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David Altman and S. S. Penner

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DAVID ALTMAN AND S. S. PENNER

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

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An analysis has been carried out for isentropic expansion through a representative rocket nozzle. The rate of change of temperature of an element of gas with distance and time in the vicinity of the nozzle throat is discussed in some detail. By use of Daniels' rate constant for the formation of nitric oxide from nitrogen and oxygen, it is shown that the temperature changes so rapidly that the reaction $2NO \rightleftharpoons O_2 + N_2$ produces insignificantly small composition changes below about 2800°K when the temperature in the rocket chamber is 3000°K.

I. INTRODUCTION

PERFORMANCE calculations for a propellant system in a rocket motor require the determination of thermodynamic properties at rocket chamber and nozzle exit conditions. It is customary to perform rocket calculations on the assumption that equilibrium among the internal energy states is maintained.[1,2] This assumption is also made in the present discussion without, however, proving its validity. In fact, a more detailed analysis of the rate of attainment of equilibrium among the internal energy states may lead to a refinement of performance calculations in rockets. Relevant experimental and theoretical data can be found in the literature.[3,4,5,6]

It is the purpose of this paper to consider flow through a nozzle with reference to composition changes which may occur as the result of chemical reactions. The flow equations which are used correspond to the well-known one-dimensional approximation.**

The numerical analysis of the changes in chemical composition during isentropic expansion described in the present paper is related to the general problem of gas reactions in flow systems which has been discussed by a number of authors.[7,8,9,10] In order to calculate the extent of changes in chemical composition during flow, it is necessary to know the rates of the various reactions involved, as well as the rate of change of temperature and pressure with time. Theoretical estimates of the order of magnitude of the reaction rates[11] or extrapolations from low-temperature measurements may be sufficient in some cases, since only relatively fast reactions will permit extensive composition changes during isentropic expansion through the rocket nozzle. The present analysis is limited to a study of the changes in composition according to the reaction

$$2NO \rightleftharpoons O_2 + N_2.$$
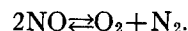
Rate constants for the formation of nitric oxide from oxygen and nitrogen are available in the literature.[12,13,14] These rate data are combined with the time-temperature relations for an adiabatic flow process in a rocket nozzle in order to predict the extent of composition change pro-

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[1] F. J. Malina, J. Franklin Inst. 230, 433 (1940).
[2] H. S. Seifert, M. Mills, and M. Summerfield, Am. J. Phys. 15, 1–21, 121–140, 255–275 (1947).
[3] H. O. Kneser, J. Acous. Soc. Am. 5, 122 (1933).
[4] L. Landau and E. Teller, Physik. Zeits. Sowjetunion 1, 34 (1936).
[5] A. Kantrowitz, J. Chem. Phys. 14, 150 (1946).
[6] P. W. Huber and A. Kantrowitz, J. Chem. Phys. 15, 275 (1947).
** A number of papers concerned with the problem of one-dimensional flow through a nozzle have been published since the preparation of this article. Among these may be mentioned the papers by A. H. Shapiro *et al.*, J. App. Mech. 14, 317, 344 (1948), and by B. L. Hicks, D. J. Montgomery, and R. H. Wasserman, J. App. Phys. 18, 891 (1947).

[7] Th. von Förster and K. H. Geib, Ann. d. Physik 20, 250 (1934).
[8] H. M. Hulburt, Ind. Eng. Chem. 36, 1012 (1944); 37, 1063 (1945).
[9] G. M. Harris, J. Phys. and Colloid Chem. 51, 505 (1947).
[10] K. Schaefer, "On the Thermodynamics of Rocket Propulsion, I," Headquarters, Air Materiel Command, Wright Field, Dayton, Ohio, 1947.
[11] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Process* (McGraw-Hill Book Company, New York, 1941).
[12] F. Daniels *et al.*, private communication, 1943.
[13] J. Zeldovich, Acta Phys. Chim., URSS 21, 577 (1946).
[14] D. Frank-Kamenetsky, Acta Phys. Chim., URSS 22, 27 (1947).

duced by chemical reaction. The corrections which should be applied to the thermodynamic treatment of the flow process when appreciable composition changes occur are usually not large. A detailed discussion of the method has been given elsewhere for an idealized system.[15]

II. REDUCED TEMPERATURE AS A FUNCTION OF NOZZLE DIAMETER

The adiabatic expansion of 1 mole of a perfect gas through a nozzle without friction losses is considered in the following discussion. From the condition that the flow occurs isentropically, it follows that

$$dp/\rho = dT/(\gamma - 1)T, \qquad (1)$$

where ρ represents the density, T is the temperature at any point along the nozzle, and γ is the ratio of the specific heat at constant pressure to the specific heat at constant volume. By the use of Eq. (1) together with the equation of continuity

$$dv/v + d\rho/\rho + dA/A = 0 \qquad (2)$$

and the law of conservation of energy

$$Mvdv = -c_p dT \qquad (3)$$

it can be shown that

$$\frac{dr}{dT_R} = \frac{r}{2}\left[\frac{1}{2(1-T_R)} - \frac{1}{(\gamma-1)T_R}\right]. \qquad (4)$$

Here v is the velocity of flow parallel to the nozzle axis, A represents the cross-sectional area at any point which is assumed to be circular and of radius r, M is the molecular weight, c_p is the heat capacity per mole at constant pressure, and T_R is defined as T/T_c where T_c represents the chamber temperature. Equation (4) has been derived on the assumptions that $v=0$ at $T=T_c$ and that c_p is constant.***

From Eq. (4) the following well-known relations can be derived:

$$(r_e/r)^2 = (T_R/T_{Re})^{1/(\gamma-1)}[(1-T_R)/(1-T_{Re})]^{\frac{1}{2}} \qquad (5)$$

[15] S. S. Penner and D. Altman, J. Franklin Inst. 245, 421 (1948).
*** The constancy of c_p and hence of γ is assumed in the present paper for the sake of simplicity. The replacement of an average γ for a given region by a variable γ which includes changes in internal energy states and chemical composition involves a second-order correction to the physical parameters discussed in this paper.

and

$$T_{Rt} = T_t/T_c = 2/(\gamma+1), \qquad (6)$$

where the subscripts e and t denote conditions at the nozzle exit and nozzle throat, respectively.

Calculations have been carried through to determine T_R as a function of r/r_e for a ratio of chamber pressure p_c to exit pressure p_e of 20:1 for gases with $\gamma=1.67$ and $\gamma=1.20$. The values of T_{Re} were calculated by use of the customary adiabatic relation

$$T_{Re} = T_e/T_c = (p_e/p_c)^{(\gamma-1)/\gamma}. \qquad (7)$$

Results are summarized by the plots of Fig. 1. It should be noted that the minimum value of $r/r_e = r_t/r_e$, corresponding to the nozzle throat, occurs at greater values of T_R for smaller γ in accord with Eq. (6). Also the value of $T_{Re} = T_e/T_c$ increases with decreasing γ according to Eq. (7). As the chamber entrance is approached where $T_R=1$, r/r_e increases without limit. This is the result of the assumption that $v=0$ at $T=T_c$, which was made in the derivation of Eq. (4).

III. REDUCED TEMPERATURE AS A FUNCTION OF AXIAL DISTANCE

Instead of expressing T_R as a function of r/r_e, it is possible to relate T_R to the linear distance from some arbitrarily chosen origin. It is convenient to choose the origin at the nozzle throat and to designate the direction toward the nozzle exit as the positive axis, as shown in Fig. 2. Conventional designs of rocket nozzles are
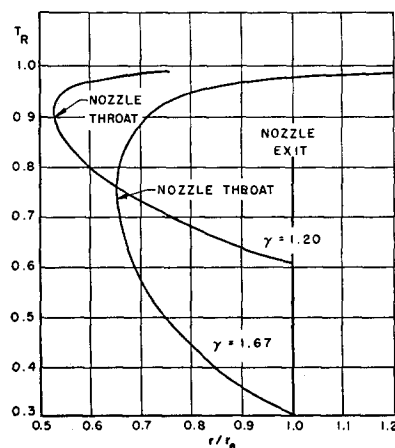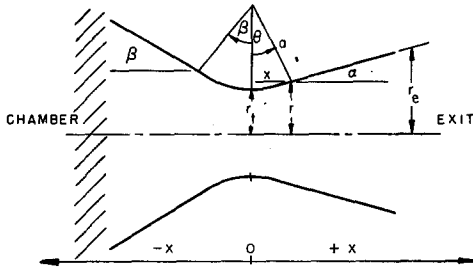

FIG. 1.

FIG. 2.

formed from two intersecting cones of half angles α and β. The throat region is rounded off with a radius of curvature a, which is frequently chosen as approximately equal to the throat diameter $2r_t$. In the present analysis, it will be assumed that $a = 2r_t$, $\alpha = 15°$, and $\beta = 30°$.

Reference to Fig. 2 shows that if r is the radius of an arbitrary point in the region of the throat and subtends an angle θ, the following relations follow from trigonometry:

$$\left.\begin{array}{l} r = (a+r_t) - a\cos\theta = r_t + a(1-\cos\theta), \\ dr = a\sin\theta d\theta, \\ x = a\sin\theta, \\ dx = a\cos\theta d\theta. \end{array}\right\} \quad (8)$$
Hence
$$dr = \tan\theta dx.$$

In general, it is evident that

$$dr = \tan\delta dx, \quad (9)$$

where

$$\tan\delta = \begin{cases} \tan\beta \text{ in the converging section} \\ \tan\theta \text{ in the throat region where the} \\ \qquad\qquad \text{nozzle contour is circular} \\ \tan\alpha \text{ in the expanding section.} \end{cases}$$

By combining Eqs. (4) and (9) and replacing dx by $a\cos\theta d\theta$, it is found that

$$\frac{d\theta}{dT_R} = \frac{r[\frac{1}{2}(1-T_R)^{-1} - (\gamma-1)^{-1}T_R^{-1}]}{2a\sin\theta}. \quad (10)$$

According to de l'Hospital's rule, the limit of $d\theta/dT_R$ as θ approaches zero is determined by differentiating the numerator and denominator of Eq. (10) with respect to T_R and taking the limit as θ approaches zero of the resulting fraction. This procedure can be shown to lead

to the relation

$$\lim_{\theta\to 0}\left(\frac{r_t}{2a}\right)\left[\frac{1}{2(1-T_{R_t})^2} + \frac{1}{(\gamma-1)T_{R_t}^2}\right]$$
$$= \frac{(\gamma+1)^3}{(\gamma-1)}\frac{r_t}{8a}, \quad (11)$$

where use has been made of Eq. (6). Since $r_t(\gamma+1)^3/8a(\gamma-1)^2$ is positive and finite, it follows that

$$\lim_{\theta\to 0}(d\theta/dT_R)$$

must also be positive and finite. Therefore,

$$\lim_{\theta\to 0}\frac{dx}{dT_R} = a\lim_{\theta\to 0}\frac{d\theta}{dT_R}$$
$$= \frac{1}{2}\left(\frac{\gamma+1}{\gamma-1}\right)\left(\frac{(\gamma-1)ar_t}{2}\right)^{\frac{1}{4}}. \quad (12)$$

It is interesting to note that as a approaches zero and the nozzle contour approaches that formed by the intersection of two cones, the reduced temperature gradient dT_R/dx approaches infinity at the throat.

IV. TIME SPENT BY AN ELEMENT OF GAS IN A GIVEN TEMPERATURE RANGE

The time dt spent by an element of gas in the reduced temperature range dT_R corresponding to the distance dx is $dt = dx/v$ where dx is always positive along the path of flow. Thus

$$dt/dT_R = (1/v)(dx/dT_R). \quad (13)$$

No correction has been made for the fact that the flow is not entirely parallel to the nozzle axis, since this correction is small for the chosen values of α and β.[1] Substituting Eqs. (3) and (10) with θ replaced in terms of x in Eq. (13) yields finally for the derivative of the residence time with respect to temperature

$$\frac{dt}{dT} = \frac{r(M/2c_pT_c^3)^{\frac{1}{2}}}{2\tan\delta}$$
$$\times\left[\frac{1}{2(1-T_R)^{\frac{1}{2}}} - \frac{1}{(\gamma-1)T_R(1-T_R)^{\frac{1}{2}}}\right]. \quad (14)$$

The value of dt/dT at the nozzle throat is

TABLE I. Derivative of residence time with respect to temperature for two types of gases.

| T_R | T (°K) | $(-dt/dT) \times 10^8$ (sec./°K) for two gases | |
		Predominantly helium ($\gamma=1.67$, $M=4$ g/mol)	Combustion gases of nitric acid-aniline motor ($\gamma=1.20$, $M=27$ g/mol)
0.99	2970	149	143
0.95	2850	7.94	14.2
0.909†	2727	—	7.12†
0.90	2700	3.35	6.18
0.85	2550	1.98	4.15
0.80	2400	1.25	4.65
0.750†	2250	0.95†	5.73
0.70	2100	0.90	6.97
0.65	1950	0.85	8.56
0.607††	1821	—	10.3††
0.60	1800	0.75	—
0.55	1650	0.95	—
0.50	1500	1.17	—
0.40	1200	1.76	—
0.302††	906	2.83††	—

† Denotes throat.
†† Denotes exit.

obtained from Eq. (14) by noting that $1-T_{Rt} = (\gamma-1)/(\gamma+1)$. The result is

$$\left(\frac{dt}{dT}\right)_t = \frac{1}{4}\left(\frac{\gamma+1}{\gamma-1}\right)^2 \left(\frac{(\gamma-1)Mar_t}{c_p T_c^3}\right)^{\frac{1}{2}}. \quad (15)$$

Equations (14) and (15) have been used to calculate the derivative of the residence time with respect to temperature dt/dT for two types of gases. A calculation has been made for a gas consisting predominantly of helium where $\gamma=1.67$ and $M=4$ g/mol, and another calculation has been made for a typical gas composition encountered in a nitric acid-aniline combination where $\gamma=1.20$ and $M=27$ g/mol. For both systems the following design parameters were assigned: $\alpha=15°$, $\beta=30°$, $T_c=3000°$K, $p_c/p_e = 20$, and $r_e=5$ cm. The results of these calculations are presented in Table I and shown graphically in Fig. 3.

Reference to Fig. 3 shows that the minimum values of $-dt/dT$ do not occur at the throat for a nozzle of the chosen contour but rather at the point of discontinuity in the expanding section of the nozzle where $\theta=15°$.

Data on the derivative of the residence time with respect to temperature as a function of temperature of the type shown in Fig. 3 may be combined with known values for reaction rates to determine the extent of changes in concentration which accompany flow through the nozzle.

In general, there is not enough information concerning reaction rates to allow more than qualitative estimates of the importance of changes of concentration resulting from chemical reaction occurring during flow through the nozzle at the high temperatures of interest in the present study. A useful method illustrating a procedure for calculating changes during flow through the nozzle is given in the following section for the decomposition of nitric oxide.

V. DECOMPOSITION OF NITRIC OXIDE DURING FLOW THROUGH A ROCKET NOZZLE

The rate constant k_f for the decomposition of nitric oxide according to the reaction

$$2NO \underset{k_b}{\overset{k_f}{\rightleftarrows}} N_2 + O_2 \quad (16)$$
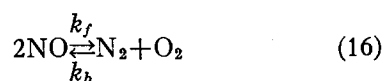
has been determined experimentally in the temperature range between 1500 and 2500°K under conditions approximating those existing in a rocket chamber and nozzle.[12,13,14] Although the reaction represented by Eq. (16) is probably not a homogeneous bimolecular gas reaction, the over-all process has been shown to be kinetically of second order.[12,13,14] Daniels and co-workers have calculated the rate constant for the decomposition of nitric oxide using the theory of absolute reaction rates and making the assumption that the decomposition of nitric oxide is a homogeneous bimolecular reaction.[12] The theoretical relation was found to be in good agreement with the experimental results obtained in a nitrogen fixation furnace after proper adjustment of the frequency factor. Daniels' rate constant will be employed in the following
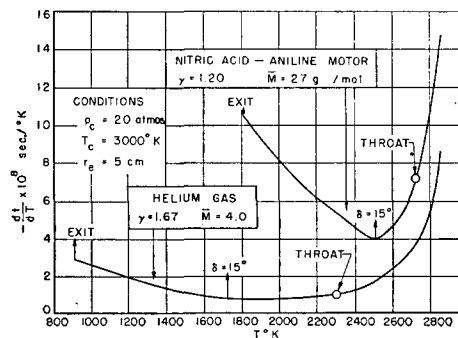

FIG. 3.

TABLE II. Equilibrium concentrations of NO, N_2, and O_2 in the rocket nozzle of a representative nitric acid-aniline motor.

T (°K)	$K_{eq} = n_{N_2}n_{O_2}/(n_{NO})^2$	n_{NO}	n_{N_2}	n_{O_2}
3000	66	0.0610	3.75	0.0655
2900	85	0.0552	3.75	0.0684
2800	110	0.0494	3.76	0.0713
2700	148	0.0436	3.76	0.0742

discussion in order to illustrate the method of application and also to predict approximately the approach to equilibrium of the NO decomposition reaction. Daniels' value for k_f is

$$k_f = 1 \times 10^9 \times [\exp(-70,000/RT)] \text{ atmos.}^{-1} \text{ sec.}^{-1}. \quad (17)$$

If p_{NO}, p_{O_2}, and p_{N_2} represent the partial pressures of nitric oxide, oxygen, and nitrogen, respectively, which are present at any time during the expansion through the nozzle, then the rate of change of the partial pressure of nitric oxide with time resulting from chemical reaction is

$$-dp_{NO}/dt = k_f p_{NO}^2 - (k_f/K_p)p_{O_2}p_{N_2}, \quad (18)$$

where the rate constant for the back reaction k_b has been replaced in terms of k_f and the equilibrium constant K_p is defined by the relation

$$K_p = p_{N_2}p_{O_2}/p_{NO}^2. \quad (19)$$

Although Eq. (18) should be used whenever calculations are carried out under conditions corresponding to a close approach to thermodynamic equilibrium, a simplification is justified when significant departures from thermodynamic equilibrium occur and the reformation of nitric oxide from oxygen and nitrogen can be neglected. In this case, Eq. (18) may be replaced by the

approximate relation

$$\Delta p_{NO}/\bar{p}_{NO} = \bar{k}_f \bar{p}_{NO}\langle -dt/dT \rangle \Delta T, \quad (20)$$

where Δp_{NO} is the change in nitric oxide concentration which occurs in a temperature interval ΔT in which $\bar{p}_{NO}$, $\bar{k}_f$, and $\langle -dt/dT \rangle$ represent average values. It may be noted that the ratio $\Delta p_{NO}/\bar{p}_{NO}$ evaluated in Eq. (20) is also equal to the fractional change in the number of moles of nitric oxide, $\Delta n_{NO}/\bar{n}_{NO}$. The ratio $\Delta n_{NO}/\bar{n}_{NO}$, however, changes only as a result of chemical reaction and therefore provides a direct measure of the composition change produced by chemical reaction. Because the reformation of nitric oxide has been neglected in Eq. (20), the calculated values of $\Delta n_{NO}/\bar{n}_{NO}$ provide an upper limit for the true value of the term $\Delta n_{NO}/\bar{n}_{NO}$ and can therefore be used for establishing a conservative temperature below which composition changes caused by chemical reaction are negligible.

In a representative rocket motor using nitric acid and aniline as propellants, the number of moles of the various gases formed at equilibrium at a pressure of 20 atmos. and a temperature of 3000°K are $n_{NO} = 0.0610$, $n_{N_2} = 3.75$, and $n_{O_2} = 0.0655$, while the partial pressure of nitric oxide is $p_{NO}^0 = 0.0610$ atmos. The equilibrium compositions at several other temperatures are summarized in Table II. These values were computed by use of the equilibrium constants given by Giauque and Clayton.[16] From the data listed in Table II it is possible to calculate the ratio $(\Delta n_{NO}/\bar{n}_{NO})_{equil.}$ for 100°K temperature intervals if thermodynamic equilibrium is maintained during expansion. The results of this calculation are contrasted in Table III with the actual changes produced by chemical reaction during flow, designated as $(\Delta n_{NO}/\bar{n}_{NO})_{kinetic}$, which were evaluated from Eq. (20). The average

TABLE III. Comparison between the kinetic and equilibrium values of $\Delta n_{NO}/\bar{n}_{NO}$.

$T_2 - T_1$ (°K)	$\bar{k}_f$ (atmos.$^{-1}$ sec.$^{-1}$)	$\bar{p}_{NO}$ (atmos.)	$\langle -dt/dT \rangle \times 10^3$ (sec. °K^{-1})	$(\Delta n_{NO}/\bar{n}_{NO})_{kinetic}$	$(\Delta n_{NO}/n_{NO})_{equil.}$
3000–2900	6.62×10^3	0.0531	52.6	0.01‡	0.0100
2900–2800	4.27×10^3	0.0400	14.2	0.0024	0.0111
2800–2700	2.76×10^3	0.0313	8.1	0.0007	0.0125

‡ The use of Eq. (20) in this temperature interval yields a value exceeding 0.01 since the back reaction has been neglected and the approach to equilibrium is very close. This value, therefore, was estimated from the complete Eq. (18).

[16] W. F. Giauque and J. O. Clayton, J. Am. Chem. Soc. 55, 4875 (1933).

value of the partial pressure of nitric oxide $\bar{p}_{NO}$ was calculated by taking into account the adiabatic change of state and a correction term for the extent of the chemical reaction by means of the equation

$$\bar{p}_{NO} = 0.0610(\bar{T}/3000)^{\gamma/(\gamma-1)} - \Delta p_{NO}\bar{T}, \quad (21)$$

where $\Delta p_{NO}\bar{T}$ equals the reduction of partial pressure resulting from chemical reaction and $\bar{T}$ is the average temperature in the interval.

Comparison of the last two columns of Table II shows that significant departures from equilibrium occur in the temperature interval between 2900 and 2800°K and that the equilibrium

$$2NO \rightleftharpoons N_2 + O_2$$
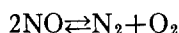
is practically frozen below about 2800°K.

A calculation similar to the one just described has also been carried out for a gas with $\gamma = 1.67$ and $\bar{M} = 4$ g/mol using the same initial concentrations of N_2, O_2, and NO. Again it was found that practically no composition changes occur below about 2800°K. This result is not surprising since the thermodynamic constants of a gas do not produce a significant change in the term $(-dt/dT)$ or in the rate of decomposition of nitric oxide. Reference to Eq. (14) shows that the design parameters which affect some control over the composition changes are r and δ. In general, however, it is not practical to design a nozzle so as to give either constant-composition or equilibrium flow since design parameters r and δ are of secondary importance when compared with the reaction rate constants.

In conclusion, it should be emphasized that the present analysis is concerned only with the decomposition of nitric oxide according to Eq. (16). If gases are present which react chemically with nitric oxide, then the over-all composition change should be analyzed in terms of the composition changes associated with each of the individual reactions.

The Kinetics of the Chromic Acid Oxidation of Isopropyl Alcohol: The Induced Oxidation of Manganous Ion

WARREN WATANABE AND F. H. WESTHEIMER
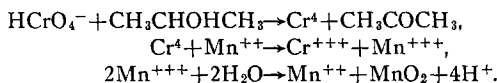*George Herbert Jones Laboratory, University of Chicago, Chicago, Illinois*
(Received July 23, 1948)

1. Isopropyl alcohol "induces" the chromic acid oxidation of manganous salts to MnO_2. The limiting induction factor (ratio of moles of MnO_2 to moles of acetone formed) is one-half.

2. In the presence of manganous ion the rate at which chromic acid is reduced by isopropyl alcohol is decreased; the maximum decrease in rate observed under a wide variety of experimental conditions is 50 percent.

3. These facts, together with the previously determined reaction kinetics, demand the formation of an intermediate chromium compound in which chromium has the valence four or five.

4. Within chemically reasonable limits, *all* the reaction mechanisms involving such transitory intermediates have been examined. In the presence of manganous salts the only possible mechanism is

$$HCrO_4^- + CH_3CHOHCH_3 \rightarrow Cr^4 + CH_3COCH_3,$$
$$Cr^4 + Mn^{++} \rightarrow Cr^{+++} + Mn^{+++},$$
$$2Mn^{+++} + 2H_2O \rightarrow Mn^{++} + MnO_2 + 4H^+.$$

In the absence of manganous salts several mechanisms (all of which are listed) are possible.

INTRODUCTION

IT has recently been shown[1] that, in the rate-controlling step of the chromic acid oxidation of isopropyl alcohol to acetone, one molecule of the alcohol reacts with one acid chromate ion and two hydrogen ions. In the over-all reaction, isopropyl alcohol undergoes a two electron oxidation; it follows, therefore, that the rate-deter-

[1] F. H. Westheimer and A. Novick, J. Chem. Phys. 11, 506 (1943).