Studies on the Chemical Equilibrium Lag during the Rapid Expansion through the Rocket Nozzle

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(Received on December 2, 1960)

The expansion process causes chemical reactions in the gas flowing through a rocket nozzle, since unstable molecules and atoms involved in the combustion product reassociate in the course of the temperature drop due to the expansion. However, when the gas expands through a nozzle in very short duration as in the case of a rocket engine, the rates of chemical reactions cannot maintain the chemical equilibrium of the system, and a relaxational phenomenon occurs; in other words, the composition of the gas reaches the chemical non-equilibrium state by way of the expansion process. The observation of such a relaxational process will give information concerning the fast chemical reaction kinetics at high temperature, and also give the descriptions of hypersonic flow with chemical reactions, since great energy changes due to chemical reactions affect the velocity of flowing gas or other parameters.

These problems occur in hypersonic flows or shock waves. First, Penner pointed out this problem in the case of a rocket engine[1], and Wegener determined the rate constant of $N_2O_4 \rightleftarrows 2NO_2$ using the hypersonic nozzle flow[2], but few experimental results have been available in a nozzle flow of a rocket engine.

The present author has constructed the automatic recording pyrometer having a short response time to observe the temperature of the nozzle exhaust gas of the JP4-nitric acid rocket, and has considered the chemical equilibrium during the rapid expansion through the *de Laval* nozzle.

Pyrometer*

In the case of the pyrometry of hypersonic gas flows, optical methods are more suitable than the methods using a thermocouple or pneumatic probe to avoid a inserting material's aerodynamic heating. The automatic recording pyrometer constructed here is a modified type of the Na D line reversal method and is similar to Heidmann or Millar's technique[3], which has been improved in regard to the accuracy of measurement in this apparatus.

The Na D line reversal method is based on the fact that the flame temperature and the brightness temperature of the source lamp are the same, when the flame containing sodium atoms has neither emission nor absorption of Na D line in reference to the background spectrum of the source lamp. In the present method, the intensity of absorption or emission of the gas was measured when the source lamp had a fixed brightness temperature, and the difference between the temperature of the gas and the source lamp was determined. The accuracy obtained in the pyrometer was ±10°K at 2000°K of the flame temperature, when the difference between the flame temperature and the brightness temperature of the lamp was 100°K. The temperature range observable by the pyrometer was from about 1500 to 3300°K,

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[1] D. Altman and S. S. Penner, *J. Chem. Phys.*, **17**, 56 (1949); S. S. Penner, ibid., **19**, 877 (1951).

[2] P. P. Wegener, ibid., **28**, 724 (1958); *Phys. Fluid*, **2**, 264 (1959).

* Presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

[3] M. F. Heidmann and R. J. Priem, *J. Am. Rocket Soc.*, **23**, 248 (1953); G. H. Millar, J. G. Winans, O. A. Uyehara and P. S. Myers, *J. Opt. Soc. Am.*, **43**, 609 (1953).

and the response time was 0.1 sec. More detailed descriptions on the pyrometer will be given in the other paper[4].

Results

The rocket test equipment was described in the other paper[5]. The temperature measurement of the exhaust gas was performed using the following propellant:

Oxidant	White fumic nitric acid with 0.3 wt.% of sodium nitrate	
Fuel	JP4	70 vol.%
	n-Butyl vinyl ether	30 vol.%

The above propellant reacted in the combustion chamber at 20 atm., and the gas produced in the chamber expanded to atmospheric pressure through the nozzle.

The exhaust gas emitted Na D line by the contamination of sodium nitrate in the oxidant, and this contamination scarcely affected the rocket performance or the flame temperature. The results are shown in Table I.

TABLE I. EXPERIMENTAL RESULTS

Exp. No.	14	19	21	
Chamber pressure	20.2	20.0	21.4	atm.
Thrust	101	100	100	kg.
Oxidant flow rate	406	405	404	g./sec.
Fuel flow rate	81	80	82	g./sec.
O/F*	5.0	5.1	4.9	
Specific impulse	207	206	206	sec.
Exhaust temperature	1870	1830	1829	°K

* Oxidant to Fuel wt. ratio

The pyrometry by the Na D line reversal method should be applied in the case of a non-luminous flame, and the exhaust gas of a rocket engine using a hydrocarbon fuel contains carbon particles, which may cause the observed reversal temperature to be different from the real temperature of the gas. The effective emissivity due to carbon particles involved in the gas was measured without contamination of sodium nitrate by the monochromator used here and was about 0.01∼0.02, which was much less than the emissivity due to sodium atoms (=0.1∼0.2). Therefore, the observed exhaust temperature has nearly the same value as the real exhaust temperature.

Discussion

Calculation of Theoretical Temperatures.—First, the temperature T_c and the composition of the gas in the combustion chamber are calculated by the assumption that the chemical equilibrium is attained in the combustion chamber at pressure P_c, and that the following enthalpy relation is held:

$$\sum_i (N_i^c/\overline{M}_c)\{H^0(T_c)-H_0^0+H_f\}_i = l\{H^0(298.16)-H_0^0+H_f\}_{\text{fuel}} + m\{H^0(298.16)-H_0^0+H_f\}_{\text{oxid}} - \Delta q_c \qquad (1)$$

where N_i^c is the mole fraction of component i of the product, and $\overline{M}_c$ is the mean molecular weight of the gas in the combustion chamber, and $\{H^0(T)-H_0^0+H_f\}_i$ is the total enthalpy of component i per mole[6], and l and m are the mole number of fuel and oxidant resoectively per unit mass of propellant, and Δq_c is heat loss in the combustion chamber per unit mass of the gas. Δq_c is assumed to be the same as Zucrow's experimental value[7]. The chemical equilibria considered here are the following seven equations:

$$\left.\begin{array}{l} H_2O \rightleftarrows OH+1/2\,H_2 \\ H_2O \rightleftarrows H_2+1/2\,O_2 \\ CO_2 \rightleftarrows CO+1/2\,O_2 \\ 1/2\,O_2 \rightleftarrows O \\ 1/2\,H_2 \rightleftarrows H \\ NO \rightleftarrows 1/2\,N_2+1/2\,O_2 \\ 1/2\,N_2 \rightleftarrows N \end{array}\right\} \qquad (2)$$

The calculation is carried out by the trial and error method using Huff et al.'s thermodynamic tables[8].

The expansion process through the rocket nozzle is assumed to be adiabatic, and the flow of the expanding gas is considered as a one-dimentional flow ignoring the diffusion or friction. Since the entropy of the gas per unit mass is constant during the expansion;

$$(1/\overline{M}_c)\sum_i\{N_i^c S_i(T_c)-\boldsymbol{R}\ln N_i^c P_c\} = (1/\overline{M}_e)\sum_i\{N_i^e S_i(T_e)-\boldsymbol{R}\ln N_i^e P_e\} \qquad (3)$$

where the suffixes c and e show the quantities of the gas in the combustion chamber and exhaust jet, respectively, and S_i is entropy per mole of i component of the gas. By this entropy relation, the temperature of the exhaust gas T_e can be calculated in the cases of both the frozen and shifting chemical equilibria during the nozzle expansion. In the former

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[4] S. Tsuchiya, *Aero. Res. Inst. Univ. Tokyo. Report*, No. 366 (1961).

[5] K. Kuratani, G. Onoue and S. Tsuchiya, *Collected Pap. Aero. Res. Inst. Univ. Tokyo*, (*Kôkû Kenkyûjo Shûhô*), **2**, 11 (1960).

[6] Heats of formation used here are the following: H_f(JP4) = −0.419 kcal./g., H_f(*n*-Butyl vinyl ether) = −48 kcal./mol., estimated by Pauling's method, H_f(Nitric acid) = −41.10 kcal./mol., at 298.16°K.

[7] M. J. Zucrow and C. M. Beighley, *J. Am. Rocket Soc.*, **22**, 323 (1952).

[8] V. N. Huff, S. Gordon and V. E. Morell, *NACA Rep.*, 1037 (1951).

case, the exhaust temperature T_e^{frozen} is calculated by the condition $N_i^c=N_i^e$, that is, the mole fractions of components of the gas are constant during the nozzle flow. In the latter case, however, the mole fractions vary according to the chemical equilibria in Eq. 2, which are shifting as the temperature of the gas is lowered during the expansion process; therefore $N_i^c \neq N_i^e$. The exhaust temperature T_e^{equil} has generally a higher value than T_e^{frozen} because the heat of reactions due to the shifting of the chemical equilibria is partly given to the expanded gas.

Since the nozzle expansion process is not strictly adiabatic, the entropy change Δs produced by heat loss at the nozzle should be considered;

$$\Delta s=\int dq_n/T \fallingdotseq q_n/T_t \qquad (4)$$

where q_n is heat loss at the nozzle per unit mass of the flowing gas, and T_t is the temperature of the gas at the throat of the nozzle. This approximation is based on the fact that the heat loss at the nozzle occurs mostly in the throat, and the value used here is Zucrow's data⁷⁾.

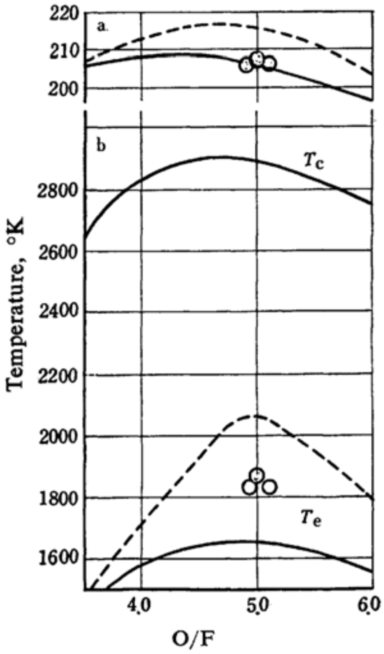

Fig. 1. Specific impulse (a) and temperature in the chamber and the exhaust (b), with correction due to heat loss in the chamber 0.05 kcal./cm²·sec., and in the nozzle 0.084 kcal./cm²·sec.;

○ : experimental value,
—— and ----: with chemical equilibria frozen and shifting, respectively.

The velocity of the exhaust gas or specific impulse I_{sp} is obtained from the enthalpy decrease of the gas due to the expansion.

$$(1/2)v_e^2=(1/\overline{M}_c)\sum_i N_i^c\{H^0(T_c)-H_0^0+H_f\}_i - (1/\overline{M}_e)\sum_i N_i^e\{H^0(T_e)-H_0^0+H_f\}_i \qquad (5)$$

$$I_{sp}=v_e/g \qquad (6)$$

The results of calculations are given in Fig. 1 by the method above mentioned, and the equilibrium compositions of the gas in the chamber and exhaust are also given in Table II.

TABLE II. EQUILIBRIUM MOLE FRACTIONS (O/F=5.0)

	in chamber T_c=2890°K P_c=20 atm.	in exhaust T_e=2070°K P_e=1 atm.
CO_2	0.23546	0.30655
CO	0.06743	0.01062
H_2O	0.43881	0.48706
H_2	0.01750	0.00338
O_2	0.03096	0.00492
NO	0.00772	0.00072
N_2	0.17260	0.18441
OH	0.02296	0.00211
H	0.00328	0.00015
N	0.00008	0.00000
O	0.00320	0.00009

Relaxation of Chemical Equilibrium.—By comparison of the observed exhaust temperatures T_e^{obs} with the calculated values, T_e^{obs} is lower than T_e^{equil} and higher than T_e^{frozen}. This fact shows that the chemical equilibria may be neither shifting nor frozen during the actual expansion through the nozzle, and that the relaxation of the chemical equilibrium occurs during the expansion process. Since the velocity of the gas reaches 1×10^5 cm./sec. at the nozzle throat and the length of the divergent part of the nozzle used here is 7 cm., the time for the gas to pass the nozzle is of the order of 10^{-5} sec. It is considered, therefore, that the rates of the chemical reactions can not maintain the equilibrium in this short time. To analyze the situations of the chemical equilibrium during the expansion, it must be necessary that the hypersonic flow through the *de Laval* nozzle be treated taking the chemical reactions into account besides the flow descriptions⁹⁾. This treatment is very difficult in the

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9) The relaxational phenomenon on the internal energy states as well as the chemical equilibria must be considered here, but the relaxation time of internal energy may be much smaller than that of the chemical reaction, and the internal energy states scarcely deviate from equilibrium in the nozzle flow discussed here.

present nozzle flow, since the chemical reactions Eq. 2, which should occur during the expansion, are very complicated. Therefore, the approximate analysis is adopted here.

Approximate Treatment of Chemically Relaxed Flow.—Here, $-(\mathrm{d}t/\mathrm{d}T)$ is considered as the parameter showing whether the composition of the expanding gas has chemical equilibrium or non-equilibrium; $-(\mathrm{d}t/\mathrm{d}T)$ equals a time to change the temperature of the gas 1°K, and when $-(\mathrm{d}t/\mathrm{d}T)$ has a smaller value, the chemical equilibrium tends to be relaxed[1]. To derive the value of $-(\mathrm{d}t/\mathrm{d}T)$, the temperature, pressure and velocity of the expanding gas are calculated in relation to the coordinate taken in the direction of the nozzle axis. The calculation is based on the following fundamental equations:

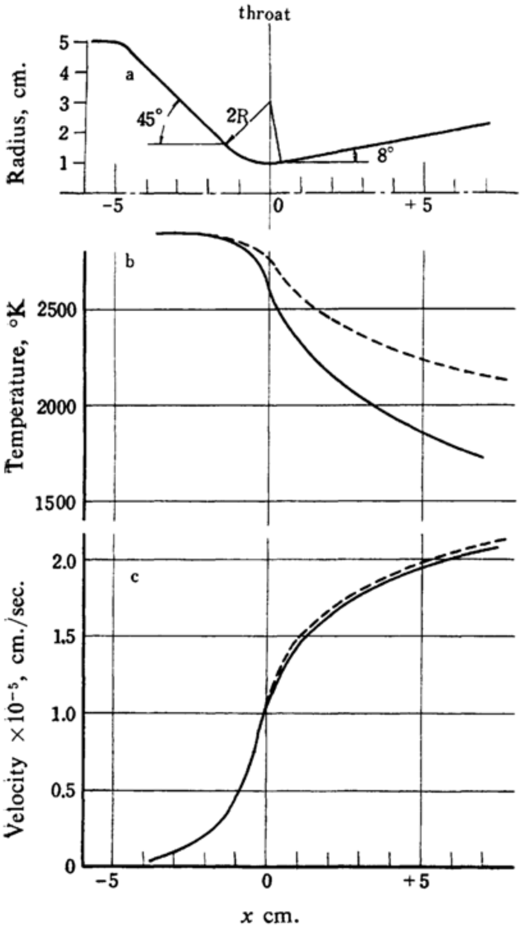

Fig. 2. Section of the nozzle parallel to the nozzle axis (a), and temperature (b) and velocity (c) profiles during the expansion process at O/F=5.0, without correction due to heat loss in the nozzle;

—— and ----: with chemical equilibria frozen and shifting, respectively.

$$\left.\begin{array}{rl} (\mathrm{d}\rho/\rho)+(\mathrm{d}v/v)+(\mathrm{d}A/A)=0 & \\ & \text{conservation of mass} \\ v\mathrm{d}v+\mathrm{d}h=0 & \text{conservation of energy} \\ \mathrm{d}s=0 & \text{isentropic relation} \\ P=(R/\overline{M})\rho T & \text{equation of state} \end{array}\right\} \quad (7)$$

where ρ is the density of the gas, v velocity of the gas, A area of the nozzle section, h enthalpy per unit mass of the gas. In the case of chemical equilibrium flow, the equations of chemical equilibria must be added to the above fundamental equations. The results are shown in Fig. 2, where the section of the *de Laval* nozzle used in this experiment is also shown. From the calculated temperature and velocity profile through the nozzle, $-(\mathrm{d}t/\mathrm{d}T)$ can be easily derived, and relations of $-(\mathrm{d}t/\mathrm{d}T)$ and the temperature of the gas are given in Fig. 3 in the cases of both frozen and equilibrium flow. At the divergent part of the nozzle, the order of $-(\mathrm{d}t/\mathrm{d}T)$ is 10^{-8} sec./deg., and is of much greater value near the combustion chamber. It is, therefore, probable that the nozzle flow of the gas may have chemical equilibrium near the throat of the nozzle and the relaxational phenomenon may occur after the gas passes the throat.

Then, the chemically relaxed flow of the gas can be treated by the following approximation: the combustion product in the chamber at pressure P_c expands to a pressure P^* and a

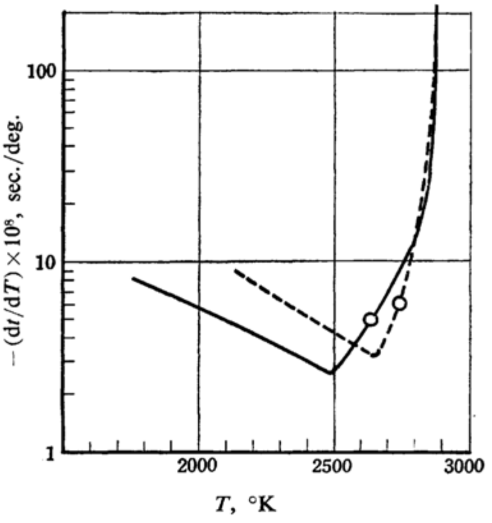

Fig. 3. Calculated curve of $-(\mathrm{d}t/\mathrm{d}T)$ during expansion through the nozzle in relation to the temperature of the gas at O/F=5.0, without correction due to heat loss in the nozzle;

○ : value of $-(\mathrm{d}t/\mathrm{d}T)$ at the throat,
—— and ----: with chemical equilibria frozen and shifting, respectively.

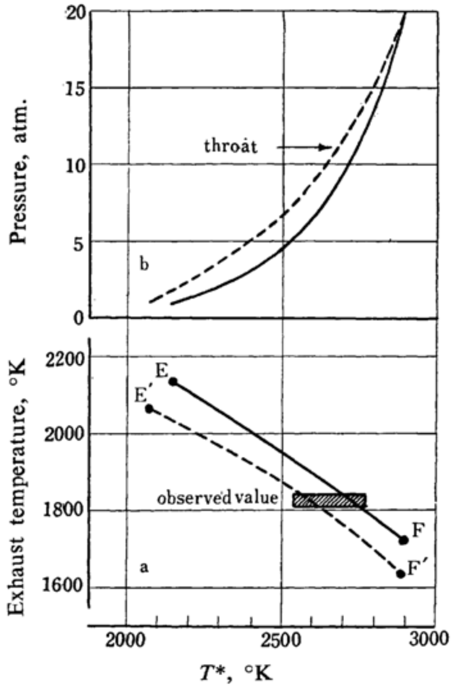

Fig. 4. Calculated exhaust temperature by 'suddenly frozen' approximation (a) and pressure of the gas (b) against T^* at O/F=5.0;

—— and ----: without and with correction due to heat loss in the nozzle, respectively. Points F and E in curve (a) correspond to the exhaust temperatures with chemical equilibria frozen and shifting, respectively.

temperature T^* with the chemical equilibria shifting, and from a pressure P^* to the exhaust pressure P_e with the chemical equilibria frozen. This approximation means:

$$\text{at } T > T^* \text{ and } P > P^*, \quad -(\mathrm{d}t/\mathrm{d}T) = \infty,$$
$$\text{at } T < T^* \text{ and } P < P^*, \quad -(\mathrm{d}t/\mathrm{d}T) = 0,$$

in other words, the expansion through the nozzle proceeds from P_c to P^* at infinitely low speed and from P^* to P_e at infinitely high speed. Recently, the author has treated the expansion process of hydrogen gas with recombining reaction of hydrogen atoms more strictly, and ascertained that the above approximation gives nearly the right illustration of the flow through the *de Laval* nozzle[10]. The foundation of this approximation is that the relaxational process ends in a very short time after the composition of the gas deviates from an equilibrium state, and that the chemical equilibria of the system are instantly frozen. In general, the relaxation of the chemical equilibrium increases the entropy of the system[11]. However, this entropy increase may be small owing to the shortness of the relaxational process, and the isentropic condition may be assumed. The same situations about the flow of diatomic gases through the *de Laval* nozzle have been considered also by Bray and by Hall and Russo[12].

The calculated results by this 'suddenly frozen' approximation are shown in Fig. 4. The pressure P^* and the temperature T^* at which the relaxation of chemical equilibrium occurs in the present nozzle flow, can be determined by a comparison of the observed exhaust temperature T_e^{obs} and the exhaust temperature T_e^{sf} calculated by the 'suddenly frozen' approximation. T_e^{obs} agrees T_e^{sf} at $T^* \fallingdotseq 2600°\mathrm{K}$ and $P^* \fallingdotseq 10$ atm. This means that the chemical equilibrium may be relaxed near about 2600°K and 10 atm. during the expansion. The position, where the temperature and pressure of the gas reach the obtained T^* and P^*, is slightly outside the throat of the nozzle. The $-(\mathrm{d}t/\mathrm{d}T)$ at this position is about 5×10^{-8} sec./deg., and the relaxation is estimated to occur at $-(\mathrm{d}t/\mathrm{d}T)^* = 3\sim8\times10^{-8}$ sec./deg.

The obtained limiting value of $-(\mathrm{d}t/\mathrm{d}T)$ for keeping the chemical equilibrium of the system can be related to the chemical reaction rate, but the kinetic mechanism is too complicated to analyze the present expansion through the nozzle, in which the recombination of atoms and the oxidation of carbon monoxide or hydrogen may be the main reactions, as Table II shows. Altman and Carter say that $-(\mathrm{d}t/\mathrm{d}T)$ ranges from about 7 to 3×10^{-7} sec./deg. at a divergent part of a nozzle in a rocket having a large thrust like the V-2, since $-(\mathrm{d}t/\mathrm{d}T)$ is approximately proportional to a square root of thrust. Considering the atomic recombining reaction rate, they estimate that the expansion through such a nozzle proceeds with the chemical equilibria shifting[13]. This estimation is consistent with the present experiment.

If a more simple system is treated, the rapid expansion through the *de Laval* nozzle can be used as a new technique for the measurement of fast reaction rate at high temperature.

Summary

The pyrometer fitted for the temperature measurement of exhaust gas of the rocket, was constructed, and the exhaust temperature of

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[10] S. Tsuchiya, to be published.

[11] W. W. Wood and J. G. Kirkwood, *J. Applied Phys.*, **28**, 395 (1957).

[12] K. N. C. Bray, *J. Fluid Mech.*, **6**, 1 (1959); J. G. Hall and A. L. Russo, *Cornell Aero. Lab. AFOSR TN* 59-1090 (1959).

[13] D. Altman and J. M. Carter, "Combustion Process", Ed. by B. Lewis, R. N. Pease and H. S. Taylor, Princeton Univ. Press, Princeton (1956), p. 51.

the JP4-nitric acid rocket having 100 kg. of thrust, was observed. From the obtained exhaust temperature, it has been ascertained that the expansion of the gas through the present nozzle proceeds with chemical equilibria neither shifting nor frozen, and that relaxation occurs. From the approximate analysis of chemically relaxed flow, the relaxational process is assumed to occur at $-(dt/dT)^* = 3 \sim 8 \times 10^{-8}$ sec./deg., $T^* \fallingdotseq 2600°\mathrm{K}$ and $P^* \fallingdotseq 10$ atm.

The author wishes to express his sincere thanks to Assistant Professor K. Kuratani for his kind encouragement throughout this work. His thanks are also expressed to Mr. G. Onoue for his help in constructing the apparatus.

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