THE EVALUATION AND CONTROL OF HAZARDS DUE TO SELF-HEATING

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SYNOPSIS

Self-heating presents hazards in many industrial situations ranging in scale from linseed-oil soaked rags to large stacks of raw or finished materials and in type from aerial oxidation under ambient conditions to condensation reactions in solvents in closed process plant.

This paper is concerned with the assessment and limitation of the risks associated with unstable and oxidizing solids and liquids in open and confined situations. The principal sub-division in the treatment is between solid and liquid substances.

Theory is presented which will enable the conditions defining the critical self-heating state, in any case, to be determined. Additionally, the temperature-time dependence of super-critical self-heating is derived. An experimental method for the evaluation of relevant kinetic and physical parameters for use in conjunction with the theoretical expressions is also derived.

Examples of practical self-heating situations, some of which have been experienced and others which were foreseen, are quoted qualitatively.

Recommendations are made for the limitation of the potential hazards of self-heating materials.

Introduction

Self-heating and its more spectacular associate, spontaneous combustion, has been a familiar phenomenon throughout history. Farming communities have faced the hazard continually in ricks and compost heaps. Since the industrial revolution when large coal tips were established spontaneous combustion has become a familiar occurrence in mining areas. Frequently in the early days of the transport of untreated wool and hides by ship, fires occurred in holds which jeopardized and in many cases destroyed the vessels. However it is only relatively recently, within the past three decades, that a scientific appreciation of and approach to the problem has emerged. Principally this has resulted from the development and manufacture of materials of increasing instability as industrial intermediates, the greater financial investment in chemical industry, and the vast increase in scale of operations in some directions.

The range of self-heating situations is enormous and involves every material capable of exothermic reaction. The reaction may be by aerial oxidation, by decomposition, or by the agency of other materials, *e.g.* water or water vapour. In the first case occasionally, especially in the case of organic materials, attack by micro-organisms may initiate the aerial oxidation. Often impurities or small quantities of materials designed to be present in a large volume of otherwise stable material will initiate the reaction of the bulk. In process vessels and storage a variation in the design or ambient temperature may render marginally stable conditions unstable. Again, the accumulation of quantities of material may lead to a volume which exceeds the safe size under the conditions obtaining—analogous to an atomic pile " going critical ". Occasionally fires occur in which a material escapes from a safe environment into a self-heating situation. This is typified by lagging fires where, for example, oil is absorbed onto an inert but hot thermal insulator.

Particular care is necessary in process vessels where chemical reactions are occurring. In many situations relatively stable reactants are used and an unstable product results. In the interest of plant utilisation and production it is desirable that the reaction is completed in the shortest possible time and that a high yield should result. Thus water cooling may be employed in the initial stages but is superseded at a later stage by steam heating. Under these conditions the failure of, for example, a stirrer which normally maintains the product in a dispersed state will create a hazardous situation. Process vessels are usually strong but may not be vented adequately. Such a circumstance may be, and in fact often has been, beyond the strength of the vessel to contain.

The theoretical treatment of self-heating has been possible, in principle, since theories of reaction kinetics became established by Arrhenius' classical work almost a century ago. This, coupled with the then established laws of heat transfer, made it possible to state the essence of the problem *mathematically in differential form. However no analytical treatment was possible*, even with the equation in its simplest form, because of the complex relationship of temperature and reaction rate. More recently Semenov[1] and Frank-Kamenetskii[2] evolved approximations for this relationship in their work on the autoignition of gases. This made it possible analytically to relate the various parameters of importance in a unidimensional case. Much more recently Chambre[3] and Genenski[4] evolved the method, based on the Frank-Kamenetskii approximation, to deal similarly with cylindrical and spherical symmetries. This work, exclusively thermal, has been expanded, typically by Thomas and Bowes[5] and by Thomas[6] to include mass transfer, various orders of reaction and reactant consumption considerations, and the effects of, for example, heat transfer at the boundary. A wealth of literature is available on the development of better approximate methods than that of Frank-Kamenetskii but it is true to say that the power of the original method remains unassailed.

A Theoretical Treatment of Self-heating

The theoretical approach adopted here is of an essentially simple nature. The rigorous treatment of these problems is complex and for the purposes of this paper unnecessary. The broader objective of preventing excessive deterioration in self-

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heating materials is the more desirable in industry and this, of course, encompasses the fire or explosion hazard.

Any material capable of self-heating will generate heat which is dissipated to the surroundings at rates controlled by the particular physical situations obtaining in each case. Under " stable " conditions, heat generation balances heat loss by the normal mechanisms of conductive, convective, and radiative heat transfer. Hazardous situations are created when this balance is lost, that is, when heat generation outstrips heat loss. Such a situation implies a continuing temperature rise in the self-heating material.

It is usual in the initial stages of a self-heating process for the heat transfer processes to be controlling. Rates of reaction are low and the mass transfer of oxygen, when appropriate, is unimportant. Such is not the case in the later stages of reaction when temperatures are high. But this condition is not within the frame of reference which is adopted here, since in that case the dangerous state will already have been reached.

Thus the theoretical approach is based on purely thermal considerations. The cases considered are of self-heating of liquid and solid materials. In practice each substance should be considered separately since the following assumptions adopted in the derivation of a working theory may not strictly apply. For liquids it will be assumed that the " well stirred " state exists and thus the temperature will be uniform throughout the bulk. The controlling heat transfer process will be considered to be external to the container. Such an assumption may not be valid in the case of very viscous liquids. With solid self-heating materials the controlling heat transfer mechanism is usually conduction within the bulk. This arises by virtue of the usually disperse nature of the solid in particulate or powder form. Again this assumption may not be valid where a homogeneous block of material is to be considered.

If the conductivity of the material in the case of liquid self-heating and the heat transfer mechanism at the boundary in the case of solid is ignored, self-heating is valid if the function hr/k, in which h is the heat transfer coefficient, r is the characteristic semi-dimension, and k is the thermal conductivity, has a value greater than 25. In most cases air cooling represents the worst case, in which $h = 5$ Btu/h°F ft², the value of k for organic liquids is normally not greater than 3 Btu/h°F ft: thus if r is larger than 1·5 ft the subsequent theory applies well. In dispersed solids $k = 0.32$ Btu/h°F ft hence the corresponding value for r is greater than 0·1 ft.

Difficulties may arise where containers are very small or with compact materials. These may be dealt with by reference to the treatment of Thomas.[7]

The theoretical approach will be concerned primarily with liquids because of the more explicit treatment possible. The complementary results obtained elsewhere for solid materials will be quoted but not derived.

Consider a liquid in a container of volume V and of surface area S, of density ρ, and heat capacity c.

Consider further that the exothermic decomposition reaction is of elementary form, i.e. zero order. This is not a crucial assumption but reduces the number of terms necessary in the treatment. The rate of reaction may be expressed in the usual Arrhenius form: $A \exp(-E/RT)$, where A is the reaction rate at very high (infinite) temperature, E is the energy of activation for the decomposition reaction, R is the gas constant, and T is the absolute temperature. If ΔH is the heat of reaction on a mass basis then for the situation so far defined the rate of heat generation is $\Delta H V \rho A \exp(-E/RT)$.

Heat is lost from the surface of the container by the controlling mechanism assumed earlier in the manner represented by the rate equation:

$$Sh(T - T_0)$$

where h is the relevant heat transfer coefficient and T_0 is the temperature of the cooling medium.

The rate of heat accumulation in the material is represented by the differential term:

$$V \rho c \frac{dT}{dt}$$

where dT/dt is the rate of liquid temperature rise.

The rate of heat accumulation, of course, balances the excess of heat generation over heat loss hence:

$$V \rho c \frac{dT}{dt} = \Delta H V \rho A \exp\left(-\frac{E}{RT}\right) - Sh(T - T_0)$$

or:

$$\frac{dT}{dt} = \frac{\Delta H A}{c} \exp\left(-\frac{E}{RT}\right) - \frac{Sh}{V \rho c}(T - T_0) \quad . \quad (1)$$

Fig. 1 illustrates the four situations of importance in this context.

The heat generation curve has the familiar " sigmoid " shape and the heat loss curves are straight lines (assuming that in the range of temperature involved h and c are constant). The points of intersection of the straight lines with the heat generation curve represent the conditions where the rates of accumulation of heat within the liquid are zero. This state is defined by putting $dT/dt = 0$ in equation (1), i.e:

$$\Delta H A \exp\left(-\frac{E}{RT}\right) = \frac{Sh}{V \rho}(T - T_0) \quad . \quad (2)$$

This equation has three roots two of which may be imaginary. Refer again to Fig. 1: an " ambient " temperature, $T_{0,1}$, is associated with three real roots, i.e. three temperatures attainable in principle where the rates of heat accumulation within the liquid are zero. $T_{1,1}$ and $T_{3,1}$ are temperatures of stable equilibrium in as much as any tendency for the system to increase in temperature causes the heat loss rate to exceed the generation rate. $T_{2,1}$ is a temperature of " meta-stable " equilibrium since the reverse is true. Thus a situation defined by temperatures lying between $T_{1,1}$ and $T_{2,1}$ will be stable. Above $T_{2,1}$ continued self-heating will occur up to $T_{3,1}$. Temperature $T_{3,1}$ is the final temperature obtained in the self-heating process and has values of the order of flame temperatures.

The attainment of stable equilibrium is the requirement here hence values of temperature above the meta-stable value are not considered at this point. It is to be seen from Fig. 1 that for a single physically defined system the lines representing heat loss have a constant slope of $Sh/V \rho c$. These lines are parallel and defined in position by the ambient temperature, T_0. Increasing T_0 bodily shifts the heat loss line to the right.

In so doing the temperature range of the stable region is diminished by the approach of T_1 and T_2 toward each other. At a value of $T_0 = T_{0c}$, temperatures T_1 and T_2 coalesce at T_c. This point defines the " critical " state of the system. T_{0c} is the absolute maximum value of the cooling medium temperature under the physical conditions obtaining which will yield a stable situation. T_{0c} and T_c may be related by a simple expression since the slopes of the Arrhenius curve and the heat loss curve are identical at T_c, i.e. from equation (2):

$$\frac{\Delta H A E}{R T_c^2} \exp\left(-\frac{E}{RT_c}\right) = \frac{Sh}{V \rho} \quad . \quad (3)$$
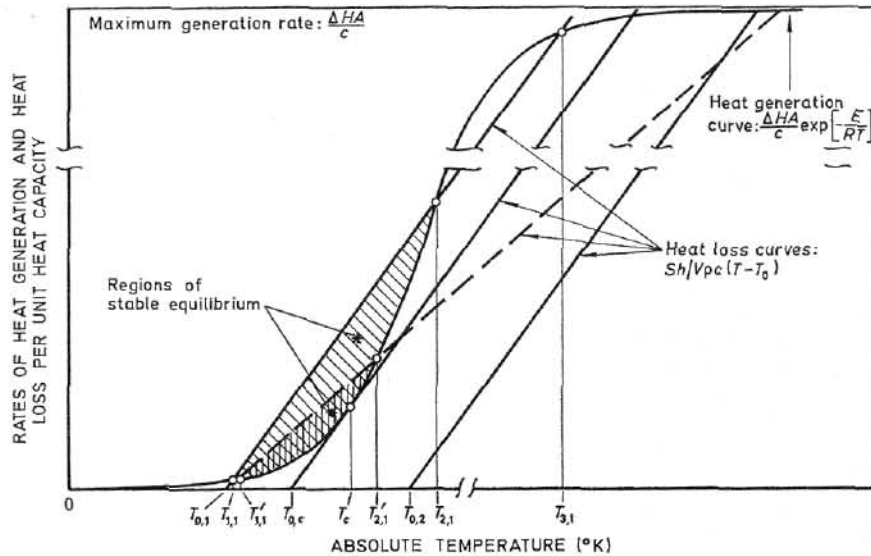
Fig. I.—Stable, meta-stable, and critical self-heating curves

and equation (2) states:

$$\Delta HA \exp\left(-\frac{E}{RT_c}\right) = \frac{Sh}{V\rho}\,(T_c - T_{0c}).$$

Eliminating the exponential we get:

$$T_{0c} = T_c - \frac{RT_c^2}{E}\ . \qquad . \qquad . \quad (4)$$

An ambient temperature of $T_{0,2}$ is not associated with any stable condition and leads inexorably to total reaction.

The dotted line in Fig. 1 denotes the effect of different physical situations. The slope of the heat loss lines is reduced by either or both an *increasing volume–surface ratio* of the container and a *reducing heat transfer coefficient*. Such a reduction in slope with an ambient at $T_{0,1}$ leads to a reduced region of stable temperature lying between $T'_{1,1}$ and $T'_{2,1}$. Sufficient reduction in the slope will lead once more to a critical condition and thence to the super-critical state with inevitably total reaction resulting.

It is of obvious importance to be able to calculate whether or not a system will self-heat uncontrollably in a given situation which may be defined by other factors, *e.g.* storage tank capacity or in the event of, say, failure of a reactor cooling supply. This may be done by a trial and error solution of equation (3) for T_c and further substitutions into equation (4) for T_{0c}.

In the foregoing treatment no mathematical assumptions have been made. An accurate assessment of the practical situation and a knowledge of the kinetics leads to a correspondingly accurate value for the critical conditions within the validity of the approach.

Self-heating liquids often stabilise at a point above the meta-stable or critical temperatures. This is the case where there is little or no confinement, where boiling can occur and the vapours can escape. In this condition the rate of evaporation accommodates the excess of heat generation over heat loss as latent heat. Although material is lost in this way the self-heating hazard is limited. Where there is confinement of the vapours however, continuing temperature *rise is possible*. The restriction of the escape of vapours raises the pressure within the container and thus the boiling temperature of the liquid. This in turn increases the rate of heat generation. Hence a second meta-stable state may be defined by whether or not the escape of vapours can ultimately maintain the pressure within the container at a constant value. Fig. 2 indicates the situation qualitatively. This problem is difficult to

state quantitatively in symbolic form by virtue of the differing flow regimes through the container vent as the internal pressure rises, the non-exact vapour pressure-temperature relationship, and the probable presence of gaseous products of reaction in the vapour phase. Nevertheless, for a particular situation, a trial-and-error calculation will yield values for the hazard to be expected. By way of example the following " simple " situation may be considered: liquid in a container, as before, at temperature, T, and vapour pressure, P, having a vent of area, a. The flow of gases will be considered to be sonic in conjunction with a zero external absolute pressure and the effects of a free space within the container will be ignored. No account will be taken of gaseous products of reaction and of the fact that the mass concentration (if appropriate) of reactant is diminished at this later stage of reaction. Then:

$$Rate\ of\ heat\ generation = \Delta H\,V\rho A \exp\left(-\frac{E}{RT}\right)(as\ before)$$
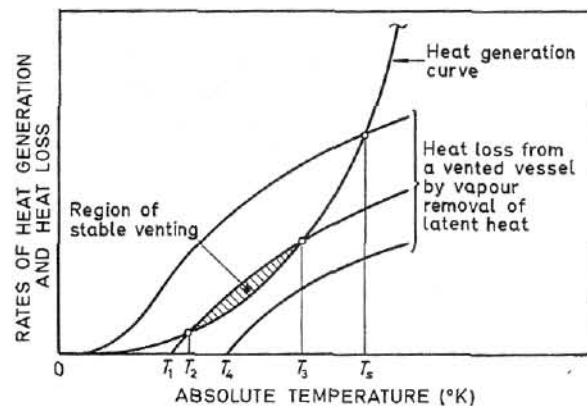
0°K and T_s °K represent the stable venting extremes of temperature when pressures external to the vessel are zero absolute.

T_1, T_2, and T_3 °K represent the boiling temperature at " normal " external pressure, the stable internal boiling temperature when venting to an ambient temperature corresponding to T_1, and the meta-stable conditions respectively.

T_4 °K corresponds to venting to a " high " external pressure. No region of stability results.

The heat loss curves are depressed toward the temperature axis for smaller vents.

Fig. 2.—Stable and meta-stable venting conditions

Rate of heat loss $\qquad = \dfrac{\lambda G}{M}$

where λ is the latent heat of vaporisation, G is the mass flow-rate of vapour, M is the average molecular weight of the vapour. This will be by far the greatest heat loss term and others are ignored.

Vapour pressure equation: $\quad P = K \exp\left(-\dfrac{\lambda}{RT}\right).$

This is the Clausius–Clapeyron equation in which K is a constant (which does not apply with accuracy); and:

The flow equation $\quad G = aC_D k'(Pd)^{\frac{1}{2}}$

Here C_D is the orifice discharge coefficient, k' is a function of the ratio of vapour specific heats only, and d is the vapour density (this under ideal gas conditions is P/RT). Eliminating P, G, and d gives:

$$(RT)^{\frac{1}{2}} \exp\left(-\frac{(E-\lambda)}{RT}\right) = \frac{aC_D k' K}{\Delta H V \rho A M} \qquad . \qquad (5)$$

This may be solved by trial and error for T and thus P may be obtained. These values are the meta-stable values for defining the hazard in the enclosed container under the conditions outlined above. Equation (5) indicates that the area of vent to the volume of the vessel ratio is a material factor in assessing the hazard.

Some of the foregoing is applicable to solids, especially those that decompose rather than oxidise. These present a hazard similar to liquids especially when contained in process plant where venting facilities are not provided. The principal differences between self-heating solids and liquids are that the former—except in process plant—are stored in relatively weak containers such as cardboard cartons, *etc.*, whereas liquids are always kept in mechanically relatively strong containers, *e.g.* barrels and tanks. However, opposing this feature to the favour of solids is the fact that where self-heating goes to completion this often results only in boilover for liquids in vented containers and in the absence of an igniting source, whereas solids inevitably inflame or explode.

The theoretical treatment for the case of solids is complicated by virtue of varying temperatures throughout the bulk of the material. The assumption of a constant temperature within the self-heating medium—justifiable in the case of liquids—is not valid.

The analogous equation to equation (1) describing the process in differential terms is:

$$\frac{\partial T}{\partial t} = \frac{\Delta H A}{c} \exp\left(-\frac{E}{RT}\right) + \frac{k}{c\rho} \nabla^2 T \qquad . \qquad (6)$$

where partial differential terms are involved and ∇ is the Laplacian differential operator. Simplified geometries yield values for $\nabla^2 T$ of:

$\dfrac{\partial^2 T}{\partial x^2}$ *for the unidimensional case*

$\dfrac{\partial^2 T}{\partial x^2} + \dfrac{1}{x}\dfrac{\partial T}{\partial x}$ *for the cylindrical case*

$\dfrac{\partial^2 T}{\partial x^2} + \dfrac{2}{x}\dfrac{\partial T}{\partial x}$ *for the spherical case*

or in general: $\qquad \dfrac{\partial^2 T}{\partial x^2} + \dfrac{m}{x}\dfrac{\partial T}{\partial x}$

where $m = 0, 1$, or 2 according to the case and x is a distance coordinate.

If the Frank-Kamonetskii exponential approximation is adopted the above equation may be transformed, for the stationary state, *i.e.* $\partial T/\partial t = 0$, to:

$$\frac{\partial^2 \theta}{\partial z^2} + \frac{m}{z}\frac{\partial \theta}{\partial z} + \delta \exp\theta = 0 \qquad . \qquad . \qquad (7)$$

where:

$$\theta = \frac{E}{RT_0^2}(T - T_0)$$

$$z = \frac{x}{r} \quad (r = \text{radius or semi-thickness of slab}).$$

$$\delta = \frac{\Delta H \rho A}{k} r^2 \frac{E}{RT_0^2} \exp\left(-\frac{E}{RT_0}\right)$$

in which the approximation referred to is:

$$-\frac{E}{RT} \cong \frac{E}{RT_0^2}(T - T_0) - \frac{E}{RT_0}\left(= \theta - \frac{E}{RT_0}\right).$$

The error in the exponent is less than 1% if $(T-T_0)/T$ is less than 10%. Equation (7) has been solved analytically by Frank-Kamenetskii for $m = 0$ and numerically by Chambre for $m = 1$ and by Genenski for $m = 2$. The corresponding critical conditions, analogous to those considered earlier are:

$m = 0; \quad \delta_c = 0.88; \quad \theta_c = 1.19.$

$m = 1; \quad \delta_c = 2.00; \quad \theta_c = 1.38.$

$m = 2; \quad \delta_c = 3.32; \quad \theta_c = 1.61.$

It is worth transforming equation (2) into a form equivalent to equation (7) for comparison purposes. In this case δ becomes:

$$\delta = \frac{\Delta H A \rho}{h} \frac{V}{S} \frac{E}{RT_0^2} \exp\left(-\frac{E}{RT_0}\right)$$

and equation (2):

$$\delta \exp\theta = \theta \qquad . \qquad . \qquad . \qquad (8)$$

This indicates that $\delta_c = 1/e$ and $\theta_c = 1$ for critical conditions. It must be added however that for liquids more exact solutions for critical temperatures are obtained from equations (3) and (4); for example $\theta_c = 1$ predicts:

$$\frac{E}{RT_{0c}^2}(T_c - T_{0,c}) = 1$$

whereas equation (4) states exactly:

$$\frac{E}{RT_c^2}(T_c - T_{0,c}) = 1.$$

Fig. 3 indicates the locus of critical conditions for the four corresponding values of δ_c and θ_c. The extent of the curve for solids defines all critical states that may be encountered in practice. Interpolation in that region of the curve is possible if a reasonable assessment of the actual geometry in a particular case can be made in terms of the " planarity ", " cylindricality ", or " sphericity " of the shape of the material.

Similarly, for liquids the straight lines joining the fixed point (corresponding to a non-viscous liquid) to the appropriate points on the curve for solids, governed by the shape of the container, will allow assessments of the critical condition for viscous materials.

Where aerial oxidation of a particulate solid is concerned the actual area of particle surface for oxidation is of obvious
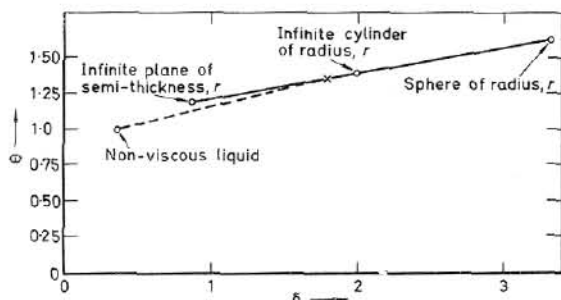
Fig. 3—Plot of critical self-heating parameters as defined in the text

relevance. Kinetics may have been obtained for one size of particle only. These kinetics may be extended to other particle sizes by modifying the Arrhenius coefficient by the ratio of the particle dimensions squared, *i.e*:

$$A_2 = A_1 \left(\frac{d_1}{d_2}\right)^2 \qquad . \qquad . \qquad . \qquad (9)$$

where A_1 and d_1 are the Arrhenius coefficient and dimension for the established kinetics, and A_2 and d_2 are the corresponding values for any new case.

It is to be noted that the expressions for δ involve the scale terms, r^2 for solids and V/S for liquids.

It is desirable in certain cases where super-critical conditions *obtain to discover the extent of the developing hazard.* The object is to ascertain whether any remedial action is possible and, in the worst case, the available time to put emergency procedures into effect. *These considerations demand a deeper enquiry into the self-heating process by discovering the time dependence of temperature.* This is not possible in any case analytically with the exact differential thermal equations. It is however possible in the adiabatic case (not considered here) if the Frank-Kamenetskii exponential approximation is adopted, and in the case of a liquid if a simple series is substituted for the approximate exponential in the integration.

Here I shall deal with the liquid case by way of example. Other workers[8, 9] have treated the more complex problem of super critical self-heating in solid materials.

The general equation as quoted earlier is equation (1):

$$\frac{dT}{dt} = \frac{\Delta HA}{c} \exp\left(-\frac{E}{RT}\right) - \frac{Sh}{V\rho c}(T - T_0).$$

If we make the substitutions:

$$\delta = \frac{\Delta HA\rho}{h}\frac{V}{S}\frac{E}{RT_0^2}\exp\left(-\frac{E}{RT_0}\right)$$

$$\theta = \frac{E}{RT_0^2}(T - T_0)$$

$$\tau = \frac{V\rho c}{Sh}$$

the equation transforms to the approximate:

$$\tau\frac{d\theta}{dt} = \delta \exp\theta - \theta \qquad . \qquad . \qquad (10)$$

or:

$$t = \tau \int_0^\theta \frac{d\theta}{\delta \exp\theta - \theta} \qquad . \qquad . \qquad (11)$$

Equation (11) cannot be integrated analytically as it stands except as stated earlier in the adiabatic case when:

$$t = \frac{\tau}{\delta}(1 - \exp\theta).$$

A polynomial in θ which may be substituted for $\exp\theta$ in which a degree not greater than two is desirable. Let this be $f(\theta)$. Then:

$$f(\theta) = \alpha + \beta\theta + \gamma\theta^2.$$

Confining our interest to θ in the range $0 \leqslant \theta \leqslant 2$ and requiring of the polynomial that $f(\theta) = \exp\theta$ for $\theta = 0$ and $\theta = 1$ and further that $f(\theta)$ and $\exp\theta$ touch at $\theta = 1$, then:

$$f(0) = 1$$

$$f(1) = e$$

$$f'(1) = e$$

then $\alpha = 1$, $\gamma = 1$, and $\beta = e - 2$ or 0.72.
Thus:

$$t = \frac{\tau}{\delta}\int_0^\theta \frac{d\theta}{1 + [0.72 + (1/\delta)]\theta + \theta^2} \qquad . \qquad (12)$$

The nature of the roots of the quadratic in θ determines the solutions of the integral. Three cases may be distinguished.

(*a*). No real roots, *i.e.* $\{[0.72 - (1/\delta)]^2 - 4\}^{\frac{1}{2}} < 0$, or $\delta > 0.368$—this predicts that thermal explosion will occur.

(*b*). Equal roots, *i.e.* $\delta = 0.368$—this defines the critical condition.

(*c*). Two real roots, *i.e.* $\delta < 0.368$—these roots encompass the range of stable temperatures. In this case, by the properties of quadratic expressions,

$$\theta_2 - \theta_1 = \{[0.72 - (1/\delta)]^2 - 4\}^{\frac{1}{2}}$$

in which θ_2 and θ_1 are functions of the stable extremes of temperature.

In the context of this section, namely—supercritical conditions, *case (a) is relevant.* The general solution of the integral here is:

$$t = \frac{2\tau}{\{4 - [0.72 - (1/\delta)]^2\}^{\frac{1}{2}}} \times$$

$$\left\{\tan^{-1}\frac{2\theta + [0.72 - (1/\delta)]}{\{4 - [0.72 - (1/\delta)]^2\}^{\frac{1}{2}}} + \tan^{-1}\frac{[(1/\delta) - 0.72]}{\{4 - [0.72 - (1/\delta)]^2\}^{\frac{1}{2}}}\right\}$$

$$(13)$$

In practice this means that, since self-heating times are long when conditions are just super-critical, steps may be taken to remedy the situation. *These steps are to increase the* surface-to-volume ratio of the material by, for example, pumping from a large container into a number of smaller ones, to increase the heat transfer coefficient by using water sprays to supersede air cooling, or simply increasing the flow-rate of coolant where possible—or to reduce the temperature of the cooling medium, *i.e.* reverting from steam heating to water cooling in, for example, a process vessel. The effects of these measures may be clearly seen by reference to Fig. 1 where the upper intersection of the cooling curves and the heat generation curve is moved to a point corresponding to a temperature greater than that of the self-heating material at that instant.

Remedial steps with solids are limited by virtue of the relative unimportance of superficial surface heat transfer. In practice the actions possible are: *the breakdown of the stock into numerous smaller units, or the blanketing of the* material. The latter involves either preventing the ingress of air to oxidisable material or complete quenching with, for example, water.

Practical Situations Involving Self-heating

In this section specific situations are considered in a general way. These situations are based on the experience of circumstances which have or which might have given rise to hazard. The six sub-sections below, it is felt, indicate the range of potential hazard which might arise. However the range is not comprehensive.

Storage of solid materials reactive with air

The storage of solid materials which may react with air comprises a very large field. Instances are: finely divided oxidisable materials, *e.g.* steel turnings, activated charcoal, *etc.*, and materials of natural organic origin, *e.g.* sawdust, coal tips, hay ricks, *etc.* For the latter a complicating feature of the self-heating process is the contribution made by attack by micro-organism. The later stages however are exclusively chemical reaction.

Steel turnings present problems both in theory and in practice. There is very little published information on the kinetics and none of this is in a sufficiently unambiguous form to use with confidence. The reaction is not simple since there is usually contamination with liquid water. Water vapour may also contribute over part of the heating process. Furthermore, turnings are always contaminated with cutting oils which are, to some degree, unsaturated and thus readily oxidised.

Recommendations may not be made concerning the storage of steel turnings without recourse to experiment. Experience indicates that spontaneous combustion in turnings cannot be combatted with conventional fire-fighting methods. This is due to the ability of hot iron to react with water exothermically—generating hydrogen—and to the high volumetric heat capacity of the material. Even total immersion of the self-heating mass is ineffective because such means do not reduce temperatures below critical values unless persevered with. Steel turnings appear to be somewhat " sensitized " after they have self-heated. Possibly this is explained by the development of a greater surface area for reaction or even the preferential oxidation of intermediates generated by a previous heating.

Fires occurring from the stacking of activated charcoal are commonplace. Recommendations exist for stacking which, if adhered to, ensure adequate air-cooling. A point of importance is that fresh charcoal, bagged in units of one hundredweight, may still be warm on delivery and recommended stacking may prove ineffective in preventing spontaneous combustion.

Materials of natural organic origin are prone to attack by micro-organisms. Some workers have held that the same is true for some inorganic materials such as coal, iron pyrites, *etc.* Opinions differ here but where the suspicion exists that this may be so tests should be performed to ascertain the facts. The determination of chemical kinetics, of course, enables the prediction of critical conditions. Where these conditions are in the range 50–75°C—normally safe in most stacking situations—attack by micro-organisms may raise the bulk temperature to supercritical conditions. Where this may be suspected but tests have not been made, temperature monitoring of the stack is necessary. Colonies of micro-organisms establish themselves at an exponential rate. The time to reach equilibrium is governed by the rate at which they can raise the temperature of their environment and this in turn controls their reproduction rate. Experience indicates that this is of the order of months, typically six to nine months. Thus any monitoring must extend over that length of time before valid conclusions can be reached.

Such is the experience with wood shavings. In a real situation wood shavings were stacked to a depth of about 25 ft. Approximate kinetics indicated that such a stack should have had a critical temperature of about 60°C. The open-air stack self-heated to smouldering temperature however. Study revealed in this case that the relevant micro-organisms were capable of maintaining stable colonies at temperatures up to 75°C. This agency had raised the temperature of the material from the stable value $T_{1,1}$ (Fig. 1) to values greater than $T_{2,1}$. The process however occupied seven months. In this case the only remedial action possible, and in fact necessary since this was a raw material not waste, was to dig out the smouldering pockets, sub-divide the stack, and reduce its height to about 12 ft. Prevention of further heating was achieved by this means.

Coal tips present a danger of spontaneous ignition which is well established. Usually, however, where there is no danger to life or property—and there usually is not—tips are allowed to smoulder. Normally this involves only internal fire which roves throughout the bulk as favourable combustion situations develop. Cavities within the mass develop which present perils to children and animals or workmen. Where the situation is known to exist, depending upon the scale of combustion, remedial action—limiting the extent of the fire and preventing access—may be taken to preserve life and property. Occasionally, however, a situation develops in which it is of paramount importance to extinguish the fire. The scale of the problem in this context is so huge, in general, that insufficient extinguishing resources are available. Even if they were, the time necessary to fight the fire would be very long. Digging out is only a possibility where combustion is incipient. (This, of course, applies to all cases under this heading.) Practically the only measure capable of achieving success commensurate with the labour involved is to eliminate the access of air. This may be attained by the complete blanketing of the tip with, for example, a layer of ground limestone which, to be fully effective, requires continual moistening. Because of the enormous heat capacity involved, months—perhaps years—must elapse before the combustion can be said to have stopped. This method of limiting established combustion and supercritical self-heating has been used with success in many instances.

Storage of thermally unstable solids

Examples of the storage of thermally unstable solids range in hazard up to explosives and detonators. The concern is with materials capable of decomposition, polymerisation, or oxidation where the oxygen is released from chemical combination within the material. Explosives form a different category and, although what is relevant in general here is relevant to them, established codes of practice and Acts of Parliament effectively limit their hazards.

Peroxide and organic nitrates forming industrial intermediates and, in combination with other materials, proprietary products, *etc.*, are the major interests. With these, kinetics provide the data necessary to define critical states.

Typical of the problems involved was a case where a thermally unstable powdered solid issuing from a wet process required drying for packaging and sale. The situation involved optimising the performance of a tray drier—basically improving the yield by raising the drying temperature and increasing its capacity by using more trays. Associated with various proposed drying temperatures were corresponding layer thicknesses. Problems such as the elimination of dead air spaces and hot spots as well as monitoring and control were considered. Recommendations were made in the light of available kinetic data and chemical engineering concepts.

Another case involved the elimination or otherwise of proprietary blends of organic nitrates as the cause of a fire. The more obvious causes seemed unlikely and much of the other stock was of a non-self-heating character. These blends

were stored in sacks and drums to form stacks of sizes in which it was not possible to establish spontaneous combustion.

In this case experiments were performed on the materials involved and the effects of scale of container were studied. It transpired that the critical ambient temperature relevant to the storage of single containers was about 110°C. This value is reduced for accumulations of containers but in all probability was not less than 90°C for these situations. Thus, in this case, self-heating was probably not the cause of the fire. No adequate explanation for the fire has been forthcoming.

Lagging fires

Lagging fires are common in industry. Occasionally they are due to combustible laggings; much more often they are the result of spillages of combustible liquids. The liquid is absorbed by the lagging material and held in a non-mobile state with, initially at least, ample air supplies. The prevailing physical and chemical conditions determine whether or not self-heating becomes supercritical. The chemical kinetics will depend upon the degree of saturation of the lagging material in as much as the air-to-fuel surface ratio will depend upon this. Thus the overall kinetics cannot be precisely determined without experiment in any case since the amount of the spillage and its distribution may not be foreseeable.

In principle the problem is one of self-heating in cylindrical symmetry with a superimposed temperature gradient. Assuming all the necessary parameters can be ascertained, then a simple approach is to consider that the corresponding critical value $\delta_c = 2\cdot00$ may be used to evaluate T_c. If T_c is below the lagging temperature at any point then self-heating must be considered to be possible. Such an approach will over-estimate the hazard. A better theoretical estimate of the critical condition is due to Thomas and Bowes.[10]

The occurrence of lagging fires can largely be eliminated if an experimental determination of the self-heating properties of likely contaminents of various laggings is undertaken. Foamed glass is found to be suitable in practically all cases since, because of the non-absorbent nature of the insulation, the accumulation of material is eliminated.

Storage of thermally unstable liquids

Chemical kinetics define the critical conditions with liquids. Where self-heating is likely, suitable precautions in the way of vents or ancillary dumping vessels should be provided. Where these precautions are not possible, *e.g.* with sealed containers and drums, the quantity and/or the location of storage vessels should be carefully determined. The super-critical self-heating of these materials leads to venting of vapour and products. Generally these, whilst being flammable—perhaps spontaneously so—add little to the hazard of a container explosion. The next section deals with venting more fully.

Where drum storage is anticipated local conditions of ambient temperature and solar radiation levels are relevant. In this case the preservation of a finite ullage is the prime concern. Such a condition will maintain the container free from distortion at the very least. Horizontal storage of drums is more preferable in this context. In the event of super-critical heating the flat drum ends, being the weakest areas, will relieve the pressure and the contents will flow into a non-self-heating configuration.

Process vessels must be protected against plant failure or the errors of operatives. These may be typified by, for example, stirrer failure, and live steam application to a joint cooling–heating jacket.

Venting of reactions in vaporizing solvents

Of the reactions carried out in vaporising solvents a typical one is a condensation reaction in water solution though, of course, solvents of all descriptions are used. However the vent requirements may be ascertained quantitatively by balancing the vent flow of solvent vapour (carrying latent heat) and the heat generation rate by reaction, the two being linked by the vapour pressure–temperature relationship for the solvent. Experience here has indicated that this approach is satisfactory.

Experiments in this context were performed by Rutledge[11] on a solution of hydrogen peroxide undergoing catalytic decomposition in water. It was found that stable conditions existed for orifices larger than 4 mm, in a 500 ml vessel, and resulted in finite internal pressures (about 2 lbf/in² gauge). However for a 3 mm vent no stable condition existed and internal pressures rose to exceed 900 lbf/in² gauge rapidly.

Venting of solid reactions yielding gaseous products

In the venting of solid reactions yielding gaseous products the consideration is of materials not associated with solvents. In this case, as there is very little heat capacity in the vented gases—unlike vaporising materials where latent heat is absorbed—the temperatures rise the more rapidly. Once again critical thermal conditions may be defined, however stable venting is rather less likely since (see Fig. 2) the corresponding heat loss curves are not likely to intersect with the heat generation curve. The difference is, as stated above, that there is no latent heat of vaporisation associated with gaseous products.

The Experimental Determination of Self-heating Potentialities

Experimental methods for determining self-heating potentialities differ accordingly as the self-heating reaction is aerobic or anaerobic. In the former case the experiments must be performed in a way which allows the free circulation of fresh air but which minimises cooling effects. Also, since this case is relevant to solid materials or liquids absorbed onto a solid substrate, reaction takes place at the "solid" surface. An estimate of the mean surface (per unit volume, say) must be made if results are to be extended to the same materials in in different size ranges. Where the self-heating reaction is anaerobic, that is to say, for example, decomposition, polymerisation, or condensation, the kinetics may be established by conventional means. In addition, with these materials, small-scale tests may be performed—as for aerobically reacting substances—which will render the determination of kinetics unnecessary.

Consideration of the self-heating equation indicates that critical conditions may be related, for the same material in the same geometrical configuration, to differing accumulations by:

$$\left(\frac{V}{S}\right)_1 \frac{1}{T_{c,1}^2} \exp\left(-\frac{E}{RT_{c,1}}\right) = \left(\frac{V}{S}\right)_2 \frac{1}{T_{c,2}^2} \exp\left(-\frac{E}{RT_{c,2}}\right)$$

for the liquid case, and:

$$\frac{v_1^2 d_1^2}{T_{0,c,1}^2} \exp\left(-\frac{E}{RT_{0,c,1}}\right) = \frac{v_2^2 d_2^2}{T_{0,c,2}^2} \exp\left(-\frac{E}{RT_{0,c,2}}\right)$$

for "solids". The suffices $_1$ and $_2$ correspond to values of the various parameters in the two accumulations. Thus it will be appreciated that any comparable situations involving the same materials may be related. The value of E, the

energy of activation for the reactions concerned, however remains to be evaluated. Where kinetics may be determined (anaerobic reaction) the value of E is readily available. If the mechanism of self-heating involves aerial oxidation however, conventional methods are not suitable.

Experimental determinations of self-heating propensities are fraught with errors which may not be entirely eliminated especially where " solid " materials are concerned. Against this background it is felt reasonable to simplify the existing theory for solids so that results can be obtained, the applications of which are useful so long as the simplifications are always borne in mind. If the scale of a self-heating experiment is sufficiently small, large errors in assuming a linear temperature gradient within the solid are avoided. The heating equation then becomes:

$$\frac{dT}{dt} = C \exp\left(-\frac{E}{RT}\right) - D(T-T_0) \qquad . \quad (14)$$

where C and D are combinations of the parameters:

	Liquids	" Solids "
D	$\dfrac{Sh}{V\rho c}$	$\dfrac{2k}{c\rho}\dfrac{\phi}{r^2}$
C	$\dfrac{\Delta HA}{c}$	$\dfrac{\Delta HA}{c}$

where ϕ is a shape factor, i.e. " sphericity " or " planarity " as the case may be, of constant value if comparable situations are studied.

The temperature-time record for an experiment performed at an ambient temperature just supercritical is represented by Fig. 4. From a number of such experiments reasonable values for C, D, and E may be estimated. At low temperatures reaction is insignificant and, as indicated, corresponding values of T and t may be inserted into the integrated form of equation (14) ignoring the contribution of self-heating:

$$D = \frac{1}{t_2 - t_1} \ln\left(\frac{T_0 - T_1}{T_0 - T_2}\right) \qquad . \quad (15)$$

When self-heating has raised the temperatures to above ambient values, the measurement of temperature gradients and their corresponding temperatures yield:

$$E = \frac{RT_3 T_4}{T_4 - T_3} \ln\left[\frac{(dT/dt)_4 + D(T_4 - T_0)}{(dT/dt)_3 + D(T_3 - T_0)}\right] \qquad . \quad (16)$$

and:

$$C = \left[\left(\frac{dT}{dt}\right)_4 + D(T_4 - T_0)\right] \exp\left(\frac{E}{RT_4}\right) \qquad . \quad (17)$$
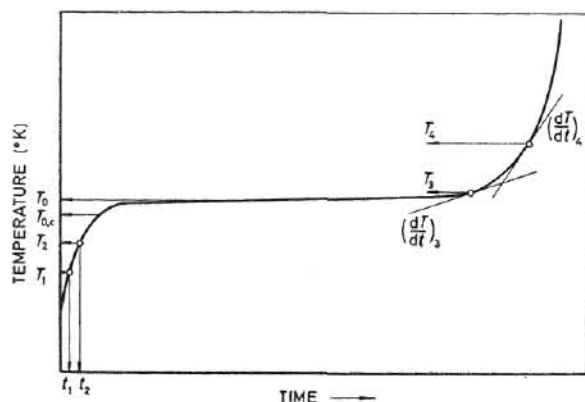

Fig. 4.—Experimentally determined self-heating curve

Errors are potentially large in that reliance is placed on the accurate measurement of actual temperatures as well as temperature gradients. It is felt however that reasonable care and the use of sensitive instruments should minimise these.

It is to be noted that, approximately, in all cases:

$$\delta_c = \frac{D}{C}\frac{E}{RT_{0,c}^2}\exp\left(-\frac{E}{RT_{0,c}}\right) \qquad . \quad (18)$$

where δ_c has the value appropriate to the circumstance.

Summary

In conclusion it may be stated that where self-heating may be foreseen a quantitative treatment of the hazard is possible. Well-attested theory is available which in connection with a few simple small-scale experiments where appropriate will wholly define the hazard in a large number of possible configurations. As has been stated in the introduction and reiterated throughout, each situation should be considered individually and an application of the relevant conclusions must take into account the simplification imposed by the treatments. No account has been taken of mass-transport processes or reactant consumption which, at some stage in all self-heating operations, must compete with and eventually supersede thermal control. Hence the thermal theory whilst accurately defining most critical conditions is always conservative. Also the hazard of super-critical states is always overestimated.

It is recommended that where the danger is known to exist strict adherence to the principle of maintaining sub-critical conditions must be ensured. That is:

(1). Maintaining accumulations of material in masses of sub-critical size.

(2). Maintaining " ambient " temperatures at less than critical values.

(3). Ensuring adequate venting of process vessels and containers.

Plant failure and operational inexpertise are the two most common causes of disasters in industry. Although these in themselves cannot be eliminated, plant may be made intrinsically safe at the design stage—by obviating the more costly alternative of modification to existing equipment.

In all cases a disaster programme may be drawn up which will minimise the risk to plant and personnel.

Acknowledgments

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DISCUSSION

THE CHAIRMAN (Mr. R. J. Kingsley) asked the author to comment on lagging fires.

Dr. GUGAN said that there seemed to be a lack of knowledge on the subject. Many people were aware of the dangers and hazards of lagging fires but so far as hard facts and figures were concerned there was very little in the literature.

Lagging material usually had cylindrical symmetry, and throughout it carried a distributed temperature, high on the inside and low on the outside. The effect of the escape of combustible material on to a lagging depended upon the exact situation. Assuming that it escaped uniformly on to the lagging, then one had a liquid which would otherwise be mobile and would escape from the situation but was unable to escape because of the lagging material. Whereas it may have been non-hazardous in its original situation it presented a large surface area for oxidation on the lagging material. There might be some complication due to catalysis by the lagging material but, in general terms, one could apply the theory for self-heating in cylindrical circumstances if one knew the kinetics which were relevant. He was helped here by Thomas and Bowes in their work at the Fire Research Station. He referred to some of their theoretical results contained in the Fire Research Note 585 (January 1965). The equation relating to critical conditions quoted in the Note should enable one to define, again if one knew the kinetics, which was a potentially dangerous situation and which was not, and which was critical. As far as he knew, this equation had not been tested by the results of experiments on laggings of conventional form. He believed that it had been tested in a plane situation but not in a cylindrical situation. That was really as far as it went.

Since the Symposium the results of experimental work had been published by the Fire Research Station in their notes 665 and 666 (June 1967). It appears that the experimental results and the theoretical conclusions yield fair agreement only

THE CHAIRMAN wondered whether there was evidence that molecules containing oxygen were rather more liable to this particular hazard than others.

Mr. F. J. OWEN said that his question was on filter cake fires where a filter cake had been discharged into an open 40 gal drum. It had been left standing and a day or two later was found to be smouldering. He asked it that kind of situation had been investigated.

Dr. GUGAN said that he knew of similar circumstances in a vessel where a solid product was being generated involving a reaction in solution. The material was normally kept in a dispersed state by an impeller which failed, and the material being less dense than the solvent collected as a cake at the surface of the liquid. In that case it went on fire. These seemed rather similar circumstances in that there was wet material in much the same sort of symmetry, a shallow cylindrical block or slab-type block which went on fire. He knew of situations like that. In many cases one realised the hazard by hindsight.

Mr. A. D. CRAVEN asked the Chairman if he was worried about the oxygen atoms in the substrate or the oxygen atoms in the potential fuel.

THE CHAIRMAN replied that it was in the fuel.

Mr. CRAVEN said that he could give at least one instance where conditions were reversed from those described. It was in a low-temperature storage vessel where the temperature inside was below ambient and insulation was effected by cork lagging. That caught fire spontaneously somewhere between the cold container and the outside, on a sunny day. The fuel involved was a pure hydrocarbon with no oxygen in the molecule.

Mr. B. J. PRIESTLEY pointed out that in the paper it was stated that the theory applied where hr/k was greater than 25. He was interested to know on what basis this figure was arrived at. Would it not vary anyway with temperature difference over the ambient surroundings?

Dr. GUGAN said that this particular section was attributed to Thomas and Bowes at the Fire Research Station who had done some practical work on establishing the values of this parameter for which the theory did work. He took the point that the temperature regime at which one worked might be important and that needed looking into.

The first section of the paper was what he considered to be a general review of the theory and, as such, refinements were quoted which provide a better theoretical basis. The point had not been taken further, however, because the prime objective of the paper was to present a simplified approach consistent with the needs of the working engineer.

Ref. 7 of the paper deals fully with the significance of α, the thermal diffusivity (hr/k), which is opposite to solid and viscous liquid situations, and Fig. 2 of that paper shows the variation of δ_c with α. The value of α, taken to be 25, was that at which it was considered the various values of δ_c were sensibly equal values for $\alpha = \alpha_0$.

Thermal diffusivity was, in general, temperature dependent and allowance should be made for its variation over the temperature range considered. However, as Ref. 7 indicates, the critical conditions (corresponding to δ_c) were strongly influenced by the value of α in which r (the characteristic dimension of the accumulation) had the most profound effect. The effect of temperature difference over the surroundings was expected to be of great significance in this context.

Mr. PRIESTLEY asked what happened in a situation where one had a self-heating, self-generating system with a smaller radius that that quoted in the example? Was the implication that it would never rise to a danger point or was it the point that the temperature rise would be smaller?

Dr. GUGAN replied that one could define critical temperature even if one was within the value quoted ($hr/k = 25$) of this function. In one of the particular cases mentioned if the radius was less than 0·1 ft, it meant that the subsequent theory was not strictly valid.

Ref. 7 showed the relationship between δ_c and α (equation (15) which might be stated for a particular material and symmetry as:

$$\delta_c = \frac{K_1}{K_2 + (1/\alpha)}$$

δ_c, as defined in his paper, was a function of r_c and T_{0c}. Substitution of this function into the above equation yielded a relationship in which the variation of T_{0c} with r_c was not immediately apparent but might be discovered by inspection.