It is also instructive to see in dimensional units the maximum temperature rise that can occur without thermal runaway. Since $\theta_c = 1$, then

$$\frac{RT^2}{E} = T_c - T_o$$

where the gas temperature at criticality is denoted as T_c. This gives a quadratic equation in T_c, whose solution is:

$$T_c = \frac{E}{2R} \pm \sqrt{\left(\frac{E}{2R}\right)^2 - \frac{T_o E}{R}}$$

and it can be shown that physical results correspond only if the minus sign is taken for the second term. This gives

$$T_c = \frac{E}{2R} - \frac{E}{R}\sqrt{1 - 4R\frac{T_o}{E}}$$

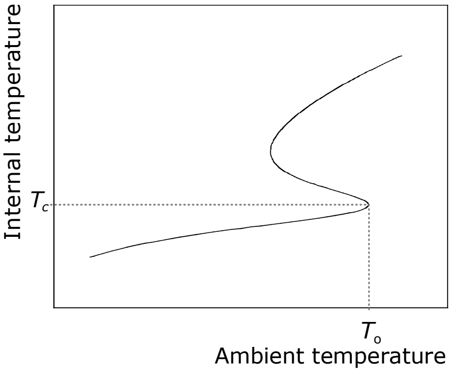

Figure 5 Full solution for T, as function of T_o (schematic)

Now, since $RT_o/E \ll 1$, we can expand the square root expression as a power series in T_o/E, giving

$$T_c \approx \frac{E}{2R} - \frac{E}{2R}\left[1 - \frac{2RT_o}{E} - \frac{2RT_o^2}{E^2} + \ldots\right]$$

or

$$T_c - T_o \approx \frac{RT_o^2}{E}$$

Using the above example values, the difference ($T_c - T_o$) ≈ 30 K. The above treatment was simplified, since only the physically stable part of the solution was developed. In fact, the curve of the steady-state Semenov solution has two additional branches[23], as shown in Figure 5. For certain ambient temperatures below T_o, three solutions for T are possible, but only the lowest value corresponds to a stable, unignited state—the middle branch is unstable, while the top branch would represent an ignited state if the Semenov model were suitable for describing for actual combustion, not just conditions leading up it (which it is not).

A number of authors[24,25] give a further-approximated version of the above development by explicitly assuming that $T_c \approx T_o$. In that case, the equation giving the AIT, i.e., the value of T_o which corresponds to critical conditions, which in our development is:

$$eQAVc^n e^{-E/RT_o} = hS\frac{RT_o^2}{E}$$

becomes, instead:

$$QAVc^n e^{-E/RT_o} \approx hS\frac{RT_o^2}{E}$$

For common hydrocarbon combustion reactions, $n = 2$, and therefore, $c^n \sim \left(\frac{P}{RT}\right)^2$, where P = pressure. Substituting this, and taking logarithms of both sides gives:

$$\ln\frac{P}{T_o^2} = \frac{E}{2RT_o} + \text{const}$$

This relation indicates that raising the system pressure causes ignition to take place at a lower temperature, and vice versa. The relation between the pressure and the temperature can best be represented by plotting $1/T_o$ on the x-axis and $\ln\frac{P}{T_o^2}$ on the y-axis (Figure 6).

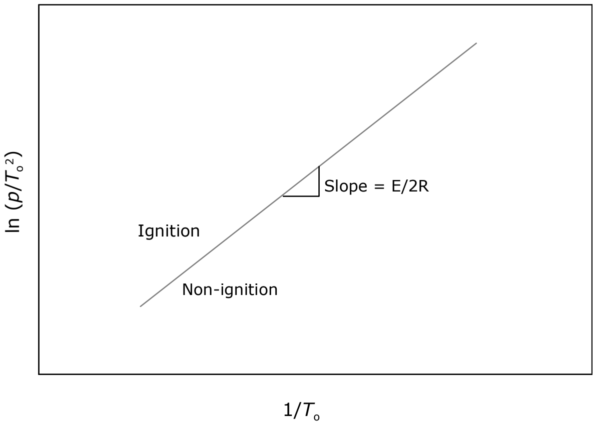

Figure 6 The relation according to Semenov theory between the pressure and the temperature needed for ignition

The above development comprised a *stationary state theory*, that is, we were only seeking to find the conditions necessary for criticality, not the time involved in heating up the system. For actual ignition problems, if the ambient temperature is larger than the T_o corresponding to critical conditions, thermal runaway will occur, that is, the gas will ignite. It then becomes of interest to assess the time required for ignition, t_{ig}. To evaluate this time, the heat released per unit volume during the period from $t = 0$ to $t = t_{ig}$ is:

$$QAc^n e^{-E/RT_o} \cdot t_{ig}$$

Assuming that there are no losses to the outside (that is, the system is adiabatic), this same heat goes to raise the temperature from T_o to T_c:

$$\rho C(T_c - T_o)$$

where ρ = density and C = heat capacity. Thus,

$$\rho C(T_c - T_o) = QAc^n e^{-E/RT_o} \cdot t_{ig}$$

ball was produced when pressure was inappropriately released in an industrial autoclave reactor[72]. The majority of cases, however, involve overheating. The overheating can occur due to various sources. It can simply be due to an ongoing fire engulfing a tank. In other cases, overfilling or another cause of overpressure will produce a discharge of the gas through a pressure-relief valve (PRV). If this discharging gas ignites, then an external source of heating exists close to the tank. Further discharge will result in continued flames, which, if impinging on the tank, will progressively raise its temperature and weaken steel that is present above the liquid line. The process leads to runaway, since normally a PRV cannot be practically provided which will keep up with the increasing pressures and flows[*]. The tank then ruptures, resulting in a massive fireball (Color Plate 43) and flying metallic fragments.

While most BLEVE incidents have involved flammable gases, it is not necessary that the gas be flammable for a BLEVE to occur. A BLEVE is basically a physical explosion, and heating from the combustion of the substance itself is only one of the ways that excessive over-pressure can occur. Prugh examined case histories for major BLEVE accidents during the period 1926 – 1986 and identified that, apart from propane/butane/LPG, accidents have involved[73,85]:

acrolein
ammonia
butadiene
carbon dioxide
chlorine
2-chloro-1,3-butadiene
diethyl ether
ethylene
ethylene oxide
gasoline
hydrogen
methyl bromide
phosgene
propylene
vinyl chloride
water

A number of the older accidents happened because of absence of proper valves and safety precautions against overfilling. Shown in Color Plate 44 are views of the fireball from the BLEVE that took place on 21 June 1970 in Crescent City, Illinois upon derailment of a train hauling propane tank cars. After the 1970s, this source of accidents in the US significantly decreased due to tighter regulations and greater safety awareness. But the most disastrous BLEVE took place in relatively recent times—1984—in Mexico[74], killing approximately 500 persons and injuring another 7000. 'Tub rockets' were propelled as far as 1.2 km in the incident, which entailed nine separate explosions, some of which were severe enough to register seismically. BLEVE fireballs from this disaster are shown in Color Plates 45 and 46, while the aftermath is illustrated in Color Plate 47.

A BLEVE is defined as an explosive release of expanding vapor and boiling liquid when a container holding a pressure-liquefied gas fails catastrophically[75]. But a failure of a tank holding a pressure-liquefied gas does not necessarily lead to a BLEVE. In general, if, for whatever reason, a fissure arises in a vessel holding a pressure-liquefied gas, there are three outcomes[76]:

(1) The fissure stops growing; there is no BLEVE, only a partial failure with jet release.
(2) Rocketing (partial failure with a liquid and vapor jet propelling the fragments).
(3) Total loss of containment and boiling liquid, expanding vapor explosion (BLEVE). This can occur either all at once or in two stages, as explained below.

For a BLEVE, as opposed to the other two failure modes, to occur, the liquid fill must be *below* a certain level. This is because a minimum energy must be available in the vapor volume to cause the crack in the metal to fully propagate[77]. This finding, of course, should not be taken to imply that tanks should be overfilled. Propane tanks are normally filled to 80% capacity. If a tank is overfilled, when it is subjected to heating (by a rise in ambient temperature, for example) the pressure inside the tank may rise sufficiently to cause discharge from the PRV. Many accidents have been reported where a discharge of this kind ignited, then caused flames to be applied to the tank, heating it further. This chain of events has ended in a BLEVE in many such incidents. Additional studies of non-BLEVE tank failures have been published[78].

Research by Birk and colleagues[76] at Queen's University in Canada and by Venart[79] at the University of New Brunswick identified the following sequence of steps as being characteristic of a BLEVE caused by flame impingement, and these are considered in some detail below.

- When flames impinge upon a tank, the liquid-filled portion stays cool due to heat-sink effects, but the steel around the vapor space rapidly heats up. Stresses increase, while strength has decreased due to the elevated temperature.
- Stresses in the tank wall are especially concentrated at the liquid/vapor interface.
- A crack develops in the tank wall, commonly located in the vapor-space portion, but near the liquid/vapor interface.
- Venting of the vapor results in a pressure drop within the tank and the liquid contents become superheated.
- The superheated liquid flashes, rapidly converting a sizable fraction of the liquid into vapor.
- If the vessel is fairly full, then vapor bubbles in the liquid cause the liquid volume to swell, resulting in a choked, two-phase liquid/vapor flow through the wall break. But if the vessel's fill level is low at the time of the BLEVE, then the two-phase outflow will comprise a mist/vapor discharge, rather than a highly turbulent liquid/vapor discharge.

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[*] This is true for the case of normal *vapor*-discharge PRVs. It would appear to be readily possible to equip many types of tanks with a secondary, *liquid*-discharge PRV. Since the mass of material which can be discharged from a given opening is vastly greater for liquids than for vapors, anti-BLEVE safety could be provided. The secondary PRV would be set to discharge at some suitably higher pressure than the primary PRV.

very soon thereafter. While the study did not produce closed-form expressions for prediction, the effect of oxide layer thickness was characterized. When all other conditions are held constant, the ignition time equals a constant, plus a term proportional to the oxide layer thickness. The constant represents the heat-up time, while the second term represents the time needed to remove the oxide film, once thermal equilibrium has been reached. The theory also indicates that there is a maximum oxide layer thickness, beyond which ignition will not occur. Their theory states that a layer which is 6.8% of the radius represents this limiting condition.

Clouds of boron particles ignite at lower temperatures than what is needed for single-particle ignition. The minimum ignition temperature decreases with (a) increasing cloud radius, (b) decreasing particle radius, (c) increasing particle concentration, (d) decreasing particle velocity, and (e) decreasing atmospheric pressure. Particles with a radius of 3 μm forming a cloud with a radius of 0.6 m at a mass fraction loading of 5% ignite at an atmospheric temperature of about 1030ºC under zero-velocity conditions[163]. If the mass loading is increased to 25%, ignition becomes possible at 630ºC. A minimum temperature for ignition of boron dusts in air[170] is reported to be 730ºC. Dust clouds with about 12% of magnesium added to the boron show ignition temperatures about 150ºC lower than for boron particles alone[171]. In a CO_2 atmosphere, boron powder (ultra fine, 0.05 μm size) was found not to be ignitable up to the maximum temperature tested, 960ºC[1396].

Brake fluid

Ohlemiller and Cleary[123] investigated the effect on the flash point and fire point of brake fluid when contaminated with gasoline. Using a non-standard open-cup test apparatus, they found that the flash point dropped from 100ºC for pure brake fluid to room temperature (22ºC) when 10 vol% of the mixture was gasoline. The fire point dropped from 130ºC for pure brake fluid to 22ºC for a mixture with 15 vol% gasoline.

Calcium resinate

Used in various paints, leather processing, and cosmetics, calcium resinate ($C_{40}H_{58}CaO_4$) is reported to be a self-heating substance[1542].

Camping fuel

According to DeHaan[172], a typical camping fuel has a Reid vapor pressure of 43.3 kPa at 38ºC. Camping fuel is a complex mixture of hydrocarbons, but dominated by hexane and related compounds. Its flash point is not fixed, but may be around –33ºC. See also: *Gasoline* (white gasoline).

Candles

Candles are one of the oldest forms of open-flame devices in a home, but in a modern residence candles involve some unique ignition hazards. Factors to consider are:

- the combustion is not confined to an engineered combustion device; some candleholders are grossly inappropriate for the application (e.g., they are combustible or are unstable and can be tipped over);
- the open flame has no protection or shielding and candles are often burning while unattended;
- unlike matches and lighters, a candle flame can burn for hours, thus items that take fairly long to ignite can be threatened.
- attempting to extinguish a candle fire with small amounts of water available to a householder is likely to exacerbate the fire in a manner similar to pouring water of burning liquid fires.

Sanderson has documented additional aspects of candle fires[173]. Candle flames were studied very early by Michael Faraday, and his classic 1861 textbook still makes worthwhile reading[174].

Candle fires in the US, while still a small fraction of all residential fires[175], have experienced a significant upsurge in recent years (Figure 14). In response to this, in 2002 ASTM issued a specification, ASTM PS 59[176], establishing safety requirements for candles.

CPSC[177] has compiled US statistics on the general nature of candle fires, see Table 9. NFPA published detailed statistics[175] on US fires for the years 1994-1998, as shown in Table 9 through Table 11. Over the years, CPSC has issued a number of recalls for products that are a combined candle/candleholder due to improper designs where either the candleholder was made from a combustible material and tended to catch fire, or else there was a propensity (typically with a glass or ceramic construction) for the candleholder to shatter and spill out burning material.

Some very high temperatures are found in a candle flame. Gaydon and Wolfhard[170] measured a peak temperature of

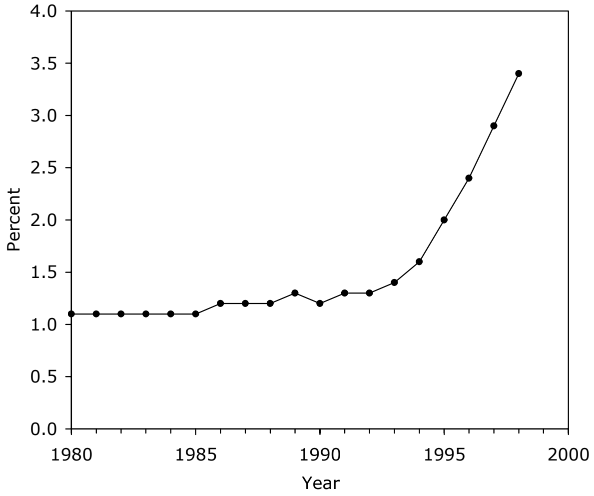

Figure 14 Candle fires in the US, as a percent of total residential fires

It has been suggested that propionic acid could be used to retard the self-heating effects in oiled sawdust, however, this is unlikely to be an economical solution.

WOOD PULP

Buchanan[2098] reported values of 210 – 265ºC for the AIT of various types of wood pulp.

SHINGLES AND SHAKES

Roofing shingles (produced by sawing) and shakes (produced by splitting) that are not fire-retardant treated are ignitable by 38 mm fire brands, but with a probability of significantly less than 100%[1049]. When shingles/shakes are weathered, they become more readily ignitable.

Wood-burning appliances

Wood-burning appliances include fireplaces, wood-burning stoves, wood-burning fireplace inserts, and similar devices. Pellet stoves, which burn small pellets compressed from wood sawdust, are a specialized form of wood-burning appliance. US statistics[289] on fires from these appliances are shown in Table 226 and Table 227.

An early study by Voigt [2143] showed that flue pipe temperatures typically ranged up to 450 – 480ºC. Temperatures on the metal base of stoves went up to 500 – 600ºC. Based on his test results, Voigt recommended that clearances of 300 mm be observed from wood ceilings or joists. For single-wall flue pipes passing through combustible walls, he recommended that either a ventilated air space of 100 mm be provided, or else that the annulus size could be reduced to 50 mm if it was packed with thermal insulation. Peacock[296] examined the results from a number of laboratory studies and concluded that peak external surface temperatures of wood-burning appliances may reach up to 300 – 450ºC, with flue gas temperatures reaching to about 700ºC. However, under improper use conditions, i.e., overfiring, the temperatures can be higher. Figure 128 shows the consequence of overfiring a fireplace with too much wood—a structural wood member inside the wall was ignited right above the fireplace.

Table 226 Equipment involved in wood-burning appliance fires

Source of fire	Percent
appliance	55
chimney	35
chimney connector	10

Table 227 Causes of wood-burning appliance fires

Cause	Percent
improper maintenance	27.5
combustibles (occupant goods) too close	18.1
improper equipment design	10.0
exterior fire from sparks	9.2
improper operation	7.5
ignition of structure	6.7
improper fueling technique	5.5
equipment malfunction	4.4
improper installation	2.4
improper chimney	1.3
use of flammable liquids	1.2
chimney fire	0.2
other	0.3

Figure 128 Ignition of wood wall-framing member from an overfired fireplace
(Courtesy Tim Bradley)

The process of burning wood pellets creates small burning embers which go up the chimney. Roof fires have occurred when such embers leaving the chimney landed on a wood-shake roof[2144].

Wool

The AIT of wool blankets[443] was reported by NIST in 1947 as being 205ºC. The method used, however, appears to give anomalously low values with other materials. Lawson[2145] reported that the minimum flux for ignition of wool fabrics is about 33 kW m^{-2} for piloted ignition and 84 kW m^{-2} for autoignition, but it is not clear what measurements were made to obtain the values.

Self-heating fires are known to occur in bales of greasy wool[1710]. Walker and coworkers examined the problem in a series of very extensive studies[2146-2149]. Self-heating problems do not occur with wool that is sheared—only with wool removed by chemical means or by a rotting process. For the latter, again no problems have been found for grease-free and completely dry wool; however wet (with water in excess of that needed to saturate the interstitial atmosphere) or moist (water content below that needed for saturation) wool will self-heat. The amount of water required to cause interstitial saturation is about 33%, dry basis (‘re-gain’), but ‘wet’ wool can easily contain 100% moisture. Bales of wool at around 400 kg m^{-3} density may show significant, albeit sub-critical, self-heating if they have as little as 18% moisture and are thus substantially below the moisture needed for saturation. Significantly accelerated