

Self-Ignition Temperatures of Materials From Kinetic-Reaction Data

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Results of experimental determinations of the kinetic constants of the self-heating reaction are presented for wood fiberboard, cotton linters, sugar pine, cork, crepe rubber, GRS rubber, natural, synthetic, and blended foam rubber (with and without additive), various oils (raw linseed, cottonseed, rapeseed, sperm, olive, castor, and neatsfoot) applied to cotton gauze in a ratio of 1 part of oil to 6 parts of cotton by weight, ammonium perchlorate, and nitrocellulose plastic. Under the assumption that self-heating follows a first-order reaction, these constants were used to calculate the critical radii of spherical piles for each of four surface temperatures likely to be experienced in long-period storage. Calculated self-ignition temperatures of piles of $\frac{1}{8}$ -inch-diameter to 22-inch-diameter spheres of wood fiberboard and $\frac{1}{8}$ -inch-diameter to 2-inch-diameter spheres of cotton linters were in reasonable agreement with previous measurements by N. D. Mitchell (National Fire Protection Association Quarterly **45**: 162, 1951).

1. Introduction

Previous workers studying the self-ignition behavior of materials have experienced difficulties in the determination and specification of a unique ignition temperature. Because of the critical heat balance that exists during the ignition process, the measured "ignition temperature" is dependent upon the characteristics of the testing apparatus, the degree of control of the ambient temperature conditions, the time of exposure, and other experimental factors. It is highly dependent also upon the size of the specimen under test. This is due to the fact that self-ignition of a material is only possible when the rate of heat generation within the material exceeds the rate at which heat is lost by radiation, convection, and conduction to the surroundings. Since the heat generated is a function of the volume of the material, while the heat lost is a function of its surface area, the measured ignition temperature should decrease as the linear dimensions increase.

The incidence of fires resulting from self-ignition makes desirable an understanding of the relationship between the self-heating reaction and the physical parameters involved. The present paper proposes and illustrates the manner in which kinetic-reaction data obtained under conditions of negligible heat loss may be used to predict critical surface and ambient temperatures as a function of size and shape for a variety of materials.

2. Analysis and Nomenclature

In the analysis, the following symbols and units will be used:

A	heat-generation coefficient	cal sec ⁻¹ cm ⁻³
B	radius or half-thickness	cm
B_c	critical radius of sphere	cm
c	specific heat	cal g ⁻¹ °K ⁻¹
e	Napierian base	-----
E	activation energy	kcal mole ⁻¹
h	surface heat-transfer coefficient	cal sec ⁻¹ cm ⁻² °K ⁻¹
k	thermal conductivity	cal sec ⁻¹ cm ⁻¹ °K ⁻¹
m	coefficient in eq (1)	-----
R	gas constant = 0.0019872	kcal mole ⁻¹ °K ⁻¹

t	time	sec
T	temperature within material	°K
T_A	self-ignition (critical ambient) temperature	°K
T_B	critical surface temperature	°K
T_O	critical center temperature	°K
T_m	mean temperature = $(T_O + T_B)/2$	°K
x	space coordinate	cm
ρ	density	g cm ⁻³

Analyses of self-heating have been made under the assumption that heat is generated within the body according to a first-order reaction law. Although this may be an oversimplification for complex materials and over extended temperature ranges, the assumption appears to be applicable for many materials in the relatively low-temperature ranges where self-heating becomes important and the ignition process is initiated. Provided the rate of the self-heating process within the material is not limited by diffusion of the reactants and/or products, or by depletion of the fuel supply, a steady-state condition can exist when the heat generated within the material is equal to the heat lost to the surroundings. The particular condition of interest is the one that produces the maximum self-heating which is still steady state. Either a slightly higher ambient temperature or a slightly larger bulk size results in a greater quantity of heat being generated than can be dissipated, and ignition results. Since this steady-state condition is critical with respect to ignition, the corresponding surface temperature and size of material are referred to as the critical surface temperature and the critical size. The ambient temperature corresponding to given critical steady-state conditions with given heat losses is considered the critical ambient or self-ignition temperature. There exists for each material and for each set of heat-loss conditions a series of corresponding self-ignition temperatures and critical sizes.

Consider a homogeneous material of half-thickness B generating heat in accordance with the first-order reaction law $Aex\rho - E/RT$ and losing heat from its surface. The steady-state heat-conduction equation which applies for the condition when the heat lost

through the surface is equal to the heat generated within the material may be written:

$$k \left[\frac{d^2 T}{dx^2} + \frac{m}{x} \frac{dT}{dx} \right] + A e^{-\frac{E}{RT}} = 0. \quad (1)$$

The critical condition of ignition in the theory of thermal explosions originally proposed by Frank-Kamenetzky [1]¹ requires the solution of this non-linear equation. Chambré [2] presented analytic solutions in terms of known functions for the sphere ($m=2$) and cylinder ($m=1$) to supplement that for the semi-infinite slab ($m=0$). Recent analyses by Genensky [3] for a sphere and by Thomas [4] for all three geometries have been made employing the assumption common to the previous solutions, namely, that temperature differences within the material are small in comparison with the temperature. Enig, Shanks, and Southworth [5] have provided solutions in the form of convenient tables of the center and surface temperatures for sphere, cylinder, and semi-infinite slab geometries without this restrictive assumption. From the tables it is useful to note that for a given surface temperature T_B , the critical radius for the cylinder and the critical half-thickness for the semi-infinite slab are given very closely by $0.775 B_c$ and $0.514 B_c$, respectively, where B_c is the critical radius for the sphere. Assuming that the heat generated within the material at a mean temperature T_m is lost from its surface according to Newton's law of cooling, the following relation may be used for calculating the critical ambient temperature for a sphere:

$$T_A = T_B - \frac{A B_c}{3h} e^{-\frac{E}{RT_m}} \quad (2)$$

where T_m is a mean temperature, here assumed as $T_o + T_B/2$.

Since the analysis by Thomas employs Newtonian surface cooling as a boundary condition, the ambient temperature is obtained directly. From the graphical relations given, it is again useful to note that for a given ambient temperature T_A , the critical radius for the cylinder and the critical half-thickness for the semi-infinite slab are given very closely by $0.782 B_c$ and $0.520 B_c$ respectively.

The experimental method used in this study for determination of the constants of the first-order reaction involved self-heating conditions which differed from those of the self-heating process described. Instead of a fixed ambient temperature, the temperature within the adiabatic test furnace surrounding the specimen was controlled to maintain negligible loss of heat. Under these conditions, the specimen temperature remained uniform throughout its mass and the heat generated within the body increased its temperature according to the relation:

$$\rho c \frac{dT}{dt} = A e^{-\frac{E}{RT}}. \quad (3)$$

By transposing terms, taking logarithms and plotting $\ln dT/dt$ versus $1/T$, the resultant line has a slope of $-(E/R)$ and intercepts the $\ln dT/dt$ axis at $\ln A/\rho c$. For each material the determination of the values of A and E , as well as of its more common thermal properties, permits the solution of the general self-heating problem including the case where size and temperature become critical and ignition results.

3. Experimental Apparatus

In the determination of the kinetic constants, use was made of an improved version, figures 1 and 2, of an adiabatic furnace previously described [6]. Although the basic operation remains the same, refinements have been made and are here summarized:

Addition of guard heaters and associated control system. In order to reduce heat losses and to maintain minimum temperature gradients within the furnace enclosure, the Dewar flask has been enclosed within a close-fitting cylindrical shell. The shell consists of two concentric stainless steel cylinders containing two electric heating elements and an insulating fill. The shell contains the bottom and center guard heating elements while a top-guard heating element has been placed within the Dewar flask plug composed of several layers of asbestos board. A thyatron control system as shown in figure 3 permits adjustment of the guard-heater cycle.

Use of multiple-junction thermocouple. The sensing element for the servo controller consists of eight No. 30 gage (B&S) copper-constantan thermojunctions arranged in series to measure the mean temperature-difference between the specimen and its ambient medium.



FIGURE 1. Adiabatic furnace with control and recording equipment.

¹ Figures in brackets indicate the literature reference at the end of this paper.



FIGURE 2. Adiabatic furnace, showing Dewar flask and specimen container removed from insulating shell.

The changes and additions described permit improved performance of the system. The controller can sense temperature differences of the order of 0.01°C while the rate of temperature drift as observed with an inert specimen has been reduced to approximately 0.25°C/hr over the temperature range 30° to 300°C .

4. Results

4.1. Determination of A and E

Table 1 lists some thermal and kinetic constants for a number of materials. Some of the values of k and c were determined during this investigation, while others were obtained from handbook sources. The values of A and E were determined over the indicated temperature ranges from experimental temperature-versus-time data and the use of eq (3). For some of these materials, there is reasonable agreement with published values obtained by other methods. These values were determined over limited temperature ranges before loss of weight became appreciable. An analysis that includes the effect of weight loss may be applied for the higher temperature ranges. Analysis of several cellulosic materials has actually shown that when weight changes are taken into consideration, the values of the kinetic constants were not much different from those obtained at the lower temperature ranges.

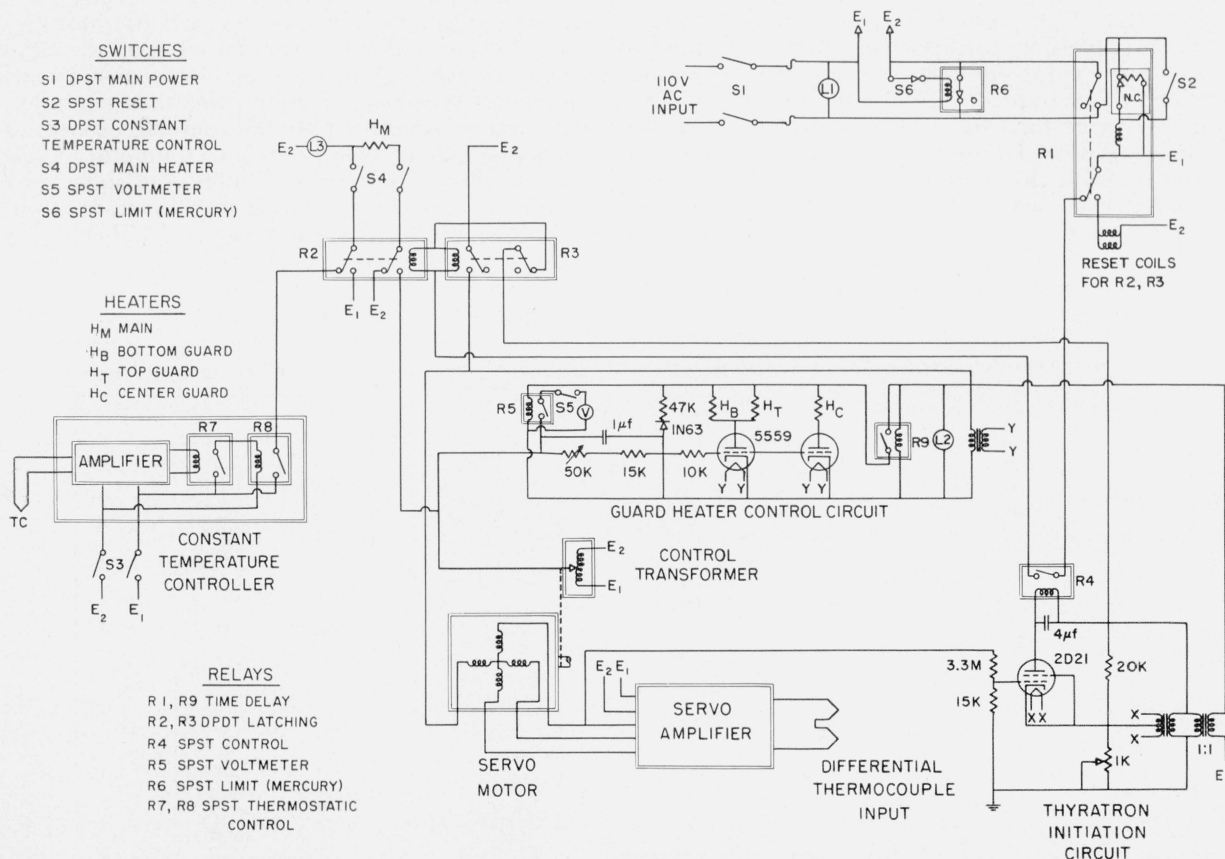


FIGURE 3. Circuit diagram of furnace-control system.

TABLE 1. Physical and kinetic properties

Material	Temperature range	Property				
		ρ	c	k	E	A
	$^{\circ}C$	$g\ cm^{-3}$	$cal\ g^{-1}\ ^{\circ}K$	$cal\ sec^{-1}\ cm^{-1}\ K^{-1}$	$kcal\ mole^{-1}$	$cal\ sec^{-1}\ cm^{-3}$
Wood fiberboard.....	80-225	0.25	0.33	0.00012	25.7	1.97×10^9
Cotton linters.....	180-260	.32	.32	.00010	34.5	5.30×10^{11}
Sugar pine.....	140-310	.36	.32	.00024	20.3	2.11×10^6
Cork.....	170-225	.13	.48	.00010	19.1	2.50×10^5
Crepe rubber.....	210-310	.92	.5	.000282	23.4	1.06×10^6
GRS.....	220-330	1.10	.5	.000299	23.6	1.11×10^7
Foam rubber, 100% natural.....	100-180	.108	.5	.000096	27.6	7.48×10^{10}
Foam rubber, 100% synthetic.....	115-210	.129	.5	.000100	26.2	4.96×10^9
Foam rubber, blended, with additive.....	110-190	.118	.5	.000098	29.0	4.25×10^{11}
Foam rubber, blended, without additive.....	110-200	.104	.5	.000095	28.5	1.10×10^{11}
Raw linseed oil ^a	90-120	.309	.34	.00011	21.0	3.50×10^9
Cottonseed oil ^a	75-120	.338	.34	.00011	24.1	2.42×10^{11}
Rapeseed oil ^a	90-140	.316	.34	.00011	20.1	6.13×10^8
Sperm oil ^a	120-160	.313	.34	.00011	20.1	1.56×10^7
Olive oil ^a	115-160	.308	.34	.00011	18.7	2.41×10^7
Castor oil ^a	140-160	.314	.34	.00011	27.8	8.33×10^{11}
Neatsfoot oil ^a	140-170	.316	.34	.00011	24.7	3.82×10^{10}
Ammonium perchlorate.....	205-270	.91	.35	-----	41.2	1.22×10^{16}
Nitrocellulose plastic.....	135-170	.82	.34	.00051	42.0	2.43×10^{19}

^aApplied to cotton gauze in ratio of 1 part of oil to 6 parts of cotton by weight. All property values refer to oil-cotton combination.

4.2. Determination of Critical Size and Temperature

The critical surface temperatures of spherical piles of wood fiberboard and cotton linters were computed, using the measured values of the kinetic and thermal constants, and the tables given in reference [5]. These computations were performed over the radius range corresponding to the specimen sizes reported by Mitchell [7]. Equation (2) was then used to calculate the corresponding critical ambient temperatures. The value of the surface heat-transfer coefficient was assumed as 4.4×10^{-4} cal/sec cm^2 $^{\circ}K$. Using this value for the surface heat-transfer coefficient, the critical ambient temperature was also determined from the relations given in reference [4]. The results of these calculations are shown in table 2 for two materials for which published experimental data [7] are available. With the exception of the smallest size specimens, for which the assumption of an arithmetic mean temperature for eq (2) introduces

considerable error in the calculated self-ignition temperature, the results are seen to be in reasonable agreement.

Table 3 lists the critical radius B_c of a sphere corresponding to several critical surface temperatures for each of the materials listed in table 1. Curves have been plotted in figure 4 showing this relationship for seven materials. In this temperature range (20° to 100° C), of practical interest for ordinary storage, the critical size calculations were based upon the assumption of the applicability of the kinetic constants which were determined over higher temperature ranges. It was further assumed that the thermal properties remained constant over the whole temperature range. Critical dimensions for cylinders and slabs may be estimated from the previously mentioned constants of $0.775B_c$ and $0.514B_c$, respectively. As h becomes very large, the self-ignition temperature is equal to the

TABLE 2. Comparison between measured and calculated self-ignition temperatures, T_A

Size		Wood fiberboard			Cotton linters		
Thick-ness $2B_c$	Half-thick-ness B_c	Self-ignition temperature			Self-ignition temperature		
		Meas-ured ^a	Calculated ^b		Meas-ured ^a	Calculated ^b	
			Ref 7	Ref 5 and eq 2		Ref 4	Ref 7
<i>in.</i>	<i>cm</i>	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$
$\frac{1}{8}$.159	317	183	260	304	257	307
$\frac{1}{4}$.318	252	218	243	270	274	291
$\frac{1}{2}$.635	212	215	223	248	267	272
1	1.27	202	200	202	222	251	253
2	2.54	180	180	180	201	233	233
4	5.08	150	159	160			
8	10.2	130	140	140			
12	15.2	122	129	129			
22	27.9	109	114	114			

^a Specimens $\frac{1}{8}$, $\frac{1}{4}$, and $\frac{1}{2}$ in. thick were cubes; specimens 1 in. and larger were octagonal prisms.

^b Based on spheres of radius equal to half-thickness.

TABLE 3. Computed critical radius of a sphere, B_c

Material	Critical surface temperature			
	20 $^{\circ}$ C	48.9 $^{\circ}$ C	82.2 $^{\circ}$ C	100 $^{\circ}$ C
	<i>cm</i>	<i>cm</i>	<i>cm</i>	<i>cm</i>
Wood fiberboard.....	4.49×10^3	680	114	50
Cotton linters.....	4.25×10^6	3.29×10^5	2.86×10^4	9.43×10^3
Sugar pine.....	2.19×10^3	501	125	66
Cork.....	1.43×10^3	363	99	55
Crepe rubber.....	1.43×10^4	2.58×10^3	511	206
GRS rubber.....	1.71×10^4	3.03×10^3	591	280
Foam rubber, 100% natural.....	3.36×10^3	438	64	26
Foam rubber, 100% synthetic.....	4.00×10^3	588	95	41
Foam rubber, blended, with additive.....	4.65×10^3	542	71	27
Foam rubber, blended, without additive.....	4.53×10^3	565	78	34
Raw linseed oil ^a	66	14.3	3.6	1.7
Cottonseed oil ^a	101	17.3	3.3	1.5
Rapeseed oil ^a	72	17.0	4.3	2.3
Sperm oil ^a	143	34	8.5	4.5
Olive oil ^a	110	29	7.3	4.5
Castor oil ^a	1.16×10^3	150	69	9.0
Neatsfoot oil ^a	139	37	4.1	1.9
Nitrocellulose plastic.....	7.69×10^4	3.31×10^3	167	43

^a Applied to cotton gauze in ratio of 1 part of oil to 6 parts of cotton by weight. All property values refer to oil-cotton combination.

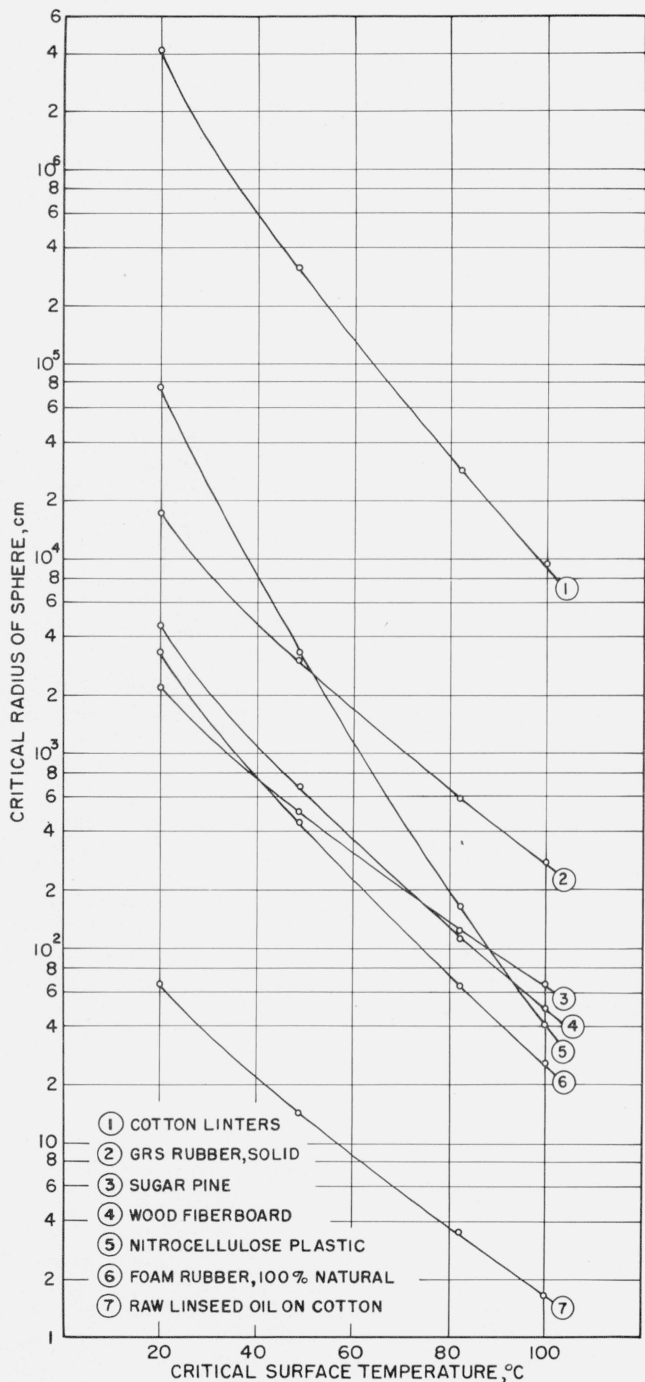


FIGURE 4. Computed critical radii and critical-surface temperatures for spherical piles of various materials.

critical surface temperature. For a finite h , the self-ignition temperature may be estimated from eq (2) or may be obtained directly from the relations presented in reference [4].

5. Conclusions

Recent analyses of self-ignition have been made under the assumption that self-heating follows a first-order reaction law. Experimental determinations of the kinetic constants of this reaction have been made for a number of materials and these constants have been used to calculate self-ignition (critical ambient) temperatures as a function of size and shape. The calculated self-ignition temperatures are in fair agreement with published experimental data for two materials, wood fiberboard, and cotton linters.

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An important contribution to this field has been made by Kazuo Akita of the Fire Research Institute, Tokyo, in a paper to be published in *J. Chem. Soc. Japan*, Section of Indust. Chem.

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