

Time-Temperature Simulation in Low-Pressure Ignition of Hypergolic Liquids

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Theme

THIS work is concerned with the ignition of hypergolic liquids at various pressures, and attempts to simulate time-temperature relationships in a droplet before it bursts into flame. It is known¹⁻⁴ that the ignitability of a propellant can be affected drastically by changes in pressure, as well as temperature and the geometry of the enclosure surrounding the impinging streams of reactants. But the reasons for this sensitivity are not clear, nor is it known whether liquid particles that differ in size also differ in ignition behavior. At atmospheric pressure, two liquids that comprise a hypergolic mixture burst into flame almost as soon as they meet. At lower pressure there is longer delay before ignition occurs. Then, below some pressure, ignition does not occur, even though slightly above this point the hypergolic mixture does ignite after a reasonable delay time. The pressure at which cut-off occurs, marking the boundary between ignition and nonignition, is not well defined and reproducibility becomes increasingly more difficult as the pressure is reduced.

Contents

Ignition, unlike combustion, is mainly a transient phenomenon, where the development of a flame represents only the final step of a series of events. When a propellant undergoes chemical decomposition, large amounts of heat are released. These exothermic reactions are accompanied by endothermic effects associated with vaporization, which is a pressure-sensitive process. The temperature of the remaining liquid changes as a result of these two competitive processes, and the temperature change during a short time interval can be calculated from thermodynamic properties

$$\Delta T = \frac{\sum(n_i \cdot H_i)_{\text{reactants}} - \sum(n_i \cdot H_i)_{\text{products}}}{\sum(n_i \cdot C_{pi})} \quad (1)$$

where n = number of moles, H = enthalpy, C_p = specific heat, and the subscript i refers to chemical species. However, thermodynamics deals with end states in energy conversion, not with rates. Chemical kinetics make it possible to deduce rates of energy conversion, from which the temperature of a hypergolic droplet as a function of time can be calculated. A rate equation typically expresses the rate of conversion of a chemical substance mainly as a function of temperature and concentration, taking the form

$$dc_i/dt = -(F_j) \times (e^{-E_j/RT}) \times (c_i^{\alpha_j}) \quad (2)$$

where c = concentration of species, t = time, F = pre-exponential factor, related to the collision frequency, E = activation energy of reaction, R = gas constant, T = temperature, α = exponent relating to reaction order, and subscripts i = chemical species

and j = chemical reaction. Expressed in terms of moles, n_i , rather than concentration, this equation becomes

$$dn_i/dt = -(F_j) \times (e^{-E_j/RT}) \times (n_i/V)^{\alpha_j} \times (V) \quad (3)$$

where V = volume.

A pseudo-rate equation, comparable to rate equations appropriate for chemical reactions, is assumed to be appropriate in describing rates of vaporization of propellant liquid

$$(dn_i/dt)_{\text{vaporization}} = -(F_j) \times (e^{-E_j/RT}) \times (n_i^{\alpha_j}) \quad (4)$$

If $\alpha = 2$, then $(dn_i/dt)_{\text{vaporization}} = -k \cdot n_i^2$ where $k = F_j \times e^{-E_j/RT}$.

Method of calculation: A computer program was developed to simulate the behavior of a droplet of a hypergolic liquid by assuming that a small amount of the droplet reacts, forming gaseous products, while, at the same time, a small amount of the droplet vaporizes. The temperature of the remaining droplet changes, and the droplet then undergoes further reaction and further vaporization, at rates determined by the new temperature and the ambient pressure. This process repeats until the liquid either reaches a high temperature, igniting, or remains cool indefinitely. The logic in the program is shown in Fig. 1. Three main activities are performed repeatedly: calculating rates of decomposition and vaporization of propellant, based on assumed activation-energy values; calculating the time required for conversion of a small amount of propellant into decomposi-

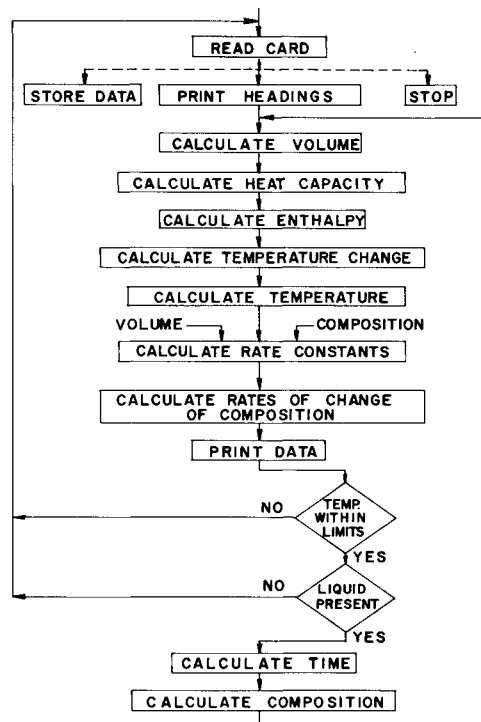


Fig. 1 Details of logic used in computer program.

Received March 15, 1973; synoptic received July 23, 1973. Full paper available from the National Technical Information Service, Springfield, Va., 22151, as N73-30865 at the standard price (available upon request). Research Sponsored by AFOSR under Grant 68-1478.

Index categories: Thermochemistry and Chemical Kinetics; Computer Technology and Computer Simulation Techniques.

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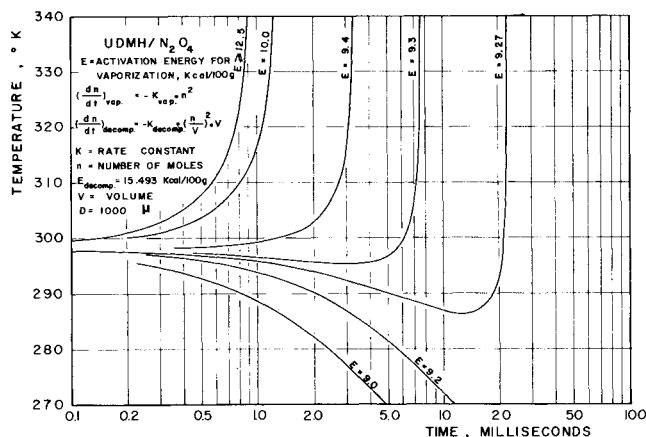


Fig. 2 Time-temperature relationships, $\text{rate} \propto \text{mole}^2$, 1000μ , UDMH/ N_2O_4 .

tion products and vapors; and calculating the temperature of the remaining liquid droplet.

It was assumed that only a negligible amount of vaporization occurs at atmospheric pressure. Different values of activation energy were chosen and calculations were performed to find the activation energy of decomposition which would bring the droplet to a high temperature in the time equal to that measured at atmospheric pressure. This same value was used consistently throughout the calculations as lower pressures were investigated. Decomposition was assumed to be second-order with respect to concentration.

If vaporization rates are expressed by a pseudo-rate expression, there is an activation energy associated with vaporization. Values of activation energy of vaporization were chosen for the lower pressures, and the corresponding time-temperature patterns were calculated. Families of curves based on different activation energies were plotted, showing the temperature of a particle as a function of time.

If rate constants did not vary with temperature, then time could be incremented in steps of reasonable size in solving these rate equations by finite-difference methods. But rate constants do vary, and small changes in composition can result in large changes of temperature. The largest change that could be permitted in any time step was found to be only 0.04°K .

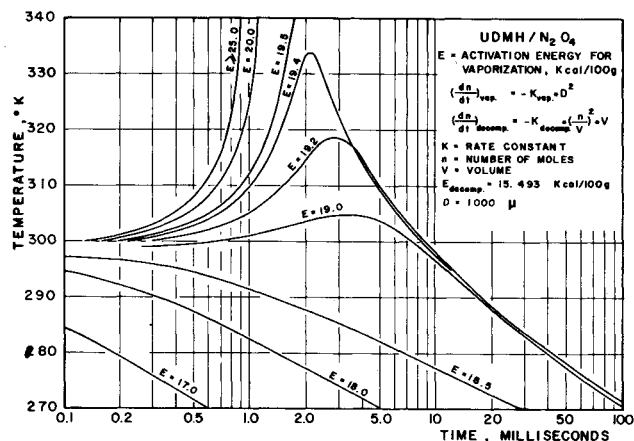


Fig. 3 Time-temperature relationships, $\text{rate} \propto \text{diam}^2$, 1000μ , UDMH/ N_2O_4 .

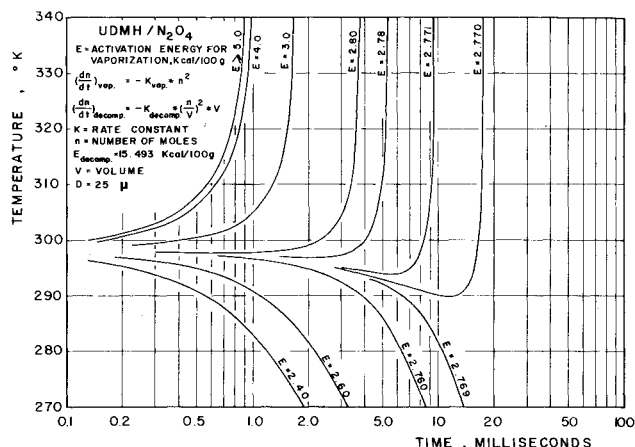


Fig. 4 Time-temperature relationships, $\text{rate} \propto \text{mole}^2$, 25μ , UDMH/ N_2O_4 .

Results: In Fig. 2, the time-temperature history of particles of UDMH/ N_2O_4 , 1000μ in diameter, are shown. Similar curves were developed for Aerozine/ N_2O_4 , $\text{N}_2\text{H}_4/\text{N}_2\text{O}_4$, and $\text{N}_2\text{H}_4/\text{HNO}_3$. At high pressure, it is mainly chemical decomposition that occurs, generating the heat which raises the temperature until the propellant ignites. At low pressures, only a small amount of activation energy is needed to vaporize liquid, and the remaining droplet cools down, finally freezing without igniting. A sharp cut-off point in activation energy appears in these curves, comparable to that observed with pressure, separating the ignition range from the nonignition range.

Calculations were also run where the rate of vaporization was assumed proportional to the surface area of the droplet. The results are shown in Fig. 3. At a narrow range of pressures, the temperature increases initially as though the droplet will ignite, but then there is a reversal and the droplet finally cools down without igniting. Work is currently being done to determine the most appropriate value for the exponent in the rate equation.

In order to investigate the effect of particle size on ignition behavior time-temperature values were calculated for particles initially 25μ , 50μ , and 100μ in diameter rather than 1000μ . In Fig. 4, time-temperature curves of particles 25μ in diameter are shown. If the assumptions made in generating Figs. 2 and 4 are correct, large particles ignite as readily as small particles do at high pressures, but only the smallest particles ignite at low pressures; also, the ignition delay time of large particles may be longer than that of small particles. Laboratory measurements have not indicated yet whether particles of different size actually show different ignition behavior.

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