Burning Rates of Solid Propellants

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A model is proposed for the burning of solid propellants which takes into account heat transfer, diffusion, and chemical reaction processes. The chemical step influencing the rate is postulated to be a reaction between a gaseous molecule and a solid component occurring at the solid-gas interface. The combination of expressions for the rates of the heat transfer, diffusion, and reaction steps leads to relatively simple equations for the burning rate in terms of (1) the physical properties of the propellant; (2) the transport coefficients; (3) the operating conditions of the burning process, temperatures, and pressure; and (4) chemical characteristics of the gas-solid reaction, activation energy, frequency factor, and heat of reaction.

The well-established facts concerning burning rates, the effect of pressure and initial temperature, and the phenomenon of erosive burning are predicted by the proposed theory. Also specific experimental data for burning potassium and ammonium perchlorate composite propellants can be predicted from the theory. The values of the variables necessary to obtain agreement between observed and predicted results are generally realistic. However it should be emphasized that conclusions regarding the detailed mechanism of the burning process cannot be obtained from comparison with burning-rate data. Elucidation of the kinetic steps in the process will require experimental investigation of the intermediate products of combustion and a detailed study of the burning surface and gaseous flame zone.

Solid propellants used in rocket propulsion are primarily of the composite type; that is, they consist of a powdered crystalline oxidizer dispersed in a continuous phase of plastic fuel. The rate of burning of the propellant is of basic importance in determining the performance of the rocket motor. The linear burning rate is defined as the velocity of the gas-solid interface (the burning surface) as the propellant is converted into gaseous combustion products. This linear rate is related to the mass burning rate per unit surface by the density of the propellant and to the mass burning rate of component C of the propellant by its mass fraction:

$$r = \frac{m}{\rho} = \frac{m_c}{n_c}\left(\frac{1}{\rho}\right) \qquad (1)$$

The primary physical variables which can influence the burning rate in the rocket motor are pressure, initial temperature of the propellant, gas velocity parallel to the burning surface, and the characteristics of the propellant. Among the significant characteristics are the kind, size, and shape of the oxidizer crystals; the fuel-oxidizer ratio; the catalyst that may be incorporated in the propellant; and the nature of the manufacturing process for the propellant. The desirable goal is the development of a theory of burning which would explain the effects of all these variables and enable the manufacturing chemist to produce a propellant for specific burning properties.

The objective of this investigation is to propose a theory for the over-all aspects of the burning process which can lead to theoretical expressions for the burning rate. The processes of chemical reaction and energy and mass transport are occurring simultaneously during the burning process, and perhaps all with finite and different resistances. The basic problem is to combine these three rate processes in such a way as to allow for the proper significance of each.

Owing to the molecular complexity of the propellant system of fuel and oxidizer it is extremely difficult to determine the separate chemical reactions which, taken together, explain the sequence of steps that lead from reactants to final combustion products. The experimentation necessary for this resolution of the chemical kinetics of propellant burning has not been accomplished at present, nor is there any evidence to suggest that the evidence will be obtained in the near future. For example after a long period of study on double-base propellants (for example the colloidal mixtures of nitroglycerin and nitrocellulose used in guns) only the general nature of the first step in the combustion process has been reasonably well elucidated (*1*). Because of this situation it has been necessary in previous studies to make assumptions regarding both the nature of the chemical steps and their relative rates. This procedure is adopted in the theory proposed in the following sections. Hence the results apply only to the over-all results of the burning process and pretend no information about the mechanism of the chemical steps.

The model proposed for the over-all burning process attempts to account for all three transport steps. In principle it is not necessary to assume that either chemical reaction, energy, or mass transfer is the controlling feature of the process. A steady state solution of the equations provides this more general solution. However the resultant burning-rate equation would perhaps be too complicated for useful application. As an illustration of the kind of specific expression that is possible from the theory the burning-rate equation is developed for the particular postulate that the mass transfer processes occur at close to equilibrium conditions.

A number of theoretical models of the burning process have been proposed in earlier investigations, particularly for the burning of double-base propellants. These results are briefly summarized in the following paragraphs.

PREVIOUS WORK

Geckler (*6*) has reviewed the unclassified experimental and theoretical work on burning colloidal and composite propellants up to about 1952 and included a list of references. Some of the most important theoretical contributions are those of Wilfong, Penner, and Daniels (*11*); Rice and Ginell (*8*); Parr and Crawford (*7*); Friedman and co-workers (*5*); Summerfield *et al.* (*10*); and Corner (*3*).

Wilfong, Penner, and Daniels (*11*) proposed that a solid-phase chemical reaction at the propellant surface was the controlling chemical step. Experimental burning-rate data show that pressure may have a strong effect. The coefficent ϵ in the empirical representation of the pressure effect

$$r = b\,p^{\epsilon} \qquad (2)$$

may vary from 0 to 1.0. In the Wilfong theory the pressure does not affect the rate of the solid-phase reaction. Rice and Ginel (*8*) considered the burning rate to be controlled by a combination of the kinetics of the initial solid-phase reaction, the rate of heat transfer to the solid by conduction (erosive burning was not considered), the kinetics of the combustion processes in the gas phase, and diffusion from the surface to the bulk gas. This theory leads to results showing the burning rate to increase with pressure as shown by experiment. The magnitude of the pressure effect was dependent upon the order of the gas-phase reactions. Experimental burning-rate data can be correlated by the theory, although the resultant expressions are not convenient to use. The procedure used by Rice and Ginell divides the gaseous burning region into several somewhat arbitrary zones and is based primarily upon observations of the flame zone in composite propellants by Crawford and co-workers (*2, 4*).

Parr and Crawford (*7*) used the same concept of successive chemical reactions occurring in different zones of the flame. Their treatment was made more general by reducing the assumptions pertaining to the position of each separate zone, but more restricted by neglecting diffusion. As in the work of Rice and Ginell, the results do not lead to usable expressions unless the processes in all but one zone are neglected.

Summerfield *et al.* (*10*) observed (by microphotography) the burning region using ammonium perchlorate propellants. Their interpretation was that the burning surface was dry and the gaseous reaction zone thin. From this it was concluded that chemical reactions at the solid surface did not occur. Rather it is supposed that the reactants stream from the surface unmixed and unreacted. Presumably the rate is controlled by the kinetics of the gaseous combustion reaction and diffusion and energy transfer in the boundary layer near the propellant surface. From these concepts empirical expressions for the burning rate are obtained for two extreme cases: diffusion resistances are negligible with respect to that of a second-order combustion reaction, and the reactions occur at near equilibrium conditions.

MODEL OF THE BURNING PROCESS

Rather than following the separate-zone concept of Rice and Grinell (*8*) it will be supposed that the significant combustion reactions are of two types. As in the theory of Wilfong, Penner, and Daniels (*11*) it is postulated that the primary, significant reaction is at the surface; however in contrast to their concept it is proposed that this reaction is between a gaseous molecule *A* and a solid substance *C* to form intermediate, gaseous products of combustion. Prior to this other physical and chemical changes may occur, such as melting or preliminary decomposition of the solid fuel. Nevertheless it is supposed that these prior steps do not exert an important effect on the rate of the over-all process. In formulating a rate equation for the over-all burning it is not necessary to describe in detail the nature of the gaseous and solid components reacting at the surface.

The second step is the conversion in the gas phase of the intermediate components into the end combustion products. The gas phase near the solid surface will be at a temperature much higher than that of the propellant surface because the greatest energy release will be for the final steps in the combustion process. The difference in temperature between the core of gas in the rocket motor and the propellant surface exists because of the large resistance to heat transfer in the gaseous boundary layer next to the surface. Because of the relatively higher temperature of the gas phase near the propellant surface it is postulated that the second stage of the combustion occurs at conditions near equilibrium. Hence the kinetics of this second stage gaseous reaction are not important in establishing the rate of burning. The pressure effect on the rate must then originate from the kinetics of the first step, the heterogeneous reaction on the propellant surface. This concept differs in this respect from the theory of Summerfield *et al.* (*10*). On the other hand Friedman and co-workers (*5*) have proposed that the initial decomposition at the solid surface is the controlling step in the decomposition of pure ammonium perchlorate.

It may be observed that the postulated model of the chemical changes does not specify that the gaseous reactions constituting the second step occur in any particular zone away from the surface. Also since they occur at near equilibrium conditions, it is not important whether they take place as a set of successive reactions, parallel steps, or a combination of both.

The physical processes that take place simultaneously with the chemical steps complete the model. The first is the energy transfer to the solid surface as a result of the temperature difference between the core gas at T_g and the interface at T^*. In using a constant temperature T_g for the gas phase it is again supposed that essentially all the resistance to energy transfer occurs in the thin boundary layer of gas adjacent to the solid surface. The magnitude of this resistance will be affected by the thickness and turbulence in the boundary layer. It is in its effect on the heat transfer characteristics of the boundary layer that gas velocity parallel to the propellant surface (erosive burning) will be a significant variable.

The energy transferred to the propellant from the gas increases the temperature of a surface layer of propellant from its original temperature T_s to its reaction temperature T^*. As a consequence of this increase in solid temperature a fusion process may be involved, increasing the energy requirement. T^* is the temperature at which the initial chemical step occurs. Its value is fixed by the characteristics of the propellant (fuel-oxidizer ratio, kind and size of oxidizer crystals, etc.) and by the resistances of the other individual steps, both chemical and physical, that in combination result in the over-all combustion process. For a fixed system of propellant and rocket motor operating conditions T^* should not change. If the heat transfer coefficient between surface and gas changes during the burning process, owing for example to a change in the velocity of core gas, or if the pressure changes, it is expected that T^* would likewise change.

While it is not essential to describe specifically the nature of the components taking part in the surface reaction, it is necessary to postulate how the oxidizing component *A* is formed. Two possibilities exist: *A* may be formed at the burning surface by decomposition of the oxidizer, or if *A* is an intermediate product of combustion, it will be transferred to the burning surface through the boundary layer of gas in the same way as the energy transfer occurs. If *A* is formed at the surface, its rate of formation does not affect the burning rate because the process is postulated to occur near equilibrium conditions. If *A* is transferred from the core gas through the boundary layer, a diffusional resistance may be introduced. This is identified in the list of rate equations for the individual steps formulated in the next section.

RATE EQUATIONS FOR INDIVIDUAL STEPS

1. Energy Transfer to Propellant Surface

The rate of energy transfer from the core gas to the propellant surface per unit area per unit time may be written as

$$q = h\,(T_g - T^*) \tag{3}$$

The heat transfer coefficient represents the result of the combination of conduction, convection, and radiation contributions to the energy transfer. Its value increases with the velocity of the core gas parallel to the propellant surface.

2. Mass Transfer of Component A to Propellant Surface

The burning rate will be formulated first in terms of the mass of propellant component *C* which reacts per unit area per unit time, that is m_c. Species *C* is the fuel component which reacts with gaseous A in the primary combustion step

$$A\,(g) + C\,(s) \rightarrow B\,(g) + D\,(g) \tag{4}$$

If *A* reaches the solid surface from the core gas, its rate of transfer per unit area of propellant surface is given by the diffusion expression

$$m_A = k_A\,(p_g - p_{A_i}) \tag{5}$$

In accordance with Equation (4) the molal rates of disappearance of A (*g*) and *C* (*s*) are equal. Hence the mass burning rate of component *C* is related to m_A by the ratio of the molecular weights:

$$m_c = m_A \frac{M_c}{M_A} = \frac{M_c}{M_A} k_A (P_{A_g} - P_{A_i}) \tag{6}$$

3. Effect of Energy Transfer on the Propellant

The energy transfer rate to the propellant surface is related to the disposition of the energy in the solid by

$$q = [\Delta H + C_p(T^* - T_s)] \qquad (7)$$

If n_c is the mass fraction of C in the solid propellant, Equation (7) may be written in terms of m_c:

$$q = \frac{m_c}{n_c}[\Delta H + C_p(T^* - T_s)] \qquad (8)$$

Equation (8) takes into account possible fusion of parts of the propellant prior to the primary reaction by considering ΔH to be the heat of fusion plus heat of primary reaction per total mass of propellant.

4. Primary Chemical Reaction at Propellant Surface

The burning rate in terms of the disappearance of **C** may be formulated according to the kinetics of the surface reaction between gaseous **A** and solid **C** [Equation (4)]. If the activation energy for this primary chemical step is E, the rate is

$$m_c = M_c\,\gamma\,C_s P_{A_i}\,e^{-E/RT^*} \qquad (9)$$

The concentration of active centers for reaction on the solid surface is designated as C_s. The value of C_s is dependent upon the specific propellant and how it is produced. However C_s should be constant during the burning process.

5. Diffusion of Products of Primary Combustion

The components B (g) and D (g) produced in the surface reaction [Equation (4)] diffuse out into the core gas. The mass rates of these processes in terms of m_c are

$$m_c = M_c\,k_B(P_{B_i} - P_{B_g}) \qquad (10)$$

$$m_c = M_c\,k_D(P_{D_i} - P_{D_g}) \qquad (11)$$

6. Secondary Combustion in the Gas Phase

The secondary combustion reactions are postulated to occur in the core gas at a relatively high temperature. The reactions may be illustrated by

$$B\ (g) + D\ (g) \rightarrow CO\ (g) + CO_2\ (g) + H_2O\ (g) \qquad (12)$$

$$+ \text{ other final combustion products}$$

At the elevated temperature these reactions take place at near equilibrium conditions, so that their kinetics are unimportant in formulating the burning rate.

BURNING-RATE EQUATIONS

An expression for the burning rate m_c can be obtained in terms of initial and final quantities by combining the equations for rates of the individual steps as listed in the preceding section. At steady state burning the rates of all the steps are equal. Hence Equations (3), (6), (8), (9), (10), and (11) form a group of simultaneous equations which may be used to eliminate the intermediate and nonmeasurable quantities, such as T^*, q, P_{A_i}, etc. However this steady state solution method leads to a complicated result not readily usable. Useful expressions can be obtained by considering some of the individual steps to be of negligibly low resistance with respect to the others. This procedure can lead to a large number of distinct expressions for the burning rate, each based upon a particular choice for the set of individual steps which control the over-all process. Provided sufficient experimental data are at hand, it is possible in principle to test the various suppositions.

It is not the aim here to develop and test a number of separate equations for the burning rate. The chief objective is to illustrate how the proposed model can be employed to determine burning-rate equations. As experimental data accumulate concerning the detailed characteristics of the combustion process, it should be possible to draw conclusions about the significance of individual steps in the over-all process. At present one choice of controlling steps will be assumed and the resultant equation compared with observed rate data.

Because it seems well established that the mass velocity of core gas affects the rate, and also that the original propellant temperature exerts a small effect, steps 1 and 3 in the previous section will be considered significant. It will also be supposed that the diffusion of reactant A and its rate of reaction at the propellant surface are important steps in determining the burning rate. The diffusion of the products and the secondary combustion will be assumed to take place at near equilibrium conditions.

Under these conditions Equations (3), (6), (8), and (9) define the rate. Eliminating q from Equation (3) and (8) one gets for T^*

$$T^* = \frac{h\,T_g + \dfrac{m_c}{n_c}(C_pT_s - \Delta H)}{h + \dfrac{m_c}{n_c}C_p} = \frac{h\,T_g + r\,\rho(C_pT_s - \Delta H)}{h + r(\rho C_p)} \qquad (13)$$

where Equation (1) has been utilized to introduce the linear burning rate.

Table 1. Ammonium Perchlorate Propellant Descriptions (*10*)

Oxidizer		Values of parameters in Equation (15)	
Wt. %	Particle size, μ	E, cal./g. mole	I, cm./(atm. sec.)
75	16	11,400	7.7
75	120	8,000	3.1
80	16	14,800	154.0
80	120	10,800	19.3

The partial pressure of **A** at the solid surface may be obtained from Equation (6) and used in Equation (9) to obtain m_c in terms of the bulk partial pressure of **A**. This latter quantity is equal to the total pressure multiplied by the mole fraction of **A** in the core gas. The product $p\ y_A$ should be constant during the burning process but a function of the propellant composition and perhaps the oxidant grain size. With these concepts Equations (6) and (9) yield

$$r = \gamma\,C_s\,\frac{y_A}{n_c\rho}\left[p - \frac{M_A}{M_c}\,\frac{n_c\rho}{y_A}\,\frac{r}{k_A}\right]e^{-E/RT^*} \qquad (14)$$

In the formulation of Equation (14), the linear burning rate is again substituted for m_c through Equation (1).

Equations (13) and (14) determine the burning rate as a function of the parameters of the system. The transport coefficients h and k_A are affected by the conditions of the gas boundary layer at the surface and would increase with core-gas velocity, as in erosive burning. The core-gas temperature is very nearly the adiabatic flame temperature for the propellant. The quantities ΔH, C_p, ρ, n_c, y_A, and the activation energy are properties of the propellant. The surface-kinetics constants $\gamma\,C_s$ and E depend upon the propellant system and the characteristics of its manufacture, for example oxidant grain size.

Equation (14) is simplified considerably if either the diffusion of A to the solid surface occurs at near equilibrium conditions, or it is postulated that A arises from preliminary decomposition processes at the surface. In either case Equation (14) becomes

$$r = \frac{\gamma C_s y_A}{n_c\rho}\,p\,e^{-E/RT^*} = I\,p\,e^{-E/RT^*} \qquad (15)$$

The quantity I is composed of factors, $\gamma C_s y_A/n_c\rho$, which are invariant during the burning but dependent upon the nature of the fuel and oxidizer, their composition, and the physical characteristics (grain size, etc.) of the composite propellant charge.

Examination of Equation (15) indicates that the rate should be directly proportional to the pressure except as modified by the variation of T^* with pressure. At low pressures the rate will be low, and T^*, according to Equation (13), will be high, with T_f as an upper limit. Conversely at high pressures, where the rate is high, T^* will be dominated by the second term in Equation (13). It will have a low value, approaching $(T_sC_p - \Delta H)/C_p$ as a limit. The net result is that the rate will increase rapidly with pressure at low values and more slowly at high pressures. This is in agreement with observed data and with the widely used empirical expression [Equation (2)].

Experimentally it has been found by Green and co-workers (*9*) that the phenomenon of erosive burning is more pronounced at low burning rates than high ones. In the proposed theory the effect of erosive burning is due to the influence of the heat transfer coefficient on T^* in Equation (13). An increase in h results in an increase in T^* and hence an increase in burning rate according to Equation (15). The magnitude of this effect will be larger the lower the rate and therefore the smaller the second term in the numerator and denominator of Equation (13) in comparison with the first. Finally the effect of initial temperature of propellant is to increase the value of T^* in Equation (13). This in turn results in an increased rate.

COMPARISON WITH EXPERIMENTAL DATA

Because of the large number of parameters involved it is not difficult to fit burning-rate data for various propellants with Equations (13) and (14) or even (13) and (15). More critical tests of the theory are whether the predictions of the effects of important variables are correct as described in the previous section, and whether the values of the parameters needed to fit the equations to the data are realistic.

Effect of Pressure and Temperature

Geckler (*6*) presented burning-rate data for an asphalt-potassium perchlorate propellant containing 76.5 wt. % oxidizer. Its density was 1.77 g./cc. and the flame temperature 2,040°K. At 15°C. (T_o = 288°K.) the observed pressure effect on the burning rate could be represented by

$$r = 0.103\,p^{0.745} \quad (p = 100 \text{ to } 200 \text{ atm.}) \tag{16}$$

The best estimates of available information suggest a value of $C_p = 0.35$ cal./g. °C. The data correlated by Equation (16) were obtained from firings of rocket motors by means of cigarette-burning grains of propellant. Hence the mass velocity of gases past the surface was not as large as in burning solid charges of propellant in a rocket motor. Therefore the heat transfer coefficient between gas and propellant surface would be somewhat, but not greatly, larger than the value corresponding to no flow of gas past the surface. A value of $h = 8.0 \times 10^{-2}$ cal./(sec.)(sq. cm.)(°C.) was chosen to use in Equation (13). Under these conditions Equations (13) and (15) fit the data [Equation (16)] with the following values for the other parameters: $\Delta H = -200$ cal./g., $E = 14{,}900$ cal./g. mole, and $I = 1.23 \times 10^2$ cm./(atm.)(sec.).

The temperature of the burning surface obtained from Equation (13), is slightly dependent upon the pressure but is in range 880° to 900°K. from 100 to 211 atm. The melting point of pure potassium perchlorate is about 883°K.

Equation (16) can be represented by other sets of values for the parameters than those listed. The specific choice was made on the basis that the numbers should be realistic. For the same propellant Geckler (*6*) presents data on the effect of initial temperature of propellant on the rate. The approximate result is given in the form

$$\frac{d \ln r}{d T_s} = 0.013 \tag{17}$$

Equations (13) and (15), with the given values for the parameters, predict a somewhat greater increase in rate with T_s than Equation (17). The predicted value of the constant in Equation (17) is about 0.005 to 0.006 or about the same as observed for colloidal propellants (*2*).

Summerfield *et al.* (*10*) measured burning rates of ammonium perchlorate–styrene polyester propellants over the pressure range 14.7 to 2,000 lb./sq. in. abs. The measurements were obtained in a bomb with square strands of propellant. Data were observed for four mixtures containing different weight fractions and particle sizes of oxidizer as shown in Table 1.

Since there was no forced motion of the combustion gases in the apparatus, the heat transfer coefficient would be considerably lower than would exist in an actual rocket motor and somewhat less than employed in analyzing the data for the potassium perchlorate-asphalt propellant. For comparison of Equation (13) and (15) with Summerfield's data a value of $h = 3.0 \times 10^{-2}$ cal./(sec.)(sq. cm.)(°C.) was employed. The flame temperature was measured and found to be about 2,670°K. Information was not given about the other conditions, so that the following values were employed: T_s = 298°K., ρ = 1.8 g./cc., and C_p = 0.45 cal./g. °K.

The initial heat effect would probably not involve a heat of fusion, since the melting point of ammonium perchlorate is high (1,200°K.). However the heat evolved in the initial decomposition reactions might well be higher. In the computations ΔH was taken as −200 cal./g., the same as for the po-

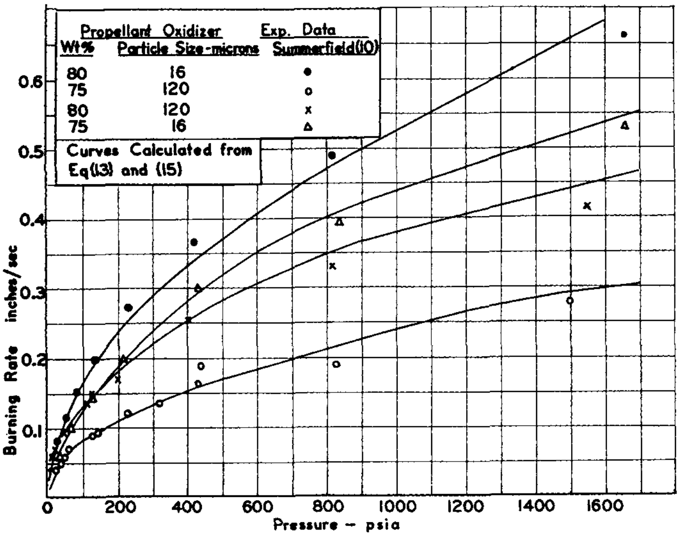

Fig. 1. Burning rates of ammonium-perchlorate propellants.

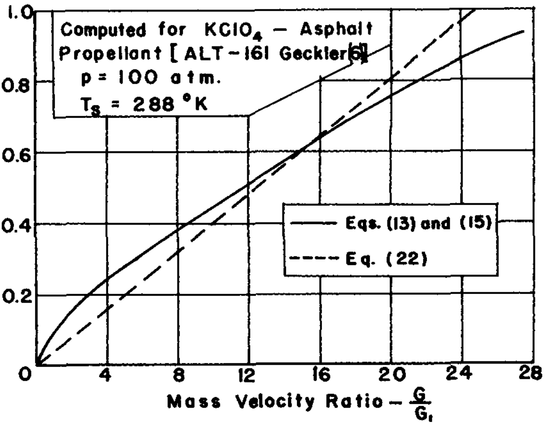

Fig. 2. Effect of gas velocity on burning rate (erosive burning).

tassium perchlorate—asphalt propellant.

Since temperature-coefficient data were not obtained, it was not possible to check the suitability of the values proposed for C_p and ΔH. However the pressure vs. rate data did permit the determination of values of E and I, which along with the chosen numbers for the other parameters best fit the data. These values are given in the last two columns of Table 1. The computed burning rate vs. pressure curves are compared with the experimental measurements in Figure 1. It is seen that some of the curves cross at low pressures. This explains the lack of systematic variation in the activation energy and the modified frequency factor I. However, as in the case of the data of Geckler, it is clear that Equations (13) and (15) can show a pressure effect that is in agreement with experiment. Chemical significance cannot be attached to the free-energy and frequency-factor numbers in Table 1 because of the complexity of combustion at the solid surface. Stated differently, the model used in developing Equations (13) and (15) is much too simple to be true in detail. All that can be said is that such a model leads to predictions that in an over-all sense (burning rates vs. pressure) agree with observation.

Effect of Gas Velocity

The numerical magnitude of the effect of heat transfer rate on the burning velocity can be evaluated from Equations (13) and (15) by considering variations in h. If the heat transfer coefficient is related to the mass velocity, the significance of erosive burning results. Such computations were carried out for the potassium chlorate propellant studied by Geckler (6).

Since potassium perchlorate gives high burning rates, the effect of erosive burning would not be as important for this propellant as for some others. Nevertheless increasing the mass velocity should increase the burning rate for any propellant, although the effect may be small in some instances. Using the property values given previously for the asphalt-potassium perchlorate propellant one can compute the rate from Equations (13) and (15) for various values of h, as shown in Table 2. Heat transfer coefficients for turbulent flow in tubes have been found to be proportional to the 0.8 power of the mass velocity. When one assumes this relationship, the heat transfer coefficient can be written in terms of G by

$$h = h_o + a\,G^{0.8} \qquad (18)$$

The quantity h_o is the coefficient at zero velocity and hence represents primarily the contribution of radiation and natural convection to the energy-transfer rate. The value of h found to correlate the experimental data of Geckler (6) in rocket motors was 0.08 cal./(sec.)(sq. cm.)(°K.). As noted previously the velocity was not large in these measurements. Therefore h_o will be chosen a small amount less than this value and the same as h_o used with Summerfield's data; that is $h_o = 0.03$. Applying Equation (18) at two mass velocities and dividing gives

TABLE 2. EFFECT OF GAS MASS VELOCITY ON BURNING RATE FOR PROPELLANT ALT-161 [GECKLER (6)]

h, cal./(sec.)(sq. cm.)(°K.)	G/G_1, mass velocity ratio calculated from Equation (20)	r, cm./sec.	$\frac{r - r_0}{r_0}$
0.030	0	2.54	0
0.046	1	2.80	0.10
0.080	4.1	3.19	0.25
0.139	11.1	3.75	0.48
0.193	18.3	4.36	0.71
0.242	25.2	4.80	0.89

$$\frac{h - h_o}{h_1 - h_o} = \left(\frac{G}{G_1}\right)^{0.8} \qquad (19)$$

Choosing $h_1 = 0.046$, the second value in Table 2, one may obtain the heat transfer coefficient at any mass velocity from

$$\frac{h - 0.030}{0.046 - 0.030} = \left(\frac{G}{G_1}\right)^{0.8} \qquad (20)$$

The ratio G/G_1 is plotted in Figure 2 vs. the burning-rate ratio $(r - r_o)/r_o$. The curve shows that the rate increases rapidly at low values of G and more slowly at high velocities. This is to be expected, since the burning rate is influenced less by the resistance to energy transfer as this resistance decreases, that is as the velocity increases.

A common empirical means of correlating erosive burning data is the expression (9)

$$\frac{r - r_o}{r_o} = k\,\frac{G}{G^*} \qquad (21)$$

This equation may be written

$$\frac{r - r_0}{r_0} = \left(\frac{k\,G_1}{G^*}\right)\frac{G}{G_1} \qquad (22)$$

Plotted on the coordinates used in Figure 2, Equation (22) suggests a linear relationship as illustrated by the dotted line, when one assumes that the erosion constant does not change. The theoretical curve in Figure 2 appears preferable to the empirical dotted line, since the effect of erosion should decrease at higher mass velocities. Stated differently, the erosive constant should decrease as the velocity increases.

CONCLUSION

A theory of burning of solid propellants has been presented which agrees with the observed effects of measurable properties upon the burning rate. However without detailed and exacting experimental studies of the several stages in the over-all combustion process it is hazardous to draw conclusions about the mechanisms involved. Hence the proposed, simple model is best regarded as a basis for developing rate equations and correlating burning-rate data.

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NOTATION

$A(g)$, $C(s)$, $B(g)$, $D(g)$ = components of the primary surface reaction
C_p = specific heat of the solid propellant, cal./g. °K.
C_s = concentration of active centers on surface of propellant, g./sq. cm.
E = activation energy for primary surface reaction, cal./g. mole
G = mass velocity of core gas, g./sq. cm. sec.
G^* = mass velocity corresponding to Mach number = 1.0
h = heat transfer coefficient between core gas and propellant surface, cal./sq. cm. sec. °K.
ΔH = heat of fusion plus heat of reaction for primary surface reactions per unit mass of propellant, cal./g.
I = constant during burning equal to $(\gamma C_s y_A)/(n_c p)$, cm./(atm.)(sec.)
k_A = mass transfer coefficient for component A, g./(sec.)(sq. cm.)(atm.)
k = erosion coefficient, defined by Equation (21)
M = molecular weight
m = mass burning rate, g. of propellant/sec. sq. cm.
m_c = mass burning rate of component C of propellant, g. of C/sec. sq. cm.
n_c = mass fraction of component C in propellant
p = total pressure, atm.
p_A = partial pressure of component A, atm.
(subscript g denotes the core gas; i denotes the solid surface)

q = rate of energy transfer to propellant surface, cal./sec. sq. cm.
R = gas constant, cal./g. mole °K.
r = linear burning rate, cm./sec.; r_0 = burning rate at zero gas velocity
T^* = temperature of primary reaction (propellant surface temperature during burning, °K.)
T_s = initial temperature of propellant, °K.
T_g = temperature of core gas during burning, °K.
y_A = mole fraction A in gas phase
ϵ = pressure coefficient in empirical burning rate, Equation (2)
γ = frequency factor in Arrhenius' representation of chemical rate equation
ρ = density of solid propellant, g./cc.

Subscripts

A, B, D = components in the primary surface reaction
g = core gas
i = gas-solid interface

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Continuous-Throughput Rectification of Organic Liquid Mixtures with Thermal-Diffusion Columns

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Experiments were carried out with cylindrical thermal-diffusion columns in which the separation chambers were sufficiently narrow so that curvature effects might be ignored. For both open and closed operation, results were obtained for the two binary systems benzene-carbon tetrachloride and *n*-heptane—benzene as well as the ternary mixture *n*-heptane—methylcyclohexane-toluene. For the binary systems, correlations are given in terms of dimensionless combinations which arise when the equations of conservation are placed in dimensionless form. The thermal-diffusion coefficients used in the correlations are literature values determined in steady-state—cell (no convection) measurements.

The historical background of thermal diffusion has been covered by Powers and Wilke (*1*). Except for the many steady-state—cell experiments (no convection), studies with liquids generally have been confined to the vertical or inclined countercurrent thermal-diffusion column conceived by Clusius and Dickel (*2*). Although for continuous throughput the product positions on a Clusius-Dickel column are usually at the extremities, with the feed position at an intermediate point, recent arrangements by A. L. Jones and his associates (*3* to *12*) include concurrent flat-plate columns operated vertically or horizontally with or without membranes as well as apparatus with porous walls. Studies have been reported recently on the Clusius-Dickel column operated with packing as well as centrifugal force (*13, 14*).

In addition to the work of Powers and Wilke (*1*), the principal quantitative investigations covering thermal-diffusion columns operated with a continuous throughput have been those of Heines, Larson, and Martin (*15*) and

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