TEMPERATURE MEASUREMENT OF REFLECTED SHOCK WAVE BY USING CHEMICAL INDICATOR*

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ABSTRACT: This report describes a new method for measuring the temperature of the gas behind the reflected shock wave in shock tube, corresponding to the reservoir temperature of a shock tunnel, based on the chemical reaction of small amount of CF_4 premixed in the test gas. The final product C_2F_4 is used as the temperature indicator, which is sampled and detected by a gas chromatography in the experiment. The detected concentration of C_2F_4 is correlated to the temperature of the reflected shock wave with the initial pressure P_1 and test time τ as parameters in the temperature range $3\,300\,K < T < 5\,600\,K$, pressure range $5\,kPa < P_1 < 12\,kPa$ and $\tau \simeq 0.4\,ms$.

KEY WORDS: temperature measurement, shock tube, chemical reaction, temperature indicator, tetrafluoromethane

1 INTRODUCTION

Most of the shock tunnels are operated in the reflected mode, i.e. the test gas behind the reflected shock in the driven section is used as the nozzle reservoir of the tunnel. The thermodynamic state of the reservoir gas is derived from the ideal shock theory and the measurements of the initial pressure and incident shock wave velocity. However, it is known that the non-ideal behavior in the gas flow behind the shock wave is accompanied by growth of boundary layer caused by viscosity which reveals that the state parameters are in significant deviation from these calculated ideal thermodynamic quintities[1]. The deviation may become serious as the shock tunnel is operated at high parameter region. It can be neither neglected nor theoretically corrected. Therefore, the direct measurement of the temperature of the reservoir gas behind the reflected shock wave is very important.

In this paper we put forward a new method of measuring the temperature of the reservoir gas in a shock tube based on the principle of comparative rate method originated in Tsang's study[2] on chemical shock tube. The essence of this method is to define a temperature scale by the measurement of the extent of the well known chemical reactions of a standard reactant which is premixed in the test gas. The reactant with this function will be called "temperature indicator" in this paper. However, most of the recommended

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reagents can not be used in determining the temperature scale for the present purpose, because all of these recommended reagents can only be used as temperature indicator in a range of temperature from $1\,000\,K$ to $2\,000\,K$, which is much lower than the temparature range operated in most shock tunnels, $3\,000\,K$ to $6\,000\,K$. Therefore, we should select a new temperature indicator and examine what fundamental base shall we use to get the temperature scale.

In this paper, we select the perfluoromethane CF_4 as the temperature indicator and examine how the final products of this reactant after shock heating and consequent rarefaction cooling will correlate with the temperature of the reservoir gas behind the reflected shock wave. The correlation will lay the foundation for developing a technique of temperature measurement in shock tube. Moreover, we are going to interpret this correlation between the extent of the reactions and the temperature of the reflected shock wave from the view point of the chemical kinectics which gives a theoretical explanation to the experimental temperature scale and establishes a base for accurate measurement of the temperature.

The dependence of the running parameters of shock tube in the correlation is also experimentally investigated for the purpose of practical application.

2 EXPERIMENTAL

The experiment is carried out in a single pulse shock tube with a 1.2 m driver section, 1.8 m driven section with internal diameter 44 mm[3,4]. A 20L dump tank is mounted to the driven section near the diaphragm through a T tube. The data of shock velocity, detected by transducers mounted on the shock tube wall, is adopted by A/D converter and processed by a PC computer. The test time of the high temperature gas behind the reflected shock waves ranging from $320\,\mu s$ to $340\,\mu s$ is determined by a transducer mounted at the end wall of the shock tube. The test gas is 99.99% pure argon premixed with 0.10% perfluoromethane CF_4 as the reactant. Its purity 99.7% is analysed by gaschromatography. The shock tube is preheated to $80°C \sim 100°C$ to avoid the absorption of any organic material on the wall. The driver gas is commercial hydrogen. In the final products three kinds of chemicals, including C_2F_2, C_2F_4 and some kind of fluorocarbon molecule with four carbon atoms, are found. However, the amount of C_2F_4 is the dominant one. Therefore, the concentration ratio of the final product $[C_2F_4]$ and the initial reactant $[CF_4]$ is selected as the characteristic quantity to determine the temperature scale. The analysis of the experiments shows that the functional relation of the ratio $[C_2F_4]/[CF_4]_0$ versus the temperature of the reflected shock wave is coincident with the Arrhenius plot and the ratio varies with the initial pressure P_1 as second power function. Collecting all the experimental data at three different initial pressures with different shock speeds, we can correlate them into a unified Arrhenius relation, which can be plotted as $\log\left[\left(\dfrac{\tau(\mathrm{ms})}{1\mathrm{ms}}\right)^{-1}\left(\dfrac{P_1(\mathrm{kPa})}{10(\mathrm{kPa})}\right)^{-2}\left(\dfrac{[C_2F_4]}{[CF_4]_0}\right)\right]$ against the reciprocal of the temperature of the reflected shock, as shown in Fig.1. The smoothed analytical expression of the result is shown as

$$\lg\left[\left(\frac{\tau(\mathrm{ms})}{1\mathrm{ms}}\right)^{-1}\left(\frac{P_1(\mathrm{kPa})}{10\mathrm{kPa}}\right)^{-2}\left(\frac{[C_2F_4]}{[CF_4]_0}\right)\right] = 2.36 - 1.38 \times 10^4 T^{-1}$$

$$(3\,300K < T < 5\,600K) \qquad (2.1)$$

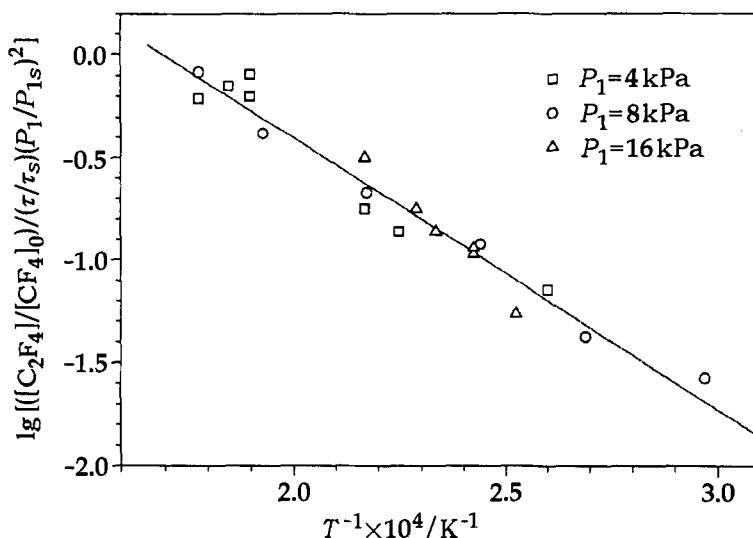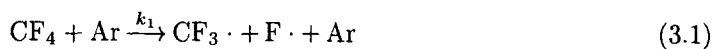This is the experience temperature scale we have found.

Fig.1 Correlation curve of relative concentration of product C_2F_4 from pyrolysis of
CF$_4$ vs reciprocal temperature

3 DISCUSSION

The expression of (2.1) is an experimental temperature scale. It can be used to determine the temperature by detecting the concentration of C_2F_4 in shock tube experiment. However, the temperature scale is demarcated by using shock speed measurement and the theory of ideal shock tube flow, so it can not be acknowledged as a more accurate scale than the common used one. The importance of the (2.1) is that the existence of the correlation between the products concentration and temperature with the associated running parameters P_1 and τ, as the parameters have been proven. The next step we have to take is to find out the internal reaction mechanism and give the temperature scale a quantitative interpretation by reaction chemical kinetics. Then the temperature scale becomes an accurate basis on the well known kinetic parameters of the temperature indicators.

In shock tube, CF$_4$ will undergo a shock heating and a consequent rarefaction gasdynamic cooling processes. In shock heating process, the dominated reaction is pyrolysis of CF$_4$, that is

$$CF_4 + Ar \xrightarrow{k_1} CF_3 \cdot + F \cdot + Ar \qquad (3.1)$$

and

$$CF_3 \cdot + Ar \xrightarrow{k_2} CF_2 : + F \cdot + Ar \qquad (3.2)$$

we have known CF$_4$ is one of the most stable organic molecules which keeps in gas phase at room temperature. The activation energy of reaction (3.1) is as high as 131 kcal·mole^{-1}. However, the activation energy of reaction (3.2) is only 86 kcal· mol^{-1}. So the reaction speed of (3.2) is much faster than that of reaction (3.1). The combination of the reaction (3.1) and (3.2) can be considered as the direct pyrolysis of CF$_4$ into CF$_2$ and two fluorine atoms with rate of (3.1) as the control step. Further, pyrolysis of CF$_2$ will be neglected due to its high activation energy and low activation entropy. After the reflected shock heating period τ, the concentration [CF$_2$] for radical CF$_2$ and [F] for F atom can be determined by

rate equations. Their solutions are

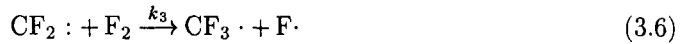$$\frac{[CF_2]}{[CF_4]_0} = 1 - \exp(-k_1[Ar]_5\tau) \cong k_1[Ar]_5\tau \tag{3.3}$$

where subscript 5 refers to the state of reflected shock wave and subscript 0 refers to the original concentration at the same state, and

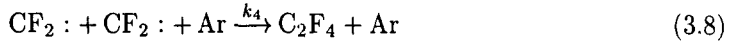$$\frac{[F]}{[CF_4]_0} = 2\frac{[CF_2]}{[CF_4]_0} \tag{3.4}$$

In the cooling period, the fastest reaction is the recombination of F atoms

$$F \cdot + F \cdot + Ar \longrightarrow F_2 + Ar \tag{3.5}$$

The consequent reactions are

$$CF_2 : + F_2 \xrightarrow{k_3} CF_3 \cdot + F \cdot \tag{3.6}$$

$$CF_3 \cdot + F_2 \xrightarrow{fast} CF_4 + F \cdot \tag{3.7}$$

and the recombination reaction

$$CF_2 : + CF_2 : + Ar \xrightarrow{k_4} C_2F_4 + Ar \tag{3.8}$$

We can see that the abstraction reaction of CF_2: with F_2 lead to the recover of the reactant CF_4. However, a competitive channel, the recombination of two CF_2: radicals with a third body Ar atom (3.8) will lead to a new product C_2F_4. That is what we have observed in the experiments.

After the cooling period some of the high temperature pyrolysis product CF_2: returns to CF_4 through (3.6) and others turn to C_2F_4 by reaction of (3.8). The branching ratio $r \equiv [C_2F_4]/[CF_2]$ can be expressed as the rate ratio of reaction (3.8) and (3.6), that is

$$r = k_4[Ar]_1(\rho_6/\rho_1)k_3^{-1} \tag{3.9}$$

where ρ_6 is the gas density after the rarefaction cooling. ρ_6 is proportional to the initial density ρ_1 and the ratio ρ_6/ρ_1 is nearly independent of shock Mach number (see appendix A). From (3.9) and (3.3), we have

$$\frac{[C_2F_4]}{[CF_4]_0} = k_1k_4k_3^{-1}[Ar]_1^2(\rho_5/\rho_1)(\rho_6/\rho_1)\tau \tag{3.10}$$

where $[Ar]_1$ is the initial mole density of argon. By introducing a reference standard state P_{1s}, its corresponding reference mole density of argon $[Ar]_{1s}$ and a reference test time τ_s, (3.10) can be expressed as

$$\left(\frac{\tau}{\tau_s}\right)^{-1}\left(\frac{P_1}{P_{1s}}\right)^{-2}\left(\frac{[C_2F_4]}{[CF_4]_0}\right) = [Ar]_{1s}^2\tau_s\frac{k_1k_4}{k_3}\frac{\rho_5}{\rho_1}\frac{\rho_6}{\rho_1} \tag{3.11}$$

If we select $P_{1s} = 10\,kPa$ and $\tau_s = 1\,ms$, the left side of (3.11) is coincident with (2.1). However, the right side of (3.11) consists of some chemical reaction rate constants. It should

be interesting to make a direct comparison between the chemical kinetic predicted scale and the experimental scale (2.1).

In the right side of Eq.(3.11), the values of ρ_5/ρ_1 and ρ_6/ρ_1 depend on running conditions of shock tube, as shown in Appendix A. They can be directly calculated and their values are nearly independent of what the temperatures have been reached. The branching ratio r is also independent of temperature, because k_3 and k_4 are some recombination rate constants, which usually do not rely on temperature. The only temperature dependent quantity in right side of (3.11) is the rate constant k_1. We have calculated the expression of k_1 by using Troe's theory[5] based on the molecular parameters of CF_4, as shown in Appendix B, and the following result is obtained.

$$k_1 = 4.7 \times 10^{41} T^{-7.5} \exp(-54\,800/RT) \mathrm{cm}^3 \cdot \mathrm{mol}^{-1} \cdot \mathrm{s}^{-1} \tag{3.12}$$

Substituting the values of $r = 0.10, \rho_5/\rho_1 = 7.9$, $\rho_6/\rho_1 = 5.0$, $\tau_s = 1 \times 10^{-3}$s, $[\mathrm{Ar}]_{1s} = 3.8 \times 10^{-6}$mol·cm^{-3} and the expression (3.12) of k_1 into Eq.(3.11), then we have

$$\left(\frac{\tau}{\tau_s}\right)^{-1} \left(\frac{P_1}{P_{1s}}\right)^{-2} \frac{[C_2F_4]}{[CF_4]_0} = 1.4 \times 10^{33} \cdot T^{-7.5} \exp(-131\,000/RT) \tag{3.13}$$

(3.13) is the chemical kinetic temperature scale we have suggested in the present paper. The comparison with the experimental result is shown in Fig.1. We will emphasize that the slope of the experimental Arrhenius plot is in agreement with the apparent activation energy predicted by kinetic theory, which is important to make sure of the validity of the temperature measurement by the present method. The mean deviation of the measured temperature by using this method is estimated as 2%.

4 CONCLUSION

A method for measuring the temperature of the reflected shock in shock tube and shock tunnel based on chemical reactions is put forward. By taking advantage of the peculiarity of the high activation energy of the pyrolysis of CF_4 and utilizing the product C_2F_4 as a temperature indicator, a temperature scale has been experimentally determined. This result has also been interpreted by reaction kinetics, and a theoretical temperature scale based on molecular characters is given. In the expression of the temperature scale, the associated running parameters and facility characteristics of shock tube are included for convenience in practical applications.

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Appendix A: The termination state of the isoentropic cooling of the shock heated gas

During the running of the shock tube, the test gas argon undergoes a reflected shock heating and a consequent rarefaction cooling. The cooling process is an isoentropic change which will sustain for a few ms and finally reach a mechanically equillibrium state, a uniform pressure P_6. The volumes of the driver section, driven section and dump tank are V_4, V_1 and V_d and initial pressures are P_4, P_1 and P_1 respectively. After the diaphragm is broken, the hydrogen gas originally stored in the driver section will undergo an isoentropic change, if we assume the penetrated reflected shock is weak, and the driven gas will be compressed by shock to the state 5, then isoentropically rarefacted to the final state P_6. Therefore we have

$$P_5[(\rho_1/\rho_5)V_1]^{\gamma_1} = P_6 V_1'^{\gamma_1} \tag{A.1}$$

$$P_1 V_d^{\gamma_1} = P_6 V_d'^{\gamma_1} \tag{A.2}$$

$$P_4 V_4^{\gamma_4} = P_6(V_d - V_d' + V_1 - V_1' + V_4)^{\gamma_4} \tag{A.3}$$

where the supperscript "$'$" denotes the final state and the subscripts denote where the gases originally stored, γ is the ratio of specific heat $\gamma_4 = 1.40$, $\gamma_1 = 1.667$. By introducing the reduced quantities $P_{61} = P_6/P_1$, $P_{51} = P_5/P_1$, $P_{41} = P_4/P_1$, $V_{4d} = V_4/V_d$, $V_{5d} = V_5/V_d$, and $\rho_{51} = \rho_5/\rho_1$, we can get the solution

$$P_{61} = P_{41}[V_{4d}/(1 - P_{61}^{-1/\gamma} + V_{1d}(1 - P_{61}^{-1/\gamma} P_{51}^{1/\gamma}\rho_{51}) + V_{4d})]^{\gamma_4} \tag{A.4}$$

Considering V_{1d} is a small quantity, we can put $P_{51}^{1/\gamma}\rho_{51} \simeq 1$ in (A.4) without making serious error. Then we have

$$P_{61} = P_{41}[V_{4d}/(1 - P_{61}^{-1/\gamma})(1 + V_{1d})]^{\gamma_4} \tag{A.5}$$

For the present work, the shock tube parameters are $V_d = 20\,\mathrm{L}$, $V_4 = 1.5\,\mathrm{L}$, $V_1 = 2.2\,\mathrm{L}$, $V_{1d} = 0.11$ and $V_{4d} = 0.075$, and the running parameters P_{41} range from 50 to 90, the termination state P_{61}, ρ_{61}, and ρ_{51} are listed in table A.1. We can see that ρ_{51} and ρ_{61} are nearly independent of the shock Mach number Ms as we expected in the discussion of the Eq.(3.11).

Table A.1 The initiation and termination state in shock tube

M_s	$T_1(\mathrm{K})$	$T_5(\mathrm{K})$	P_{41}	P_{61}	ρ_{61}	ρ_{51}	$\bar{\rho}_{51}$	$\bar{\rho}_{61}$
3.5	350	3300	50	3.2	4.8	7.6	7.9	5.0
4.5	350	5400	90	4.2	5.2	8.2	7.9	5.0

Appendix B: The rate constant of the pyrolysis of tetrafluoromethane

The theoretical expression of the rate constant of reaction (3.1) is given by Troe[5] as

$$k_1 = Z_{\mathrm{LJ}}\rho(E_0)RTQ_v \exp(-E_0/RT)\beta \tag{B.1}$$

where Z_{LJ} is the factor of collision frequency, $\rho(E_0)$ is the density of the vibrational energy levels at the energy threshold E_0 of molecule CF_4, Q_v is the vibrational partition function, R is the gas constant and β is weak collision efficiency. Z_{LJ} can be directly written down as

$$Z_{\mathrm{LJ}} = N_{\mathrm{AV}}\sigma^2\sqrt{8RT/\pi\mu}\,\Omega^{(2.2)}(T/T^*) \tag{B.2}$$

where N_{AV} is Avogadro number, σ is the collision diameter in Linnard-Jones potential between CF_4 and Ar, μ is the reduced molar weight, $T^* = \varepsilon/R$ is the characteristic temperature related to the

Linnard-Jones potential parameter ε, and $\Omega^{(2.2)}$ is the collision integral. For the collision between CF_4 and Ar, we take $\sigma = 4.1\text{Å}$[6], $\mu = 27.5\text{g} \cdot \text{mol}^{-1}, T^* = 134\,\text{K}$[6], and $\Omega^{(2.2)} = 0.69$[6]. Then we have

$$Z_{LJ} = 1.9 \times 10^{12} T^{1/2} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \tag{B.3}$$

$\rho(E_0)$ can be calculated by using the Whitten-Robinovich approximation

$$\rho(E_0) = \frac{E_0^{s-1}}{(s-1)! \prod\limits_{j=1}^{s} hc\omega_i} \tag{B.4}$$

where we have omitted the contribution of the zero point vibration of the molecule and treated the vibration as harmonic oscillator; $S = 9$ is the total number of the vibration mode of CF_4[7]; $E_0 = 548\,\text{kJ·mol}^{-1}$ is the dissociation energy for reaction (3.1); ω_i is the wave number of the i-th vibration mode, which have the values of 908^1, 435^2, 1283^3, 631^3 in cm^{-1}, where the indexes on the supperscripts denote the degree of degeneration of the mode. The calculated result of (B.4) is

$$\rho(E_0) = 4.4 \times 10^5 \text{mol} \cdot \text{J}^{-1} \tag{B.5}$$

The vibrational partition function Q_v can be expressed in harmonic oscillator model as

$$Q_v^{-1} = \prod_i^s [1 - \exp(-hc\omega_i/KT)] \tag{B.6}$$

Fitting the result of numerical calculation of (B.6) at temperature range $3\,300\,\text{K}$ to $5\,600\,\text{K}$ with a power function of T, we get the following approximation

$$Q_v^{-1} = 7.0 \times 10^{26} T^{-9} \tag{B.7}$$

The factor of weak collision efficiency as given by Troe[5] can be expressed as

$$\beta = \left(\frac{\Delta E}{F_E RT}\right)^2 \tag{B.8}$$

where F_E is the energy dependent factor and ΔE is the energy step size down. At $4\,000\,\text{K}$, the $F_E \simeq 3$ and $\Delta E \simeq 150\,\text{cm}^{-1}$ is estimated, and the corresponding value of β is derived as $\beta = 1 \times 10^{-4}$. According to the parameters of molecule CF_4 we adopted above, the final expression of k_1 has been determined as

$$k_1 = 4.8 \times 10^{40} T^{-7.5} \exp(-548\,000/RT)\,\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \tag{B.9}$$

The k_1 depends upon temperature through two factors, the power function $T^{-7.5}$ and the exponential function with activation energy $548\,\text{kJ·mol}^{-1}$. These expressions are determined in the framework of the well defined kinetic theory. In fact, we have noticed the dependence of temperature is in agreement with the experiments. However, the rigorous theory for determing the weak collision efficiency is lacking. At present, we have to depend on the experience, in which experimental studies are needed.