P_0)]^{n-1}[\alpha'(t)(P_\mathrm{T} - P_0) + \alpha(t)\,\mathrm{d}P_\mathrm{T}/\mathrm{d}t] \tag{17}$$

$$\mathrm{d}^3P_\mathrm{T}/\mathrm{d}t^3 = n(n-1)k_\mathrm{T}[P_0 - \alpha(t)(P_\mathrm{T} - P_0)]^{n-2}[\alpha'(t)(P_\mathrm{T} - P_0) + \alpha(t)\,\mathrm{d}P_\mathrm{T}/\mathrm{d}t]^2 - nk_\mathrm{T}[P_0 - \alpha(t)(P_\mathrm{T} - P_0)]^{n-1}\left[\alpha''(t)(P_\mathrm{T} - P_0) + 2\alpha'(t)\mathrm{d}P_\mathrm{T}/\mathrm{d}t + \alpha(t)\frac{\mathrm{d}^2P_\mathrm{T}}{\mathrm{d}t^2}\right] \tag{18}$$

Evaluated for $t = 0$, equations 17 and 18 reduce to

$$(\mathrm{d}^2P_\mathrm{T}/\mathrm{d}t^2)_{t=0} = -n\alpha_0k_\mathrm{T}^2P_0^{2n-1} \tag{19}$$

$$(\mathrm{d}^3P_\mathrm{T}/\mathrm{d}t^3)_{t=0} = n(2n-1)\alpha_0^2k_\mathrm{T}^3P^{3n-2} - 2n\alpha_1k_\mathrm{T}P_0^{2n-1} \tag{20}$$

It will be noted that the form of the second derivative is unchanged by imposing the condition that the relative amounts of products vary during the course of the reaction. A comparison of equations 13 and 20 will show that the first terms are identical in form. The presence of the second term in equation 20 is due entirely to the process or processes which upset the initial stoichiometry of the reaction.

Having derived expressions for the initial values of the first three pressure derivatives, it is possible to evaluate the constants contained in these expressions. The order of the reaction, n, can be determined from the values of $(\mathrm{d}P_\mathrm{T}/\mathrm{d}t)_{t=0}$ at several initial pressures. Equations 2 and 11 then permit the evaluation of k_T, and equation 12 permits the evaluation of α_0. If equation 8 is the proper form for the rate equation, then, within experimental error, a single value of α_0 will be obtained from an isothermal series of decompositions at different initial pressures. Failure to obtain a constant value of α_0 from such a series is an indication that $\alpha(t)$ is dependent on both time and the initial pressure. Treatment of this case will be discussed in the next section.

If α_0 is independent of the initial pressure, then it is possible to calculate a value for the first term of equation 20. If the reaction is a simple decomposition, this value should be in agreement with the experimentally determined initial value of the third derivative, *i.e.*, the second term of equation 20 is zero and equation 20 reduces to equation 13. If the calculated value is low, a polymerization is indicated; if it is high the presence of a secondary decomposition process can reasonably be suspected.

For an nth order decomposition a knowledge of α_0 provides a means for calculating the true rate constant as defined by the expression

$$-\,\mathrm{d}P_x/\mathrm{d}t = k_xP_x^n \tag{21}$$

since $k_x = \alpha_0k_T$.

Detailed Treatment of Data.—It has been shown that introduction of a pressure independent parameter, $\alpha(t)$, permits one to separate the initial process of a decomposition from subsequent reactions involving the products without having to specify the nature of these subsequent reactions. When calculation of a pressure independent constant, α_0, from the second derivative does not prove possible, a more detailed treatment of the data must be undertaken. In general, this situation arises when the starting material undergoes reaction simultaneously by two or more processes of different order. Considering only decomposition of pure substances, reactions which would require a detailed treatment can be considered as falling into one of two categories: (a) decomposition of a substance by two or more processes of different order, (b) decomposition of a substance followed by reaction of this substance with one or more of the reaction products. Fortunately, it is possible to distinguish between these two types from the behavior of $\log(dP_T/dt)_{t=0}$ with $\log P_0$. For type (b), the function is linear, while for type (a) it is non-linear.

For the purpose of illustrating the method, let us consider the following sequence of reactions (Type b):

$$A \longrightarrow r_1B + C \text{ (first order)} \qquad (22)$$
$$A + C \longrightarrow r_2D \text{ (second order)}$$

which can be described in terms of the following differential equations

$$dP_A/dt = -k_1P_A \qquad (23)$$
$$dP_B/dt = r_1k_1P_A \qquad (24)$$
$$dP_C/dt = k_1P_A - k_2P_AP_C \qquad (25)$$
$$dP_D/dt = r_2k_2P_AP_C \qquad (26)$$

When $t = 0$, $P_A = P_0$ and $P_C = 0$, therefore equations 23 through 26 can be evaluated for $t = 0$ and summed to give

$$(dP_T/dt)_{t=0} = r_1k_1P_0 \qquad (27)$$

Differentiation of equations 23 through 26 and evaluation of the results for $t = 0$ followed by summation of the resulting equations leads to the result

$$(d^2P_T/dt^2)_{t=0} = -k_1P_0[r_1k_1 - (r_2 - 2)k_2P_0] \qquad (28)$$

It can be seen from equations 27 and 28 that the ratio of the second derivative to the first derivative is a linear function of the initial pressure. This relationship provides a method for determining whether or not the assumed mechanism is applicable to the reaction being studied.

The same procedure can be applied to any reaction where the initial conditions are known. The initial rates of change of the components of the system can always be expressed in terms of these initial pressures, therefore the sum of the initial rates of change, $(dP_T/dt)_{t=0}$, can be evaluated. Since higher derivatives can always be expressed in terms of the initial pressures and previously evaluated derivatives, the procedure can be extended to as many terms as desired. Reconciliation of a particular reaction with an assumed paradigm is effected by comparing the behavior of the experimentally determined initial values of the derivatives with the behavior of the expressions for these derivatives obtained from the paradigm.

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STORRS, CONN.

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Preparation of $UClF_3$[1]

BY ALBERT W. SAVAGE, JR.

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A mixed halide of tetravalent uranium was prepared by five different methods. Microscopic examination and X-ray studies conclusively demonstrated that the principal product in each case was the same compound. Analytical and X-ray evidence indicated that the correct formula for the compound is $UClF_3$.

Summary of Previous Work

The reaction between uranyl fluoride and carbon tetrachloride was first studied by Gates, Andrews, Block and Young.[2] They reported investigation of both liquid phase (at 130° in a sealed tube under pressure) and vapor phase (at 450°) reactions and found the latter to be the more convenient. Their analysis of the reaction product showed a U/F/Cl ratio of 1:2:1.63, and they assumed the material to be UCl_2F_2. They further reported that this compound disproportionated on heating, forming UCl_4 and UF_4, the UCl_4 being removed by distillation.

In another experiment Gregory heated a mixture of equimolar quantities of UCl_4 and UF_4 at 600° in a quartz tube under an atmosphere of helium for 15 hours.[2] At the conclusion of this period the charge was a homogeneous mass except for a very small amount of sublimate. Heating to 500° completely melted the charge. He concluded that an addition compound was formed which had a melting point around 460°, and decomposed only very slowly at temperatures as high as 600°. The lack of any trace of fluorine in the distillate was "in agreement with the observation that UF_2Cl_2, if formed, would disproportionate on heating."

All attempts to reproduce these experiments in this Laboratory have resulted instead in the formation of $UClF_3$. This compound was first prepared by reaction of chlorine gas with UF_3 at 315°[2] at the Ames Laboratories.

Apparatus and Materials

Except as otherwise noted, all reactions between solids and gases were carried out by placing the solid in a small platinum or porcelain boat (about 4″ long and 1/2″ wide), which was then placed in a Pyrex tube 20″ long and 1 1/4″ in diameter. This tube was equipped with a stopcock at each end and lay horizontally in a cylindrical furnace 13″ long so that both ends of the Pyrex tube extended beyond the furnace, allowing any volatile uranium compounds formed to condense on these colder surfaces. Temperatures were measured by means of a thermocouple lying under the Pyrex tube. One end of the tube was connected by means of a three-way T-bore stopcock to a helium supply and to a 5-liter, 3-necked flask equipped with an electric

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(1) Work done under the auspices of the Atomic Energy Commission.

(2) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," National Nuclear Energy Series, Division VIII, Vol. 5, McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 541.