

# Thermo-kinetic explosions: Safety first or safety last?

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## ABSTRACT

Gas and vapor explosions have been involved in industrial accidents since the beginnings of industry. A century ago, at 11:55 am on Friday September 24, 1920, the petroleum barge *Warwick* exploded in London’s docklands and seven men were killed. Understanding what happened when it blew up as it was being refurbished, and how to prevent similar explosions, involves fluid mechanics and thermodynamics plus chemistry. I recount the 1920 accident as an example, together with the history of thermo-kinetic explosions prior to 1920 and up to the present day, and I review the history and the actual state of the science of explosion and the roles of fluid mechanics, thermodynamics, and chemistry in that science. The science of explosions has been aware of its societal implications from the beginning, but, despite advances in health and safety over the past century, is there still work to do?

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## I. GAS AND VAPOR EXPLOSIONS BEFORE 1920

One risk of using a public toilet in ancient Rome was of getting one’s bottom singed (or worse); methane explosions in sewers were known from classical times.<sup>1–3</sup> Mines too have always accumulated inflammable gases, in particular firedamp—methane—which has caused explosions for as long as mining itself. So, it is not surprising that it is in mining that we see the first research on preventing gas explosions.

The 1812 disaster at Felling pit near Gateshead, where 92 men were killed through a methane explosion, was one of the stimuli for the invention of safety lamps to prevent explosions.<sup>4</sup> Humphry Davy and George Stephenson were two of the key figures involved in developing safe miners’ lamps—the Davy lamp<sup>5</sup> and the Geordie lamp,<sup>6</sup> respectively—designed to supersede the use of naked candle flames to illuminate mines. Davy’s lamp used a wire gauze to supply air; Stephenson’s Geordie lamp used narrow tubes for the same purpose. There was a rather squalid dispute between the two men and their supporters over priority in the invention.<sup>4,6</sup>

Davy had an assistant when working on the safety lamp. That was Michael Faraday. Faraday later took over Davy’s position at the Royal Institution and wrote a beautiful book, *The Chemical History of a Candle*.<sup>7</sup> About mine explosions, he wrote that

“In olden times the miner had to find his own candles, and it was supposed that a small candle would not so

soon set fire to the fire-damp in the coal mines as a large one .... They have been replaced since then by the steel-mill, and then by the Davy-lamp, and other safety-lamps of various kinds.”

Early safety lamps were dimmer than candles, and the gauze or tube did not completely eliminate the risk of explosion, and improvements to the designs of miners’ safety lamps continued to be worked on throughout the 19th century.<sup>4,8</sup>

As well as gases, inflammable vapors<sup>9</sup> were likewise the cause of explosions. Thomas Graham, of Graham’s law fame, was one of those who investigated the loss of the paddle steamer *Amazon* in 1852. While the cause of the fire that led to 105 to 115 deaths when she sank off the Isles of Scilly on her maiden voyage was never absolutely established, Graham thought that the presence of volatile inflammable liquids in the store room near to the engines was a key factor:<sup>10</sup>

“The sudden and powerful burst of flame from the store-room, which occurred at the very outset of the conflagration, suggests strongly the intervention of a volatile combustible, such as turpentine, although the presence of a tin can of that substance in the store-room appears to be left uncertain. I find, upon trial, that the vapour given off by oil of turpentine is sufficiently dense, at a

temperature somewhat below 100°, to make air explosive upon the approach of a light. Any escape of turpentine from the heated store-room would therefore endanger a spread of flame by the vapour communicating with the lamps burning in the boiler room or even with the fires of the furnaces.”

On October 2, 1874, the *Tilbury*, a barge on the Regent’s Canal in London, exploded killing its crew of four; it was carrying both barrels of petroleum and gunpowder. The spot, at the edge of Regent’s Park under a bridge over the canal, is now called *Blow Up Bridge*. It was lucky, as it were, that this happened at 5 am, otherwise many more people would have died.<sup>11,12</sup> Frederick Abel, developer of guncotton and inventor of cordite, mentioned this example in a lecture “On Accidental Explosions” he gave at the Royal Institution in 1875 that was subsequently printed in *Nature*.<sup>13</sup>

“Among other “accidents” referred to as arising from a similar cause, was the recent explosion of the powder-laden barge in the Regent’s Canal. It was established by a sound chain of circumstantial evidence that this explosion must have been caused by the ignition, in the cabin of the barge, of an explosive mixture of air and of the vapour of petroleum, derived from the leakage of certain packages of the spirit which were packed along with the powder.”

The *Tilbury* accident accelerated the passing of the Explosives Act in 1875, which in the UK regulated the manufacture and carriage of dangerous substances.

The industrializing world was demanding more and more chemical products. The petrochemical industry was, figuratively speaking, exploding. Abel returned to the theme of accidental explosions a decade later for another lecture at the Royal Institution in 1885, this time entitled “Accidental Explosions Produced by Non-Explosive Liquids,” in which he specifically discussed “accidents connected with the transport, storage, and use of volatile inflammable liquids, which are receiving extensive application, chiefly as solvents and as illuminating agents.”<sup>14</sup>

Redwood wrote a very thorough report in 1894 on “the transport of petroleum in bulk”<sup>15</sup> motivated by the explosion of the petroleum tank-steamship *Tancarville* while being worked on in Newport, Wales in 1891, in which five men were killed. Redwood comments

“In a lecture delivered at the Royal Institution, on the 12th March 1875, Sir Frederick Abel called attention to the special danger arising from the accumulation of the vapour of petroleum spirit, or the similar liquid, in unventilated places and referred to several cases of fire and explosion in illustration of his remarks, including one which occurred with coal-tar naphtha in 1847. In a more recent lecture (on the 13th March 1885) he enlarged upon this theme, and gave particulars of explosions due to the use on board Her Majesty’s ships of paint-driers containing dangerously inflammable liquid hydrocarbons. For many years past Colonel Majendie has briefly described in the Annual Reports of H.M. Inspectors of Explosives, the more noteworthy of the petroleum accidents which have taken place during the preceding twelvemonths (although petroleum, not being an explosive

substance, does not come within the scope of the Explosives Act); and his reports constitute most valuable contributions to the literature of the subject.”

In his report, Redwood lists many other similar incidents that give a depressing litany even at this early date of the petrochemical industry.

“These accidents arose from the incautious handling of a material which was not generally known to contain a liquid readily converted into vapour, and in that condition capable of forming a powerfully explosive mixture with air,”

he writes. Of the *Tancarville* in particular he relates

“The evidence given at the Board of Trade inquiry conclusively demonstrated that the accident was due to the ignition of an explosive mixture of petroleum vapour and air in the ballast tank, but did not clear up the question of how the ignition took place. Samples of the petroleum were examined by Dr. Dupré and by the Author, with the result that it was ascertained that one gallon of such oil would render 200 cubic feet of air feebly, and, about 58 feet of air strongly, explosive; therefore 20 cubic feet of oil would have sufficed to render the atmosphere of the water-ballast tank, the capacity of which was about 6,000 cubic feet, explosive.”

As we shall see, the 1920 accident was to be very similar in its origin. Just the year before the accident that is our principal example, on July 15, 1919, there occurred the Cardiff dockland disaster when the oil tanker *Roseleaf* exploded, killing the 12 men working on her. This was determined to be owing to a man carrying a naked flame down into the ship.

## II. THE EXPLOSION OF THE PETROLEUM BARGE, WARWICK, ON SEPTEMBER 24, 1920

The Isle of Dogs, a tongue of land formed by a large curve of the River Thames in east London, was once marshes but by the turn of the 20th century had become a great hub of industrial activity related to the river. Samuel Hodge and Sons, engineers and ship repairers, had premises at Union Iron Works, 104 Westferry Road in Millwall, the Isle of Dogs, from the 1850s to the mid-1920s. The site of these works where the accident that killed seven men occurred is now part of a public park on the riverbank, the Sir John McDougall Gardens. My grandfather Charles James Cartwright (1882–1920) traveled across the river from Bermondsey to the Isle of Dogs every day. He worked as a welder at Samuel Hodge’s until his death in this accident alongside his brother, who was also killed, and his father-in-law, my great-grandfather, Thomas Tilling, who survived the explosion. The following account of the accident is taken from the report written by G. Stevenson Taylor, Inspector of Factories.<sup>16</sup>

The *Warwick* was a petroleum barge, designed to carry 42 000 gal of petrol in its tank [Fig. 1(a)]. It had last been used for that purpose from 17th to 20th September, 1920, before being sent for cleaning prior to work being carried out on it. On 22nd September, it was cleaned out by pumping out the remaining 19 gal of petrol and mopping up the remainder with cotton rags. Then, on 23rd September, it underwent steam cleaning by putting a steam hose into the tank. On

the morning of 24th September, the barge was towed up the river from Purfleet where the cleaning had been carried out to the Isle of Dogs. As it approached the wharf, it could be seen from the barge that a work party was ready to come aboard with acetylene torches; clearly, they were intending to get to work straight away, and this alarmed the lighterman [bargeman] on board. My great-grandfather “Tilling heard Lazell, the lighterman, tell James [the foreman] that, if they were going to use lights [i.e., flames] on the barge, he was off.” The barge was moored at 11:45.

The idea was to remove the petrol tank from the barge to alter its bulkheads according to the latest regulations. For this, the first job was to fit lifting lugs onto the tank, which entailed removing rivets from the tank top with welding apparatus. As Taylor’s report states

“Charles Cartwright (deceased) was using an oxy-acetylene burner, and with this he was seen to burn the heads from a number of rivets along the central joint in the tank top.”

At 11:55, the barge exploded [Fig. 1(b)]; “all the witnesses describe the explosion as of great violence.” One of these witnesses was Tilling, who “was on the wharf at the time of the explosion and was blown against a wall and slightly injured.”

Let us continue with Taylor, who pieces together the facts of the matter in the best detective tradition.

“The nature and extent of the damage to the tank and barge, as well as the evidence of the witnesses, definitely indicate that a violent explosion occurred within the tank itself and not in the surrounding spaces of the barge. The fire, which lasted several minutes after the explosion, and the blackening of parts of the interior of the tank by a slight sooty deposit, as well as the general nature of the damage indicate that the explosion was due to the ignition of some carbonaceous material (gas or vapour)”

wrote Taylor.

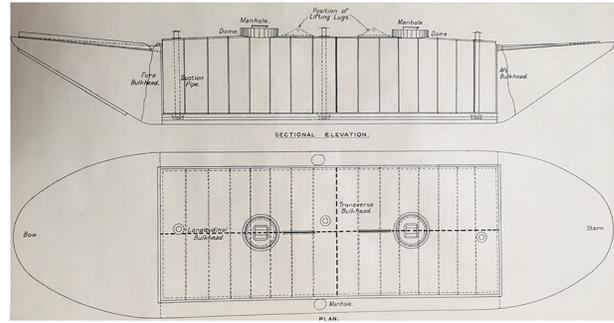
“The only hole which was burnt through the plate by the oxy-acetylene burner was a small one, which was not finished at the time of the explosion.” “Acetylene gas may ... be dismissed as a possible source of the explosion”; “it must ... be concluded that the combustible matter in the tank was present when the barge arrived at the wharf”

and

“the whole of the circumstances of the explosion are consistent with the theory that it was caused by the ignition and subsequent explosion of a mixture of petrol vapour and air in the tank.”

Taylor pointed out that “no test of the atmosphere of the tank for petrol was made after the steaming.” He then performed the following calculation:

“The quantity of petrol required to render the atmosphere of the tank explosive can be readily



**FIG. 1.** The explosion of the petroleum barge, *Warwick*, on September 24, 1920. Above: the design of the barge, showing its petrol tank. Center: the remains of the *Warwick* after the explosion. Both images reproduced from the accident report.<sup>16</sup> Below: the same view a century later, on September 24, 2020; the Thames is now a post-industrial river.

ascertained. The tank has a capacity of 7,040 cubic feet and the vapour of petrol of the quality carried in the tank is explosive when mixed with air in proportions from 1 1/2 to 6 per cent., and about 3 per cent. of vapour or 210 cubic feet would produce a violently explosive mixture in the tank. One cubic foot of petrol produces about 147

cubic feet of vapour at normal temperature and pressure, so that 1 1/2 cubic feet of petrol would produce over 210 cubic feet of vapour. The total area of the interior surface of the tank and bulkheads is over 3,200 square feet, so that an extremely thin film of petrol remaining on the whole interior surface would produce explosive conditions when vapourised. Even a film less than 1/450th of an inch in thickness on the bottom alone would be sufficient to produce such conditions, whilst 1 1/2 cubic feet of liquid could easily be disposed in and around the various angle and plate joints.”

Taylor’s findings were clear and unequivocal:

“Having reached the conclusion that the tank contained a mixture of petrol vapour and air on its arrival at Messrs. Hodge’s wharf, the source of the ignition is not difficult to trace in the light of subsequent events. It is clear from the evidence of several witnesses that an oxy-acetylene burner was used to remove rivet heads on the outside of the tank, and that just when the burner was being used to burn a hole in the plate of the tank top, the explosion occurred. An examination of the damaged tank confirms this evidence in every respect and shows that the explosion took place as soon as the flame of the burner penetrated the plate.”

Taylor laid the responsibility with the barge owners:

“I consider that adequate precautions were not taken by the owners of the barge to ensure that the tank was free from petrol vapour before handing her over for repairs.”

It turned out, Taylor found, that other barges of the same type had previously been taken to Hodge’s for the same modifications to be carried out, after the same cleaning procedure, and had not exploded. The difference in those previous cases was that the barges had lain a day at the wharf before being worked on. That must inadvertently have saved the men who had worked on them, as the remaining liquid would have had an extra day to evaporate, and the vapours would have had an extra day to disperse before work began.

Taylor was the first Senior Engineering Inspector in the newly formed Engineering Branch of the inspectorate of factories for the Home Office. Taylor had been appointed in April 1920, and the Warwick explosion was his first report in this capacity.<sup>17</sup> Around this time, there was a new drive for health and safety at work, both in Britain and beyond, with the slogan “safety first.” In 1917, the Industrial “Safety First” Committee was established in Britain, and in 1918, the British Industrial Safety First Association was formed.<sup>18</sup> Harold Lloyd’s 1923 film “Safety Last!,” famous for the scene of Lloyd dangling from the hands of a clock high on a skyscraper, played with the slogan. Ironically, Lloyd himself had lost a finger and thumb in an explosion: a 1919 filming accident with a fake bomb that was not.<sup>19</sup>

### III. POST 1920

Despite *Safety First*, despite the advance of both science and technology, an inflammable vapor– or gas–air mixture plus a source of

ignition continued to cause accidents. After 1920, such explosions have continued, even into recent decades. Just a few of these, that illustrate the variety of detailed causes of such accidents and their societal implications, are the following. The sewers of Cleveland, OH, exploded on October 20, 1944 when methane from a storage tank leaked into them and was ignited. The resulting explosions and fires killed 130 people and destroyed a large area of the city.<sup>20</sup> On September 7, 1951, a storage tank exploded at the Royal Edward Dock, Avonmouth, Bristol, while being filled with gas oil, and killed two men.<sup>21</sup> The Apollo 13 mission of April 1970, meant to be the third space mission to land on the moon, was aborted half way to the moon, and its crew was narrowly saved after an explosion aboard the spacecraft that occurred when stirring an oxygen tank for its fuel cells, which had been incorrectly assembled leaving damaged electrical insulation on the wiring, which ignited.<sup>22</sup> The Clarkston explosion of October 1971 killed 22 people at a shopping center in Scotland when a gas leak ignited. The Flixborough disaster of 1974 was an explosion at a chemical works that killed 28 people and “rattled the confidence of every chemical engineer in the country”<sup>23</sup> when a pipe joint in a poorly modified cyclohexane plant failed and the resulting gas cloud was ignited.<sup>24–26</sup> A fuel tanker explosion of July 1978 in Los Alfaques, near Tarragona, Spain, killed 217 people when a tanker lorry carrying propene leaked gas, which exploded on encountering an ignition source in a neighboring seaside campsite. *Piper Alpha* was an oil rig in the North Sea that exploded in July 1988 killing 167 people working on it when methane hydrate blocked a pump and another pump, partially dismantled for maintenance, leaked inflammable gas when mistakenly switched on to take its place.<sup>27</sup> Flight TWA800 was a Boeing 747 aircraft that exploded in July 1996 minutes after taking off from New York killing its 230 passengers and crew. Its loss was determined to be owing to an explosion in its empty central fuel tank in which inflammable vapor was ignited by a short circuit in the electrical connections.<sup>28</sup> The Buncefield accident of December 2005 at an oil storage facility in Hertfordshire killed no-one but caused an immense explosion and fire when a petrol tank was overfilled and a cloud of vapor from it was ignited.<sup>29</sup> The *Deepwater Horizon* was an oil rig in the Gulf of Mexico that suffered a blowout of inflammable gas that was ignited probably by coming into contact with the diesel generators on board;<sup>30</sup> 11 people died in that April 2010 explosion, and it produced a huge oil spill that caused environmental devastation in the Gulf of Mexico.

### IV. THE THEORY OF FLUID MECHANICS OF IGNITION, COMBUSTION, AND EXPLOSION

An explosion is a rapid increase in volume. Accompanying this, there are pressure waves and the loud bang we associate with an explosion. Whether or not a chemical reaction in a fluid leads to an explosion depends on the interaction between fluid mechanics and chemical reaction. We may call these explosions thermo-kinetic because, as we shall see, the explosion—i.e., fast reaction—can result from self-heating (thermal) or from the chemical kinetics (chemical chain reaction) or from both factors.

Combustion and explosion science<sup>31,32</sup> is now a field with some beautiful and elegant theory,<sup>33,34</sup> and experiments.<sup>35</sup> However, not everything is known. There are still areas in which more knowledge of the processes taking place is needed,<sup>36</sup> as we shall discuss. It must also be noted that, as we have seen, the impact of thermal radiation from

these explosions is a major factor in terms of human health, and this aspect is also the object of study.<sup>37,38</sup> Combustion theory began to be developed in the 1880s in France where Mallard and Le Chatelier worked on inflammability of gases, combustion and its application to mine safety.<sup>39</sup> They developed a laminar flame speed theory for the rate of expansion of the flame front in a combustion reaction.<sup>40,41</sup> At almost the same time, van't Hoff worked on autoignition of gases and suggested a criterion for when ignition would occur.<sup>42</sup>

Semenov and his student Frank-Kamenetskii took up these ideas in the 1930s in Russia. Semenov's theory<sup>43,44</sup> pertains to the case where convection is so vigorous that the temperature in the vessel is uniform; Frank-Kamenetskii's<sup>45,46</sup> covers the other limit where the transport of heat occurs by conduction only. For well-mixed systems, the reacting gas explodes when the Semenov number exceeds a critical value, when

$$\psi = k_0 c_0^n q E / (\chi S_v R T_0^2)$$

is greater than  $1/e$ . (Here,  $k_0$  is the initial kinetic constant for first-order reaction  $A \rightarrow B$ ,  $c_0$  is the initial concentration of species A,  $n$  is the order of the reaction,  $q$  is the reaction exothermicity,  $E$  is the activation energy,  $\chi$  is the heat transfer coefficient,  $S_v$  is the surface area per unit volume,  $R$  is the universal gas constant, and  $T_0$  is the constant wall temperature.) When heat is transferred by thermal conduction alone, explosion occurs when the Frank-Kamenetskii number is greater than a critical value, when

$$\delta = l^2 k_0 c_0^n q E / (\kappa \rho_0 C_p R T_0^2)$$

is greater than  $\delta_c$ . (Here,  $l$  is the reactor size,  $k_0$  is the initial kinetic constant for first-order reaction  $A \rightarrow B$ ,  $c_0$  is the initial concentration of species A,  $n$  is the reaction order,  $q$  is the reaction exothermicity,  $E$  is the activation energy,  $\kappa$  is the thermal diffusivity,  $\rho_0$  is the initial density,  $C_p$  is the specific heat at constant pressure,  $R$  is the universal gas constant, and  $T_0$  is the constant wall temperature. The critical value depends on the geometry of the system; it is 3.32 for a sphere, 2.00 for a cylinder, and 0.88 for parallel plates.<sup>46</sup>) However, in most reacting systems, heat loss occurs due to the combined effects of natural convection and heat conduction. In the 1950s, Kistiakowsky and co-workers published a series of experimental papers with the common title *gaseous detonations*.<sup>47–59</sup> Among other aspects of the conditions for explosion that they investigated was the role in explosion of temperature changes due to heat conduction. Sokolik's 1960 textbook *Self-ignition, Flame and Detonation in Gases* (published in English in 1963)<sup>60</sup> models these conditions of explosion and the role of the non-dimensional activation energy term in the peaking of heat release, crucial for any explosion.

In parallel to these works, fluid mechanics was developing. The equations for the movement of a fluid were written down in the early 19th century by Navier, Cauchy, Poisson, Saint Venant, and Stokes.<sup>61</sup> In the second half of the 20th century, with the advent of the electronic computer it became possible to solve the Navier–Stokes equations numerically. Computational fluid dynamics (CFD) methods are now ubiquitous. One can couple these computational methods with the equations of chemical kinetics to solve numerically how a reaction behaves in a fluid medium. Three physical processes combine in a reacting flow: fluid dynamics, thermodynamics, and chemical reaction. Each process has its own space and timescales, which may be very different from those of the other processes. Such differences of scales, on

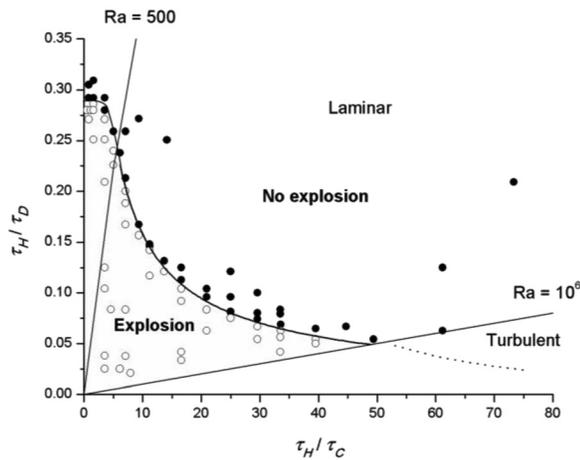
one hand, can allow simplification of a theoretical model, but on the other hand, they can also be a source of numerical difficulties. The fluid dynamics is a balance between the temporal evolution and the spatial convection of the flow properties governed by the conservation of mass, momentum, and energy. Reactive fluid thermodynamics includes microscopic heat transfer between gas molecules, work performed with pressure and associated volume change. In addition, chemical reactions determine the generation and destruction of chemical species while observing mass conservation.

One application of the theory of chemically reactive flows is to mining, as its pioneers had studied. We may note that both original types of miners' safety lamps work because the mesh or tubes function as a flame arrester. The metal absorbs heat from a flame front so that the front decays and the flame dies. This mechanism depends critically on the size of the tubes or the mesh. Moreover, as we have seen, Faraday commented on the choice before safety lamps of a small candle—one presumably having a small flame—by miners, which might provide illumination without igniting the firedamp.

Work on strong and weak ignition can be mentioned at this point. In the 1960s, Voevodsky and Soloukhin looked at variations in ignition arising from chemical kinetics and defined two regimes.<sup>62</sup> Strong ignition occurs when a single ignition point is enough to give a detonation front. Weak ignition takes place at lower temperatures when reaction is initiated at multiple points. These coalesce to produce a front. Meyer and Oppenheim showed that weak ignition occurs at different points where fluid flow velocities are low and that the induction time to reaction is sensitive to temperature variations owing to inhomogeneities.<sup>63</sup> This understanding of the different processes of weak and strong ignition is of relevance to the deflagration-to-detonation transition that we shall discuss below.<sup>64</sup>

As well as mining, a further application, this time one where explosions are wanted, but need to be controlled, is the internal combustion engine. An amount of work has been carried out under the heading of knock, or preignition, in the internal combustion engine.<sup>31,65</sup> (It should be noted that this is generally a two phase system, as droplets of fuel, not vapor, are the reactant. It has been argued that fuel involved in the Buncefield explosion, described above, may have been in the form of such a mist of droplets.<sup>66</sup>) Knock in internal combustion engines has been associated with cool flame formation, and cool flames resulting from complex thermo-kinetic interactions<sup>67</sup> in turn have been implicated in the TWA800 explosion mentioned above.

Recent theoretical work in the last two decades, which takes the Semenov and Frank-Kamenetskii approaches and moves them forward, is by the group of Cardoso in Cambridge. Following an approach first put forward by Cardoso *et al.*,<sup>69,70</sup> Liu *et al.*<sup>68</sup> proposed that in these systems the occurrence or not of an explosion depends on the relative magnitudes of three timescales: that for chemical reaction to heat up the fluid to ignition, the timescale for thermal conduction and that for natural convection. They summarized their results in a two-dimensional regime diagram (Fig. 2), in which Frank-Kamenetskii's purely conductive system and Semenov's well-mixed system appear as two limiting cases, represented by the two axes. The plane in between the two axes contains all the systems with different relative magnitudes of heat loss by conduction and by natural convection. This approach has the advantage of quantifying separately the stabilizing effects of conduction and natural convection on an explosion.



**FIG. 2.** The regime diagram summarizing simulations without consumption of the reactant, with closed circles representing no explosion and open circles, explosion.  $\tau_H$  is the timescale for heating by reaction;  $\tau_C$  is the timescale for convection, and  $\tau_D$  is the timescale for diffusion. The horizontal axis then denotes the well-mixed limit; the vertical axis represents the purely conductive limit. The relative importance of thermal conduction and natural convection in the system is shown by the Rayleigh number  $Ra$ ; when  $Ra < 500$ , heat transfer is controlled by conduction; laminar convection dominates heat transfer for  $500 < Ra < 10^6$ ; for  $Ra > 10^6$ , the flow is turbulent. The other solid and dotted lines, respectively, represent the explosion limit in the laminar and turbulent regimes. Reproduced with permission from Liu *et al.*, “Effects of natural convection on thermal explosion in a closed vessel,” *Phys. Chem. Phys.* **10**, 5521–5530 (2008). Copyright 2008 PCCP Owner Societies.

In a subsequent paper, they then extended these ideas to explore how the consumption of the reactant alters the onset of a thermal explosion.<sup>71</sup> They showed that whether or not a chemical reaction in a fluid leads to an explosion is shown to depend on four timescales: (1) that for the chemical reaction to heat up the fluid containing the reactants and products,

$$\tau_H = \frac{\rho_0 C_p \Delta T_s}{k_0 c_0^n q},$$

where  $\rho_0$  is the initial density,  $C_p$  is the specific heat at constant pressure,  $k_0$  is the initial kinetic constant for first-order reaction  $A \rightarrow B$ ,  $c_0$  is the initial concentration of species A,  $n$  is the order of the reaction,  $q$  is the reaction exothermicity, and  $\Delta T_s = RT_0^2/E$  (with  $E$  being an activation energy) is a temperature increase scale; (2) for cooling by heat conduction or diffusion out of the system,

$$\tau_D = \frac{l^2}{\kappa},$$

where  $l$  is the reactor size and  $\kappa$  is the thermal diffusivity; (3) for natural convection in the fluid,

$$\tau_C = \frac{l}{U},$$

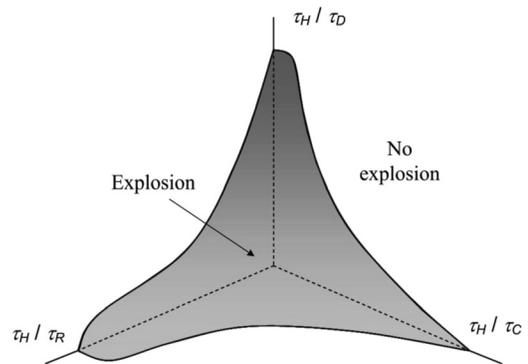
where  $U$  is a characteristic velocity; and finally (4) for chemical reaction that uses up the reactant,

$$\tau_R = 1/k_0,$$

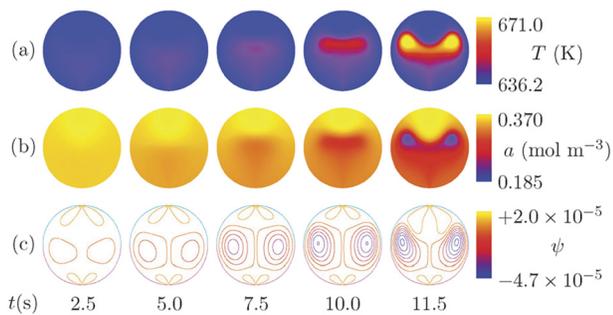
where  $k_0$  is the initial kinetic constant for first-order reaction  $A \rightarrow B$ .

The behavior of the system can be depicted on a three-dimensional regime diagram, as shown in Fig. 3, where the three ratios of the four timescales are the coordinates. There is a surface separating the region near the origin where explosions occur from the region further from the origin where the stabilizing effects of heat conduction, natural convection, and consumption of the reactant prevent explosions. The vertical axis  $\tau_H/\tau_D$  represents the purely conductive limit ignoring depletion of the reactant, i.e., the systems considered by Frank-Kamenetskii. The right-hand axis  $\tau_H/\tau_C$  gives the well-mixed limit of Semenov with no consumption of the reactant. In addition, the third, left-hand axis  $\tau_H/\tau_R$  measures the effect of the disappearance of the reactant on the heating up of the fluid; for example, if the chemical reaction in effect depletes the reactant much faster than the fluid is heating up (e.g., because the heat of reaction is very small), then  $\tau_H \gg \tau_R$  and we expect the temperature rise in the fluid to be small and explosion not to occur. The synthesis of these two limits into one—thermal and kinetic effects into a thermo-kinetic theory—is a beautiful piece of theory, bridging and bringing together points often seen as separate, but which really are not separate at all, as the figures show.

Cardoso *et al.* also performed numerical CFD simulations of the effects of combined natural and forced convection on thermal explosion in a spherical reactor with upward natural convection from internal heating caused by a chemical reaction to which they added downward forced convection driven by injecting fluid at the top and removing it at the bottom of the reactor.<sup>72,73</sup> They found oscillatory behavior for moderate forced convection. They also found that explosive behavior is favored by a balance between the natural and forced flows, owing to a nearly stagnant zone close to the center of the reactor that quickly heats up to explosion (Fig. 4). It is counter-intuitive that explosion may occur in an otherwise stable reactor by injecting cold fluid or enhancing natural convection.



**FIG. 3.** Schematic regime diagram with the three axes,  $\tau_H/\tau_C$ ,  $\tau_H/\tau_D$ , and  $\tau_H/\tau_R$ , for an exothermic reaction occurring inside a closed spherical vessel.  $\tau_H$  is the timescale for heating by reaction,  $\tau_C$  is the timescale for convection,  $\tau_D$  is the timescale for diffusion, and  $\tau_R$  is the timescale for reaction. The gray surface separates the inner region, where explosions occur, from the outer one, where they do not. Reproduced with permission from Liu *et al.*, “On the occurrence of thermal explosion in a reacting gas: The effects of natural convection and consumption of reactant,” *Combust. Flame* **157**, 230–239 (2010). Copyright 2010 Elsevier.



**FIG. 4.** Numerical simulations with computational fluid dynamics of explosion in a spherical reactor with mixed convection; evolution of the fields of (a) temperature, (b) reactant concentration, and (c) streamlines. The temperature starts rising at the bottom of the vessel, accompanied by reactant depletion, and buoyancy is triggered within the fluid. Owing to the interaction between buoyancy and forced convection, the hot region expands further to both sides of the reactor where the cooling by diffusion of colder species from the inlet stream is not so efficient. This allows the fluid to heat up by reaction, leading to explosion at  $t = 11.5$  s. Reproduced with permission from F. Gonçalves de Azevedo, J. F. Griffiths, and S. S. S. Cardoso, "Effects of kinetic and transport phenomena on thermal explosion and oscillatory behaviour in a spherical reactor with mixed convection," *Phys. Chem. Chem. Phys.* **16**, 23365–23378 (2014). Copyright 2014 PCCP Owner Societies.

The foregoing theory is for a homogeneous mixture of reactants in a vessel with its walls at constant temperature. One significant aspect where theory has been inadequate and computational fluid dynamics needed is the deflagration to detonation transition,<sup>74</sup> important in the context of the confinement of an explosion. The central theme of this review is to illustrate the consequences of pressure build up from the increase of volume in an unventilated medium. The pressure waves and loud bang of an explosion have not been discussed because our focus has been not on the waves and bang but on the timescales of the phenomenon in the context of the fluid mechanics and the chemistry leading to volume increase. Quasi-detonations and detonations and their initiation, either through transition from a flame or otherwise, have a strong gas dynamic component. Quasi-detonations are more likely in an explosion. While it is not possible to do justice to these other aspects of explosions here, for which we send the reader to recent reviews,<sup>75–79</sup> it is worth mentioning them because they show how science always needs to be interdisciplinary because it turns out that the same science is involved in the explosions of industrial accidents and in the explosions of stars.

In deflagration, there is a subsonic flame propagation velocity and in the reaction zone, chemical combustion progresses through the medium by the diffusion of heat and mass. In contrast, in a detonation, there is a supersonic flame propagation velocity, and the reaction zone is a shock wave where the reaction is initiated by compressive heating caused by the shock wave. This regime has generally needed numerical simulations of computational fluid dynamics for its understanding. A general theory of the deflagration-to-detonation transition has recently been presented together with an interesting astrophysical application to the explosion of stars. Figure 5 shows schlieren images with the coalescing of pressure waves and formation of a shock wave. Poludnenko *et al.* showed that thermonuclear combustion waves in type Ia supernovae are qualitatively similar to chemical combustion waves on Earth because they are controlled by the same physical

mechanisms and are not sensitive to the details of the equation-of-state, microphysical transport, or reaction kinetics.<sup>80</sup> They discussed how a deflagration-to-detonation transition may have been involved in some industrial accidents, such as at Buncefield. At the same time, the astrophysical application demonstrates how interdisciplinary this field at the interface between fluid mechanics and chemistry is, and how far from terrestrial concerns it can get.

## V. SAFETY FIRST?

During the past century, combustion theory has grown from its incipient state to fully fledged. The understanding of chemical reaction kinetics has evolved immensely. Fluid mechanics has developed both theory and also numerical solutions with CFD methods as computers first appeared and subsequently have doubled in speed every eighteen months or so. Engineering science—chemical, but also mechanical, civil, and other branches—has likewise advanced at an ever increasing pace. In addition, health and safety planning has progressed enormously in foreseeing and eliminating risks since the early days of factory and engineering inspectors and *safety first*. Nonetheless, gas and vapor explosions have killed many people, and in many of these cases, a container or tank was involved, as in the accident of my grandfather.

In the last 100 years, there have been developed and implemented systems for making safer such (especially) fuel tanks with a nitrogen or similar inert atmosphere, or a non-combustible atmosphere, such as carbon dioxide. Some Second World War aircraft used inerting systems, and tanker ships trialled them in the 1920s. On-board inert gas generation systems have been developed for aircraft.<sup>81</sup> Tanker ships use either gases produced in combustion by the ship engines, or they generate inert gases.<sup>82</sup> Likewise, so-called hypoxic or oxygen-reduced air systems with low-oxygen-concentration air have been developed for buildings: for archives, warehouses, electrical substations, and other buildings where reducing is preferred to eliminating oxygen.<sup>83</sup> In addition, racing-car fuel tank or fuel cell technology involves filling the tank with an open-cell foam, again to reduce the explosion risk. We can see all these safety systems as playing with the parameters of the theory that we have described above, to move from an explosive to a non-explosive part of the parameter space. So, why have such safety systems not, like miners' safety lamps, become the norm? It is arguable that in some instances, that of cars, for instance, car fuel tank explosions are (despite the mythopoeia of Hollywood) rather rare. This does not appear to be the case, however, for tanker ships. Devaney<sup>84</sup> compiled a long list of tanker ship accidents caused by explosions in fuel tanks. He asks regarding inerting,

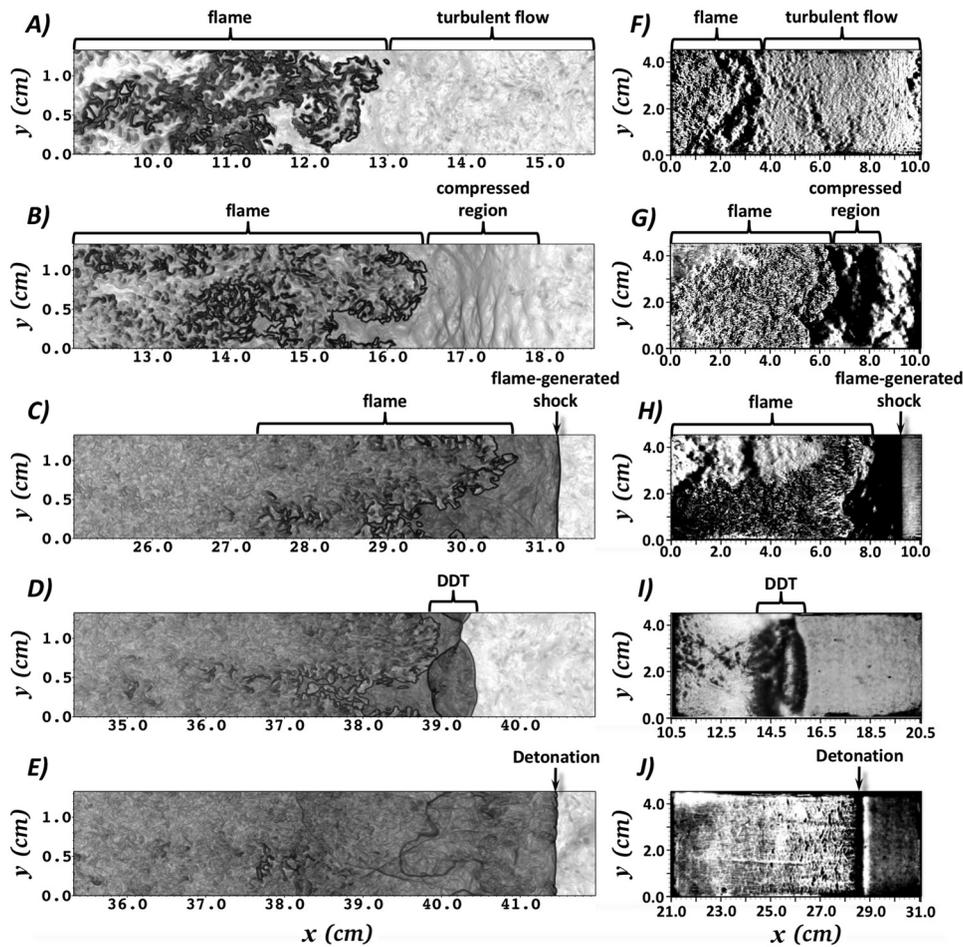
“why was the industry so slow to adopt such an obvious, effective, safety measure which probably pays for itself in reduction of tank corrosion?”

and answers his own question

“the cost[s] of implementing inerting to these ships were more than the dollar benefits of the lives and ships saved,”

because

“a tanker owner rarely suffers any loss when one of his ships blows up. His P&I [Protection and Indemnity]



**FIG. 5.** Simulated [(a)–(e)] and experimental [(f)–(j)] schlieren images of turbulent flame evolution. Once the flame front has developed, it begins to propagate toward the open end of the channel [(a) and (f)]. Pressure waves generated within the turbulent flame propagate into the unburned material and form a compressed region ahead of the flame [(b) and (g)]. As the runaway process develops, multiple pressure waves coalesce into a flame-generated shock, the strength of which grows with time [(c) and (h)]. Eventually, the shock triggers a deflagration-to-detonation transition, DDT [(d) and (i)] and gives rise to detonation [(e) and (j)]. Reproduced with permission from Poludnenko *et al.*, “A unified mechanism for unconfined deflagration-to-detonation transition in terrestrial chemical systems and type Ia supernovae,” *Science* **366**, eaa7365 (2019). Copyright 2019 AAAS.

insurance pays off the dead crew’s family, in most past cases a few thousand dollars per head. His hull insurance covers the loss of the ship. In many cases, the insured value is more than the market value and the owner comes out ahead.”

This review has demonstrated how, from the very beginning, the science of explosions has been inextricably intertwined with its societal implications. As I write, at the centenary of my grandfather’s death, I do wonder whether more could not be done, with more innovative solutions from scientific and technological ideas, to reduce further the risk of explosion, in the same way that miners’ safety lamps were developed and used. Despite great advances in both science and engineering, gas and vapor explosions continue.<sup>85</sup> I began this review with sewer explosions of two millennia ago, and I have mentioned the enormous 1944 disaster in Cleveland, OH; these still occur on occasion. A

fuel tanker blew up a century ago owing to incorrect working methods with fuel vapor. That was then, but how can it be that a century on fuel tankers are still blowing up for the same reason? Has it really been *safety first*, or *safety last*?

Whether or not further regulatory action is needed is a question that scientists involved with the societal responsibilities of science should consider. Some scientists believe that we should not concern ourselves with these matters, which they see as political rather than scientific. To my mind, that is a fundamentally misguided point of view. I myself firmly believe that we as scientists must be open to, and understand, the societal aspects of science, that science owes it to society to explain the implications of science for society, and these matters should be discussed alongside the science itself. From the point of view of the science itself, in this field, science has always engaged with the practical questions arising from explosions. The Felling pit explosion of 1812 led to the miners’ safety lamp; the Deepwater Horizon

explosion of 2010 and the resulting oil spill in the waters below the rig have led to a great quantity of research into the dynamics of two-phase plumes,<sup>86</sup> and the Buncefield explosion of 2005 is noted in the latest results on supernovae explosions;<sup>80</sup> I am sure that new scientific advances will continue to emerge from the fluid mechanics of explosion.

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## DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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