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Evaluation of the Likelihood for Thermal
Runaway for Nitrate Salt Containers in
Storage at Los Alamos National Laboratory

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March 21, 2016

Introduction

In order to handle and process the existing Los Alamos National Laboratory (LANL) Nitrate Salt drums it is necessary to quantify the risk. One of the most obvious dangers is a repeat of the original violent reaction (Clark, 2015), which would endanger nearby workers, not only with radioactive contamination, but also with large amounts of heat, dangerous corrosive gases and the physical dangers associated with a bursting drum. If there still existed a high probability of violent reaction, then these drums should only be accessed remotely. The objective of the work reported herein is to determine the likelihood of a similar violent event occurring.

Objective

In order for one of the LANL Nitrate Salt drums to undergo thermal runaway, the rate of heat production by the chemistry occurring in the drum must be greater than is dissipated to the environment. In order to get long-time thermal runaways, the chemical heat production must be very closely balanced to heat dissipation. If the chemistry produces heat much faster than it is dissipated, then thermal runaway occurs in a relatively short time frame. It is hypothesized that the combination of thermal parameters, which would lead to thermal runaway after the long storage time is so unlikely that the probability of thermal runaway now occurring is extremely unlikely.

This hypothesis is presented with several caveats: the material in the drums is well-mixed and homogeneous and the chemistry occurring in the drums can be described as one chemical reaction – namely that it follows first order Arrhenius kinetics, and the drums will not be subjected to any additional thermal insults.

This hypothesis is tested by using a computational model of the LANL Nitrate Salt drums to explore the thermal runaway times over a set of kinetic parameters. It will be shown that the slice of parameter space that could possibly lead to thermal runaway is so small that, given the caveats above, the probability of another thermal runaway occurring is beyond extremely unlikely.

Method Overview

While the exact contents of the drums are not known, it is possible to estimate the probability of another self-heated thermal runaway occurring by treating the drums as a generalized chemical system. To do so, the drums are assumed to be filled with a homogeneous, well-mixed chemical system which reacts obeying Arrhenius kinetics. Given a set of Arrhenius parameters, activation energy, pre-exponential factor and enthalpy, it is then possible to use the heat equation and a computational model to determine whether the system will undergo thermal runaway, as well as predict the time required for this to happen.

The parameter space defined by the Arrhenius parameters can be explored numerically to determine where the go/no-go regions in the parameter space exist and how long it takes to get to thermal runaway at a given environmental temperature. Figure 1 illustrates this for a two dimensional parameter space, where the enthalpy is fixed and the activation energy and the pre-exponential factor are allowed to vary. As can be seen in the figure, as well as finding the go/no-go boundary in the Arrhenius parameter space, the set of parameters, which will lead to a specific range of cook-off times can be determined. This is illustrated in the figure, where the set of Arrhenius parameters which lead to thermal runaway times of a $t_r < \infty$ is outlined in orange. If the set of Arrhenius parameters is known which lead to a known range of thermal runaway times, then it would be possible to describe the

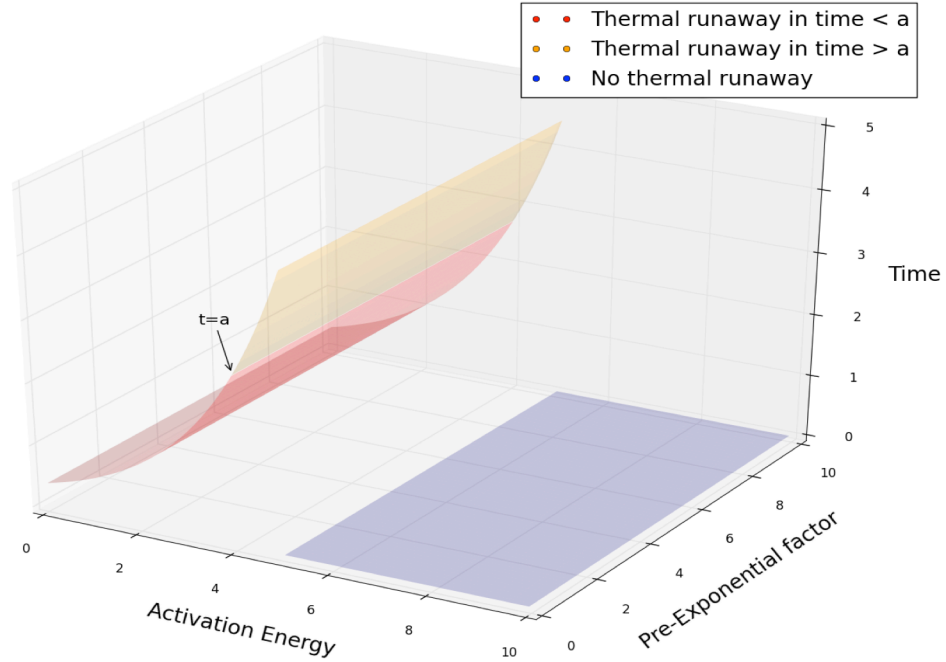


Figure 1: Illustrates the go/no-go regions for a two dimensional Arrhenius parameter space. The blue area is the set of parameters which do not lead to cook-off, while the orange area is the set of parameters which lead to thermal runaway for times greater than a.

probability that a drum would under thermal runaway in this time frame if the probability distribution function (PDF) describing the distribution of kinetic parameters is known.

Next, by assuming probability distribution, it is possible to calculate the probability of a thermal runaway occurring in a specific time frame. This is done by integrating the probability distribution function (PDF) over the range of Arrhenius parameters which describe the thermal runaway times of interest. In Figure 2, this is illustrated for a one dimensional case, where a Gaussian PDF of the Arrhenius parameters is assumed. If the probability of a thermal runaway occurring for time greater than four, for example, is to be determined, then the integral of the PDF from a to b is calculated.

$$P(t > t_a) = \int PDF(x) dx$$

The integral from a to b gives the probability that thermal runaway will occur in times between t_a and infinity. The Arrhenius parameter marked as variable a gives thermal runaway times of t_a .

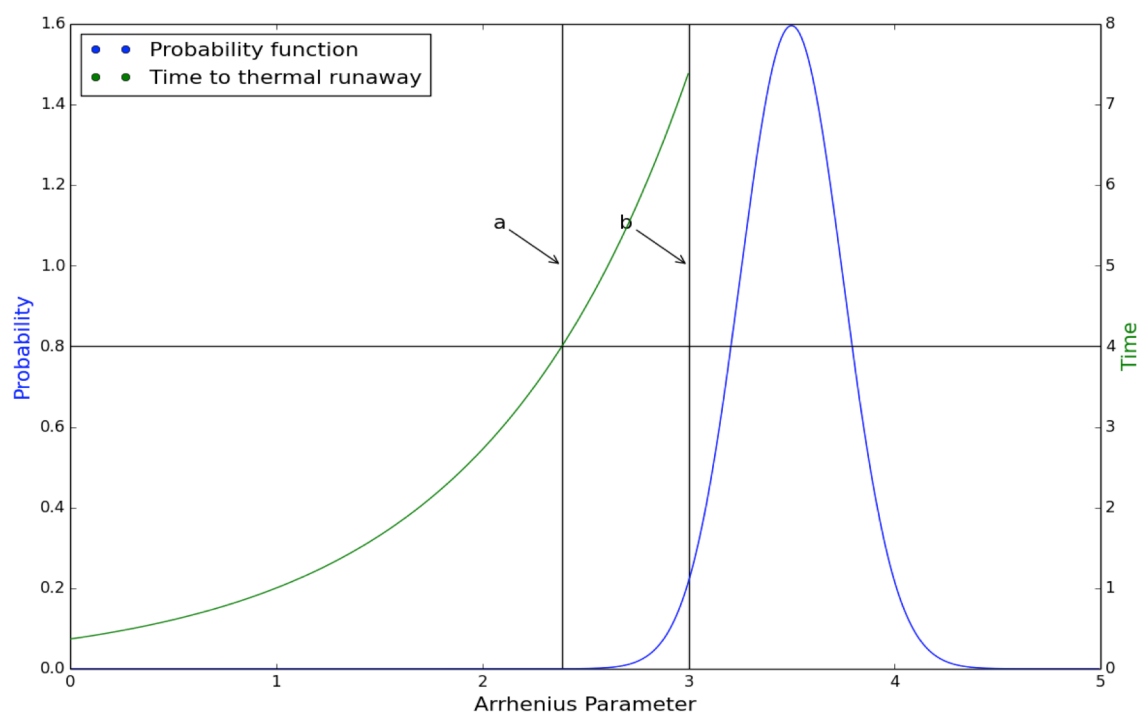


Figure 2: The time to thermal runaway (green) and PDF (blue) for a sample set of Arrhenius parameters. For Arrhenius parameters greater than three no thermal runaway will occur. The probability of a thermal runaway for time greater than four will be the integral of the PDF from a to b.

This methodology gives clear path forward for calculating the probability of one of the existing LANL Nitrate Salt drums to undergo thermal runaway—assuming an order of the Arrhenius kinetics for the well-mixed, homogeneous drums—the probability can be calculated by determining the times to thermal runaway for the set of Arrhenius parameters and applying the appropriate PDF for the system.

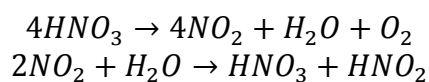
The Chemical System

The LANL Nitrate Salt drums of interest consist of nitrate salts generated from the historical plutonium recovery operations, an organic wheat based pet litter, an organic neutralizer and a variety of metals, such as lead, bismuth, iron, and aluminum, to name a few. It is well known that metal nitrates will react with cellulose/starch, the primary reactive constituents of the organic pet litter. While the pet litter also contains lignins and lignincellulose, these are not likely of concern considering the most reactive functional group on these compounds is the aromatic rings, and these are less reactive than the hydroxyl group on the cellulose and starch molecules (Summerscales, 2015). Since cellulose and starch will be the most reactive component of the pet litter and because most of the existing literature concentrates on the reaction of nitrate salts or nitric acid with cellulose rather than starch, the organic pet litter was assumed to consist of entirely of cellulose. Since both starch and cellulose react primarily through the hydroxyl functional group, reaction kinetics are similar for both. The enthalpies are also similar, meaning this can be considered a valid approximation.

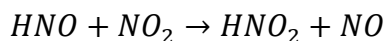
The reaction of metal nitrates and cellulose is quite complex and has not been completely described in the literature. Cellulose can react with nitrate salts in a variety of ways from oxidation of cellulose or as

nitration agents. The metal salts can also catalyze the nitration, hydrolysis and pyrolysis of cellulose. The metal nitrate salts can also react with water to undergo hydrolysis or pyrolysis, upon heating, to produce nitric acid. The nitric acid can react with the hydroxyl group on the cellulose to produce the nitrate ester nitrocellulose, whose properties have been well studied. In addition, iron nitrate salts have been shown to catalyze the production of HNO_3 and NO_x , which can directly react with the cellulose in variety of ways, such as nitration or oxidation of the cellulose.

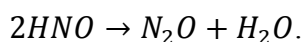
Both the nitration and oxidation of cellulose or starch proceed through the formation of the nitronium ion, NO_2^+ (V.A. Rafeev, 1999) (J. Taylor, 1947) and it seems the most likely mechanism would be the oxidation of the pet litter via the reactive hydroxyl group. The likely mechanism for oxidation would be the one proposed for the oxidation of alcohols by Aellig, *et al* (C. Aellig, 2011). However, the source of the nitric acid/ NO_2 would come from the hydrolysis/ decomposition of the metal nitrates salts. The nitric acid and NO_2 can then form the nitronium ion as follows:



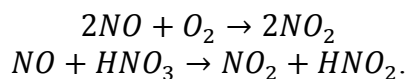
The HNO_2 then oxidizes the pet litter and gives HNO which can then be either oxidized back to HNO_2 by reaction with NO_2 as,



or the HNO react with itself as follows,



The formation of N_2O ends its potential as an oxidant, however the NO from the previous reaction can then be oxidized back into NO_2 , either by reaction with atmospheric oxygen, or by reacting with nitric acid.



This means the overall reaction forms a cycle where oxidants can be regenerated from either atmospheric oxygen present in the drum or from the metal nitrate salts. This regenerative oxidation scheme is summarized in Figure 3.

While the generic reaction scheme presented in Figure 3 shows the hydroxyl group being oxidized to an aldehyde, this would not necessarily be the case in the actual system. Many other reactions will take place and one would expect a great number of fully oxidized and partially oxidized products to form. As for most oxidative reactions, this is expected to be quite exothermic.

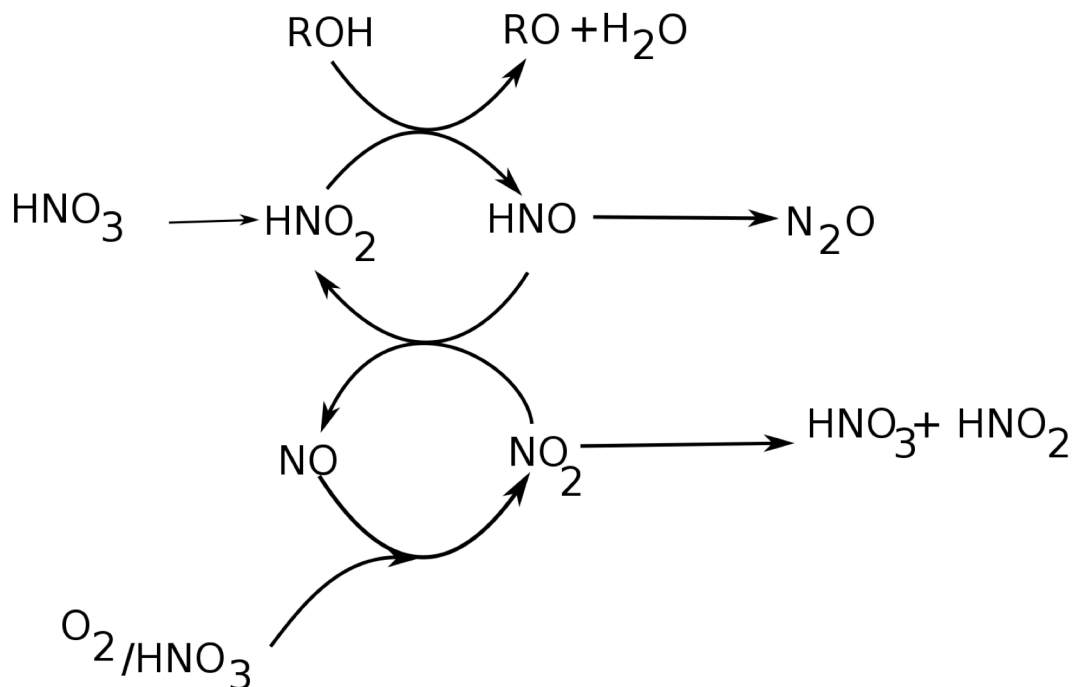


Figure3: Overall regenerative oxidation scheme showing the oxidation of the reactive hydroxyl group, ROH , to an aldehyde.

If this was a closed system, where the amount of nitric acid was fixed by the initial conditions, one would expect that the cycle would come to an end once all the oxygen from the nitric acid and atmospheric oxygen was used. For the system of interest, however, this is not the case—while the system is closed, it continues to produce excess nitric acid as the metal nitrates salts continue to undergo hydrolysis, which means the system can continue to oxidize the pet litter and regenerate the NO into NO_2 even after the free oxygen is depleted. It is expected to see an increase in NO and N_2O concentrations, as well as a decrease in atmospheric oxygen, as the reaction progresses.

Any significant increases in the concentrations of NO or N_2O , as well as a decrease in the free oxygen, can be taken as indicator that this reaction is proceeding at significant rate. This makes the monitoring the NO_x concentration, specifically the NO and N_2O concentrations, good diagnostics for determining if an exothermic oxidation reaction is occurring. It is expected to see a decrease in the free oxygen before significant increases in NO and N_2O . It is also expected that both CO and CO_2 would be produced when as the oxidation reaction progresses. Obviously, any increases in temperature would be a good indicator as well. Since the NO_2 will react with either the HNO or the water it is not expected to see significant quantities of NO_2 . The trends in the concentration of NO , N_2O and O_2 were all measured and reported in a companion report (G. Parker, Thermolytic Response of Surrogate Remediated Nitrate Salts Waste Mixtures at the Drum Scale, 2015).

Discounting the reaction of the various lignins, sugars, etc. in the pet litter, as well as reactions of the organic neutralizer, and only considering the reactions involving the metal nitrates and the cellulose, it should be noted this chemistry has not been well reported in the literature. This, combined with the fact

that the contents of the LANL Nitrate Salt drums are not well described, means the contents of the drums must be described as a general chemical system. Consequently, for this numerical analysis, the contents are considered a well-mixed, homogeneous system, where the rate of reaction can be described by Arrhenius kinetics. In order to keep the work computationally tractable only first order Arrhenius kinetics are considered. Therefore three parameters will be needed to describe the general chemistry of the drums: the activation energy, the pre-exponential factor and the enthalpy.

$$\frac{d[A]}{dt} = [A]Z e^{\frac{-E_a}{RT}}$$

The first order Arrhenius kinetics equation showing the change of concentration with time. E_a is the activation energy, Z is the pre-exponential factor, $[A]$ is the concentration of the reactant, R is the Boltzmann constant and T is the temperature in Kelvin.

In order to keep the problem computationally tractable, the Arrhenius factors must be bound in some physically meaningful manner. Therefore, they were chosen by considering the thermal decomposition of nitrocellulose, since most reactions of cellulose with nitrate salts proceed through reactions with the hydroxyl group. The Arrhenius parameters reported in the literature (Summerscales, 2015) vary quite broadly, with the activation energy, E_a , varying from 10-53 kcal/mol, while the log of pre-exponential factor varies from $\log(Z) = 7-23 \text{ s}^{-1}$. The wide range of values come from the fact that multiple mechanisms can drive the thermal decomposition of nitrocellulose and these mechanisms become active in three broadly defined temperature ranges: low ($T < 100 \text{ }^\circ\text{C}$), intermediate ($100 \text{ }^\circ\text{C} < T < 200 \text{ }^\circ\text{C}$) and high temperatures ($T > 200 \text{ }^\circ\text{C}$).

Since the reactions in the drums occur in the low temperature range, only the low end of the activation range will be considered: activation energy values of approximately 15-40 kcal/mol and pre-exponential factors of $\log Z = 6-25 \text{ s}^{-1}$. The pre-exponential factors are shifted to the low side since regions of interest in the Arrhenius parameter space are near the go/no-go boundary for thermal runaway. The maximum possible enthalpy out of the salt/pet litter system would be the enthalpy for the complete oxidation of cellulose, 4160.0 cal/g (R.S. Jessup, 1950). Therefore, it is possible to bound enthalpy of the generalized system by the maximum enthalpy. The system contains a variety pet litter to salt ratios, where the 3:1 pet litter to nitrate salt by volume ratio was considered to be the worst case scenario. This dilutes the enthalpy to 2800 cal/g.

Simulation Overview

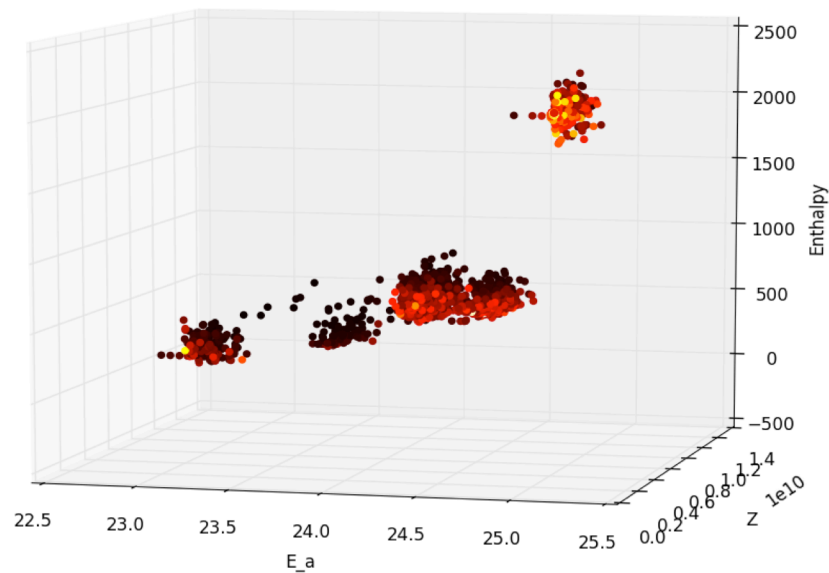


Figure 4: The set of kinetic parameters which lead to thermal runaway are shown in 3 dimensions, activation energy (E_a), pre-exponential factor (Z) and enthalpy. The lighter the color the longer the time to thermal runaway. The go/no-go surface is roughly outlined. For clarity the no-gos are not shown.

In order to calculate the probability of another thermal runaway occurring in one of the existing LANL Nitrate Salt drums, the Arrhenius parameter space for the physically relevant values of the parameters must be explored, which determined if thermal runaway could occur for each combination Arrhenius parameters, as well as the time to thermal runaway. A variety of general assumptions were made to make the problem tractable:

- The material in the drums is well-mixed and homogeneous.
- One chemical reaction was occurring and it follows first-order Arrhenius kinetics.
- The maximum enthalpy was assumed to be capped by the complete oxidation of the pet litter – 2800 cal/g.

The first methodology used a Markov chain Monte Carlo method (Hastings, 1970) for exploring the full three dimensional (activation energy, pre-exponential factor and enthalpy) Arrhenius parameter space. The heat equation with reaction kinetics was then solved for the drums for each step in the Monte Carlo scheme to determine if thermal runaway occurred and the elapsed time to runaway. If thermal runaway did not occur then the step was rejected and the next step of the Markov chain took

place from the last combination of parameters to give runaway. In order to keep parameters near the thermal-runaway boundary the probability distribution from which the Markov chain sample was weighted towards the go/no-go boundary.

Many thousands of simulations were performed with the Monte Carlo scheme described above for ambient temperatures of 20 °C and 25 °C. See Figure 4 for an overview of the 20 °C results. However, this methodology proved to be intractable due to the extremely small slice of parameter space on which the longer thermal runaway times exist, which it makes it extremely unlikely that such a method would find the longer runaway times of interest.

In order to achieve long thermal runaway times the heat produced by the chemical reaction must be very finely balanced by the heat lost to the environment—if the chemical reaction produces heat much faster than heat is lost to the environment the drum undergoes thermal runaway fairly rapidly. Conversely, if more heat is lost to the environment than is produced by the chemical reaction then thermal runaway is never achieved and all the chemical energy in the system bleeds away to the environment. As will be seen, very small changes in the rate of heat production when near the thermal runaway boundary can make it a large difference in thermal runaway times. For example, a change in activation energy of on the order of 10^{-13} % can make a difference in thermal runaway times of greater than 50 days. This means the Monte Carlo method of exploring the Arrhenius parameter space is excessively unlikely to describe the kinetic parameters of interest unless a physically unachievable number of simulations is performed. Therefore a different methodology to describe the parameter space must be used.

Since each drum contains a finite amount of chemical energy, the drums, which will have the longest possible thermal runaway times are those which have the most chemical energy--this corresponds to higher enthalpies for the case of first order kinetics. Since this is a safety calculation a worst case scenario can be used as a basis for the probability calculation, which would be the maximum enthalpy available for this system. In other words, it is assumed the pet litter is fully oxidized and the Arrhenius parameter space is reduced from three dimensions to two.

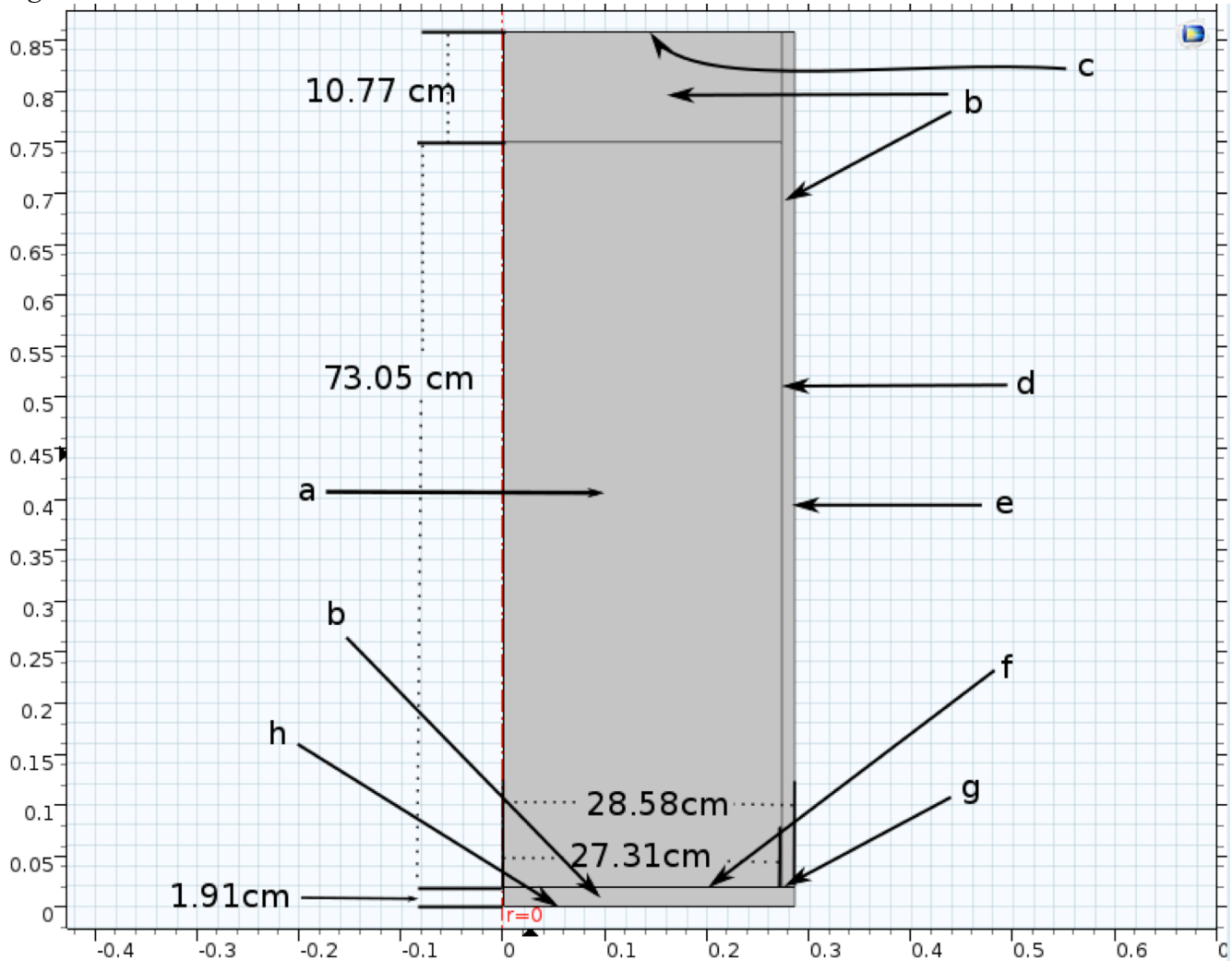
Rather than using a Monte Carlo algorithm to explore the reduced parameter space, which would still be extremely unlikely to find the parameters for longer thermal runaway times, a different approach is taken. In this approach the pre-exponential factor is fixed and the initial activation energy is picked such that thermal runaway occurs. The activation energy is then increased by discrete steps, ΔE_a , until no thermal runaway occurs. At this point the step size is cut in half for each step and the activation energy is increased from the point of last thermal runaway. This is then iterated until the difference in time to thermal runaway for two successive steps is less than 10,000 secs or the error in the numerics due to the extremely fine margins become apparent. At this point, the pre-exponential factor is increased by a discrete value and the iteration over the activation energy starts over.

This methodology allows the thermal runaway boundary to be resolved to high level of resolution, such that the difference in activation energy between the longest time thermal runaway and no thermal runaway is on the order of 10^{-15} kcal/mol. This will allow the longest time thermal runaway line to be determined to a high degree of accuracy, as well as finding the thermal runaway boundary, which will give the necessary data for determining the probability of a thermal runaway after a certain time has elapsed.

Model Setup Details

The COMSOL Multiphysics program was used to solve the heat equation with heat generation from the reactive chemistry. The symmetry of the drum was utilized to reduce the computational load by assuming two-dimensional axisymmetry. The drum was meshed with custom free triangular grid with a minimum element size of 6.5×10^{-6} m and a maximum element size of 0.003 m. The simulation was run for 600 days with an absolute tolerance of 1×10^{-9} . The simulation was stopped if the maximum temperature in the drum exceeded 420 K. This was considered a thermal runaway.

Figure 5



The dimensions, materials, etc. of the simulation are overviewed in Figure 4. The key for Figure 4 is as follows:

- a) This area is filled with the pet litter, nitrate salt and water mixture.
- b) These areas are filled with air.
- c) This lid of the drum is approximated as a thin layer in COMSOL. It is 0.12 cm thick AISI 4340 steel and uses horizontal plate natural convective heat flux boundary condition.
- d) The 0.64 cm thick cardboard liner of the drum is approximated as a thin layer in COMSOL.
- e) The drum is approximated as thin layer in COMSOL. It is AISI 4340 steel and uses vertical

- wall natural convective heat flux boundary condition.
- f) The bottom of the drum is approximated as a two layer thin layer in COMSOL. It consists of 0.12 cm thick AISI 4340 steel and 0.64 cm thick cardboard.
 - g) This is approximated as a thin layer in COMSOL. It consists of AISI 4340 steel.
 - h) This boundary is fixed to the environmental temperature.

The thermal properties, the heat capacity, density and thermal conductivity, of the various materials are overviewed in Table 1.

Material	Heat Capacity	Density	Thermal conductivity
Air	1.01 (J/(g*K))	272.35/T (kg*K/m ³)	See Text
Cardboard	140 (J/(kg*K))	840 (kg/m ³)	0.17 (W/(m*K))
AISI 4340 Steel	475 (J/(kg*K))	7850 (kg/m ³)	44.5 (W/(m*K))
Pet litter mixture	See Text	967.7 (kg/m ³)	See Text

Table 1: An overview of the thermal properties of the materials used in the simulation. The values for air were adjusted for altitude. See text for discussion on pet litter mixture.

The built in physical constants in COMSOL were used for cardboard and the steel. The thermal parameters for air were adjusted for the altitude of Los Alamos National Laboratories, where the thermal conductivity for air was found to be:

$$k_{air} = a * T + b$$

where $a = 7.95 \times 10^{-5} \text{ Wm}^{-1}\text{K}^{-2}$ and $b = 2.147 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-1}$.

The pet litter mixture is a complex mixture of pet litter, nitrate salts and water. Precision Measurements and Instrumentation Corporation (PMIC) determined the thermal parameters for the pet litter and nitrate salt mixture for a variety of ratios of pet litter to salt and water. However, the mass fraction of water of interest was not directly measured and was then found by fitting to the following forms. The form of the heat capacity used was:

$$C_p = C_1 T + C_2 M_w + C_3$$

Where $C_1 = 0.012 \text{ Jg}^{-1}\text{K}^{-2}$, $C_2 = 2.656 \text{ Jg}^{-1}\text{K}^{-1}$ and $C_3 = 1.955 \text{ Jg}^{-1}\text{K}^{-1}$. The mass fraction of water, M_w , used was $M_w = 0.068$.

Since the pet litter/salt mixture forms a porous, complex mixture, the form of the thermal conductivity was quite a bit more complex and estimated to be the following (Heatwole, 2015):

$$k = \frac{k_{wat} - k_{dry}}{2} \left(1 + \text{erf} \left(\frac{M_w - \mu(T)}{\sqrt{2}\sigma(T)} \right) \right)$$

Where M_w is the mass fraction of water, erf is the error function, k_{wat} is the thermal conductivity of water in W/(mK),

$$k_{wat} = 0.9 + 0.008387T - 1.118 \times 10^{-2}T^2,$$

and k_{dry} is the thermal conductivity of the dry 3:1 pet litter, salt mixture in W/(mK),

$$k_{dry} = 2.4 \times 10^{-4}T + 0.01323.$$

The $\sigma(T)$ and $\mu(T)$ functions are unitless temperature dependent fitting parameters and where found to be,

$$\mu(T) = 2.554 \times 10^{-4}T - 0.6134$$

and,

$$\sigma(T) = 8.258 \times 10^{-4}T - 0.04002.$$

Any effect of the dissolution or precipitation of the salt with temperature was neglected for all of these thermal parameters.

Convective heat flow boundary conditions were used for the lid and sides of the drum. The built in parameters in COMSOL for the heat transfer coefficient for the upside of a horizontal plate and vertical wall with external natural convection was used for the lid and walls of the drum. The environmental temperature, in this case, 10, 15, 20, and 25 °C was used as both the initial temperature of the drum and the external temperature. The bottom boundary condition was fixed to this temperature as well.

The thermal parameters described above were used to model the cooling test of surrogate pet litter drums (G. Parker, Data Report for the Drum-Scale Thermal Transport Characterization Study, 2015). The cooling curves were described very well by the preceding model.

Results

The times to thermal runaway for the two dimensional Arrhenius parameter space were calculated for 10, 15, 20, and 25 °C using the methodology described previously. The enthalpy was fixed to the worst case – the complete oxidation of the pet litter – which leads to the longest thermal runaway times. For each temperature the pre-exponential factor was varied between 10^6 to 10^{25} s^{-1} where the time to thermal runaway was calculated for a series of activation energies.

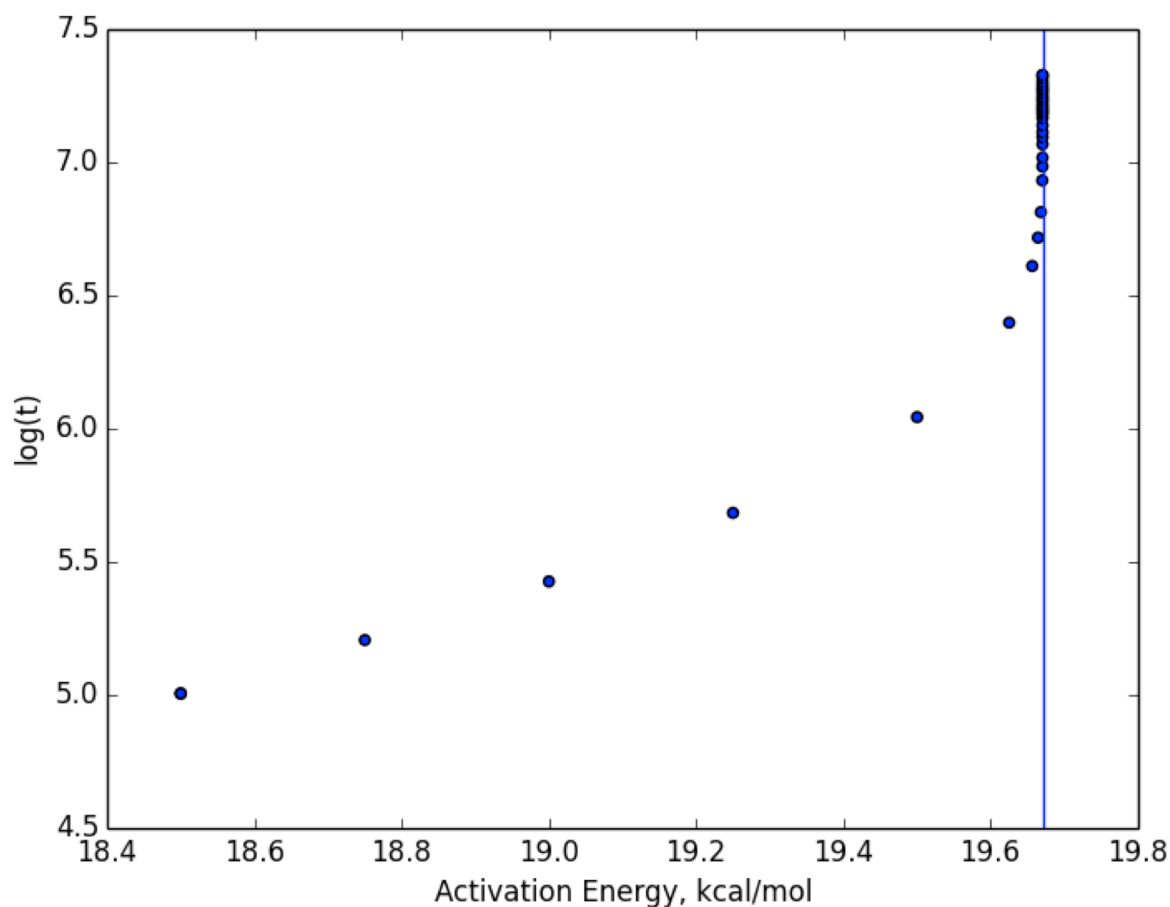


Figure 6: Plot showing the dependence of time to cook-off with activation energy. For this example the temperature is 20 °C and the pre-exponential factor is 10^6 s^{-1} . The blue line is the go/no-go boundary, where activation greater than the line will result in no thermal runaways. The strong dependence of time to thermal runaway on activation energy near the thermal runaway boundary is illustrated.

As can be seen in Figure 6, as the activation energy approaches thermal runaway boundary the time to runaway increases with smaller and smaller changes in activation energy. If there was an infinite source of chemical energy available to the system the time to runaway would asymptote to infinity as the difference between the activation energy and the go/no-go boundary goes to zero. However, since there is a finite amount of chemical energy in the drums, the system must run out of energy at some point and represents a hard boundary in time to thermal runaway. Also illustrated in Figure 6 is how strongly small changes in activation energy near the thermal runaway boundary causes large changes in the time to thermal runaway. For this example, a change in activation energy 8×10^{-11} kcal/mol leads to a 58-day increase in the time to thermal runaway.

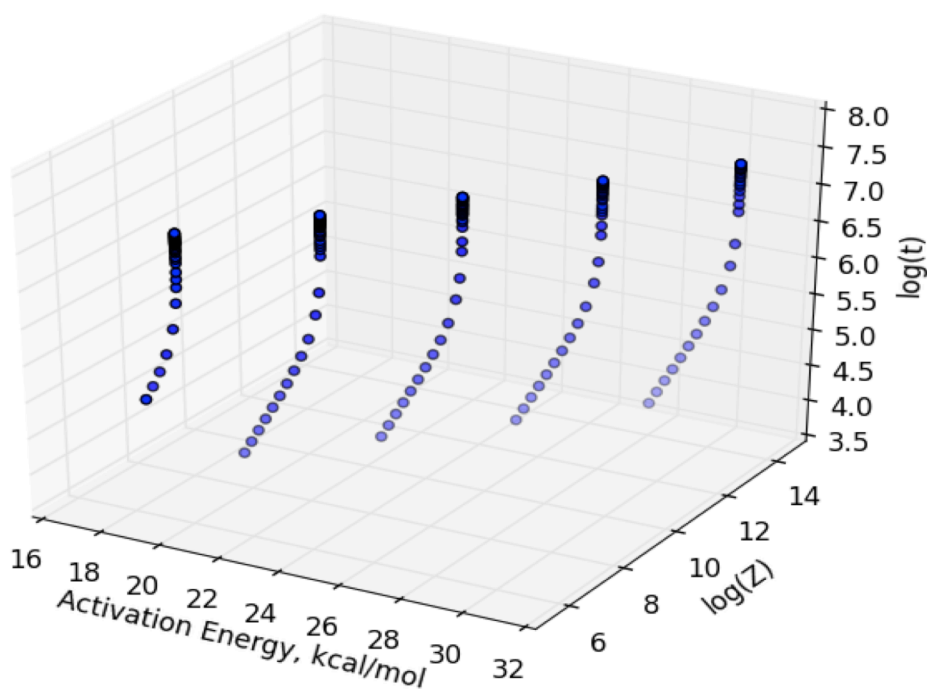


Figure 7: Showing the time to thermal runaway for a drum at 20 °C ambient temperature for a variety of pre-exponential factors and activation energies.

T (°C)	log(Z)	E _a (kcal/mol)	Time to runaway (s)	ΔE _a (kcal/mol)
25	8	22.7929	2.2195x10 ⁷	2.0x10 ⁻²⁶
25	10	25.5969	2.3233x10 ⁷	1.8x10 ⁻¹⁵
25	11	26.9958	2.3908x10 ⁷	1.8x10 ⁻¹⁵
25	15	32.5739	2.5937x10 ⁷	1.0x10 ⁻²⁶
25	20	39.5181	2.7653x10 ⁷	3.6x10 ⁻¹⁵
25	25	46.4407	3.0216x10 ⁷	8.9x10 ⁻¹⁶
20	6	19.6703	2.1267x10 ⁷	2.2x10 ⁻¹⁹
20	8	22.4404	2.2397x10 ⁷	1.8x10 ⁻¹⁵
20	10	25.1995	2.3826x10 ⁷	1.0x10 ⁻²⁶
20	12	27.9501	2.4171x10 ⁷	1.8x10 ⁻¹⁵
20	14	30.6940	2.4919x10 ⁷	1.8x10 ⁻¹⁵
20	16	33.4323	2.5937x10 ⁷	2.2x10 ⁻¹⁶
20	18	36.1660	2.6784x10 ⁷	3.6x10 ⁻¹⁵
15	6	19.3633	2.0606x10 ⁷	3.6x10 ⁻¹⁵
15	8	22.0878	2.1875x10 ⁷	8.9x10 ⁻¹⁶
15	10	24.8015	2.2875x10 ⁷	1.8x10 ⁻¹⁵
15	12	27.5068	2.3838x10 ⁷	8.9x10 ⁻¹⁶
15	14	30.2055	2.5642x10 ⁷	2.2x10 ⁻¹⁶
15	16	32.8988	2.6423x10 ⁷	1.0x10 ⁻²⁶
15	18	35.5875	2.6679x10 ⁷	1.8x10 ⁻¹⁵
15	20	38.2724	2.7142x10 ⁷	1.8x10 ⁻¹⁵
10	6	19.0559	2.0662x10 ⁷	1.8x10 ⁻¹⁵
10	8	21.7346	2.1561x10 ⁷	4.4x10 ⁻¹⁶
10	10	24.4027	2.2720x10 ⁷	4.4x10 ⁻¹⁶
10	12	27.0628	2.3750x10 ⁷	8.9x10 ⁻¹⁶
10	14	29.7164	2.4547x10 ⁷	1.0x10 ⁻²⁶
10	16	32.3647	2.5380x10 ⁷	1.0x10 ⁻²⁶

Table 2: An overview of the results of the simulation. The activation energy which gives the longest time to thermal runaway is shown for each temperature and pre-exponential factor. Also shown is, ΔE_a, the difference in activation energy between the longest time to runaway and the nearest no-go.

Table 2 gives an overview of the results generate from the set of computer simulations. The table shows the activation energy, which gives the longest time to thermal runaway for a specific pre-exponential factor. Also shown is, ΔE_a, the difference in activation energy between the longest time to thermal runaway and the closest no-go in activation energy. If there is to be thermal runaway times

greater than the longest runaway time found, ~350 days, then the combination of Arrhenius parameters must exist somewhere in the gap between the longest time runaway and its nearest no-go. Since this gap is exceptionally small it is beyond extremely unlikely that any of the existing LANL Nitrate Salt drums would contain the proper combination of kinetic parameters. See the section on probability for an extensive analysis.

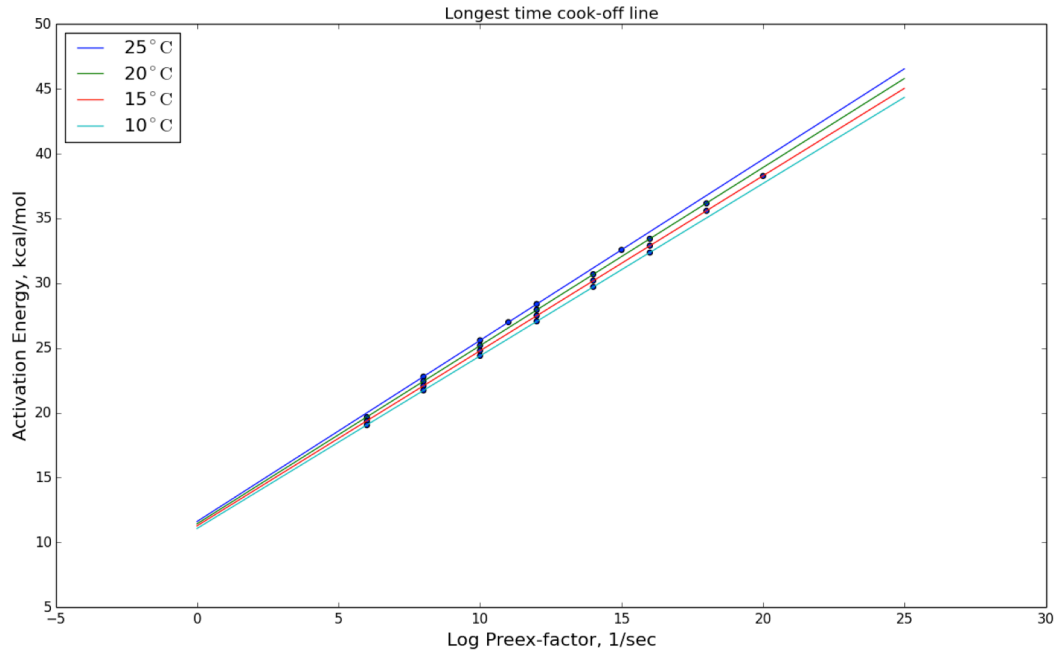


Figure 8: Shows the longest time to thermal runaway line in the activation energy, pre-exponential parameter space.

Next the Arrhenius parameters, which give the longest time to thermal runaway were plotted with activation energy and the pre-exponential factor. The activation energies were then fit to the equation of a line, $E_a = a \log(Z) + b$. The results are tabulated in Table 3.

T (°C)	a	δa	b	δb	Average $\Delta E_a, \mu_w$ (kcal/mol)	δ_w
25	1.397	0.001	11.62	0.01	8.9×10^{-16}	1.2×10^{-15}
20	1.374	0.001	11.44	0.02	1.3×10^{-15}	1.2×10^{-15}
15	1.350	0.001	11.29	0.02	1.3×10^{-15}	1.1×10^{-15}
10	1.331	0.001	11.09	0.02	5.9×10^{-16}	6.1×10^{-16}

Table 3: Showing the constants for fitting the activation energies to a line $E = a \log(Z) + b$. The constants a and b are the fitting constants, while δa and δb are the errors associated with the constants. Also tabulated is the average difference in activation energy between the longest time thermal runaway and the nearest no-go and its error.

Probability Analysis

As discussed in the previous section if a thermal runaway was to occur in the one of current LANL Nitrate Salt drums, its kinetic parameters must exist somewhere in the parameter space between the longest time thermal runaway and the parameters defining the no thermal runaway space. In order to estimate a probability of thermal runaway a PDF describing the distribution of Arrhenius parameters in the LANL Nitrate Salt drums must be found. It is possible to build a PDF based on the actual empirical information available by considering the temperature history and time to thermal runaway of the drum 68660. This approach would have several shortcomings, the foremost being the paucity of the empirical evidence available. However, since this is a safety calculation a worst case PDF will be used and will provide an upper bound on the probability of thermal runaway. As will be seen later, the probability of thermal runaway calculated using a worst case PDF is so small it is unnecessary to compare it to a PDF based on the real drums. The worst case PDF will be defined as a Gaussian distribution centered on the longest time thermal runaway line. Thus, by design, the worst case PDF will determine a higher probability of thermal runaway than one derived from the actual drums. If the worst case PDF was reflected in reality, it would be expected that approximately half the drums would have undergone thermal runaway at this point.

It should be noted that the longest time thermal runaway line does not represent a single thermal runaway time, rather it is the longest time the computational methodology was able to find. The actual calculated time to thermal runaway changes as the set of kinetic parameters on the line changes, with a general increase in thermal runaway times as the kinetic parameters increase. This means it is incorrect to say that the calculated probability for thermal runaway is for a distinct time but rather that the drums could have a set of kinetic parameters which are within the region between the longest time thermal runaway line and the no-go region. This region contains the kinetic parameters, which would lead to thermal runaway in the LANL Nitrate Salt drums for times greater than 675 days, so this analytic technique is applicable for problem and would be considered a conservative approach since it also would contain the kinetic parameters which would lead to runaway in less than 675 days as well.

The multivariate Gaussian PDF used will be centered between the longest time thermal runaway line and the go/no-go line determined in the previous section, where the activation energy can be written as $E_a = a \log(Z) + b$. It is assumed that there is no correlation between the variables of the PDF. Then the PDF centered between the longest time cook-off line and the go/no-go line can be written as follows:

$$P(x, y) = \frac{1}{2\pi\delta_y\delta_x} \exp\left(-\left(\frac{(y - (ax + b))^2}{2\delta_y^2} + \frac{(x - \mu_x)^2}{2\delta_x^2}\right)\right)$$

Where x and y are taken to be the log of the pre-exponential factor and activation energy respectively. The constants a and b are found from the equation of the longest time cook-off line. The width of the PDF, δ_x and δ_y , as well as the average position in the x coordinate, μ_x , is chosen somewhat arbitrarily. However, it should be intuitively obvious that the values of δ_x and μ_x will have only a small effect on the final probability.

In order to achieve thermal runaway in the time frame of interest the kinetic parameters must be between the longest time thermal runaway line and the go/no-go line. This space is consider to be a strip of the Arrhenius parameter space and follows the line $E_a = a \log(Z) + b$ and has some width , w . See figure 9.

The probability of a thermal runaway is simply the PDF integrated over this width. If the width was known exactly this calculation would be trivial, however, this is not the case—there is error associated with the width. The width is assumed to follow a log-normal distribution, $B(w)$, where the location and shape parameters are determined from the average ΔE_a and the ΔE_a variance.

$$B(w) = \frac{1}{\sqrt{2\pi}w\delta_w} \exp\left(\frac{-(\ln(w)-\mu_w)^2}{2\delta_w^2}\right)$$

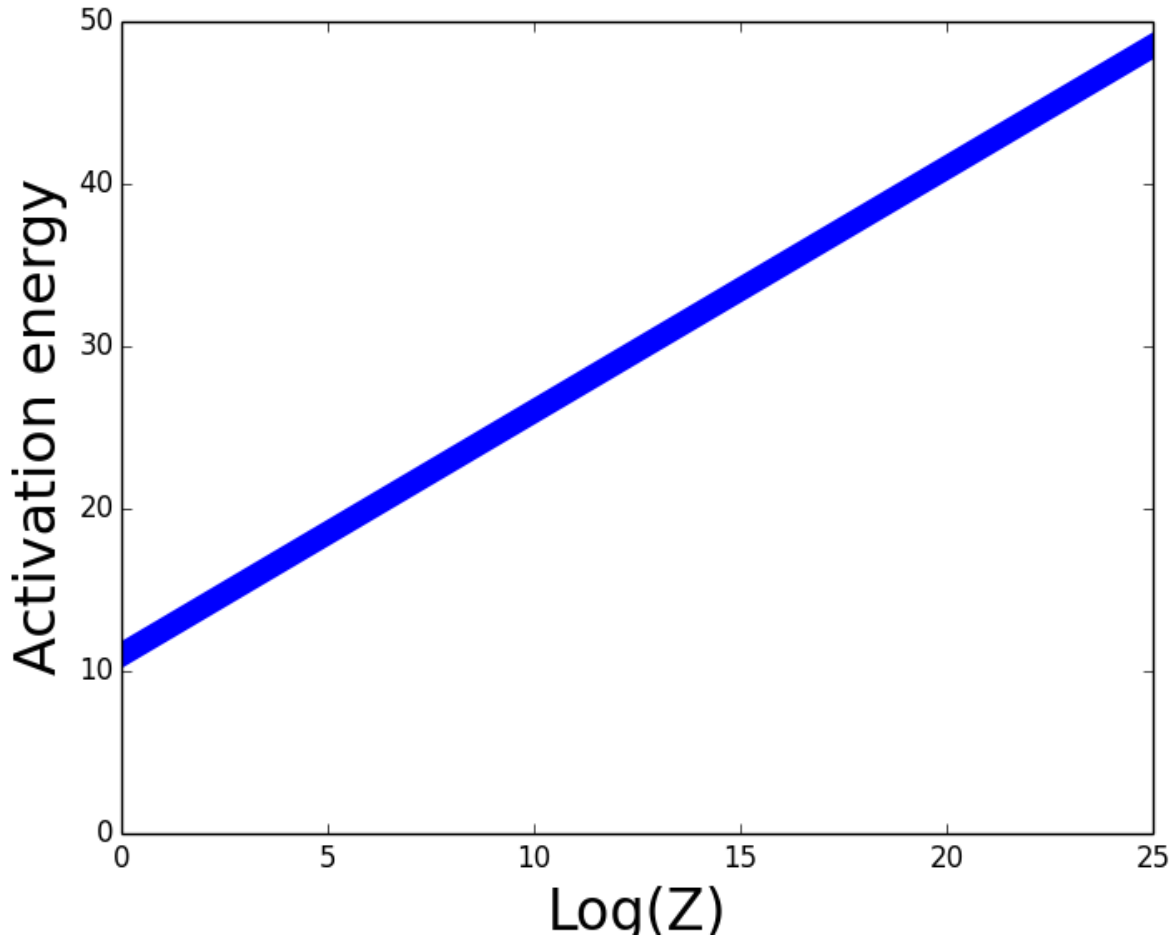


Figure 9: Showing the strip of activation energy and pre-exponential factor space that the PDF is integrated over.

The width is not exactly known, so in order to calculate the probability of interest all possible values of the width will be considered and weighted with the $B(w)$ term (Nakhleh, 2015) (McLenithan, 2008) (Ng, 1968). This leads to the following expression for the probability of interest,

$$\begin{aligned} Pr &= \int_0^\infty B(w) \int_{-\infty}^\infty \int_{ax+b-\frac{w}{2}}^{ax+b+\frac{w}{2}} P(x, y) dy dx dw \\ &= \int_0^\infty B(w) \operatorname{erf}\left(\frac{w}{2\delta_y\sqrt{2}}\right) dw \end{aligned}$$

where $P(x,y)$ is the PDF of the Arrhenius parameters.

An exact analytical solution to this expression does not exist and numerical methods for solving the integral are difficult to implement do to the very small size of the width. However, an accurate approximate solution can be found by Taylor expanding the error function around μ_w to give the following expression:

$$Pr = \operatorname{erf}\left(\frac{\mu_w}{2\sqrt{2}\delta_y}\right) + \frac{e^{-\frac{\mu_w^2}{2\sqrt{2}\delta_y}}}{\delta_y\sqrt{2\pi}}\left(e^{\frac{\delta_w^2}{2}} - \mu_w\right)$$

It should be intuitively obvious that this solution is approximately equal to the height of the activation energy portion of PDF Gaussian multiplied by μ_w , however, the above equation will be used for all probability calculation in this work. See Table 4 for an overview of the probability to thermal runaway.

In order to apply this equation to the problem at hand, several quantities must be determined. The most important quantity is the average difference in activation energy or μ_w . The calculated value tabulated in Table 3 will be used to determine a lower bound on the probability. Since this is a safety calculation an increased value of $\mu_w = 10^{-10}$ will be used to find an upper bound on the probability. The variance in width, δ_w , is scaled linearly from the μ_w value. This larger value corresponds to an approximate 50-day change in thermal runaway times this close to the no-go border. This value for is the upper bound of the probability of a drum undergoing thermal runaway with the chosen worst case PDF. A lower bound can be calculated by considering the value of ΔE_a found from the numerical work. As expected this value was approximately five orders of magnitude lower than the upper bound.

While the μ_w and δ_w terms are determined from the computational work, the δ_x , δ_y and μ_x terms must be chosen by the researcher. As expected, the δ_x and μ_x terms have no effect on the final probability. The δ_y term has a stronger effect on the calculated probability and is chosen to be 1 for the purposes of this work. This is still a much tighter distribution than would be expected to be found in the actual drums and is still considered a worst case PDF.

Temperature (°C)	Upper Bound	Lower Bound
25	4.0×10^{-11}	5.2×10^{-16}
20	4.0×10^{-11}	5.2×10^{-16}
15	4.0×10^{-11}	5.2×10^{-16}
10	4.0×10^{-11}	2.4×10^{-16}

Table 4: The upper and lower probability bounds for a thermal runaway occurring for the various temperatures. The upper bound was found by setting the average width, μ_w , to 10^{-10} , while the lower bound was calculated from the simulations.

Discussion

The applicability of this work hinges on several caveats, one of which was that the global chemical system followed first order Arrhenius kinetics. The key point is that the heat generated by the chemical

system must be extremely finely balanced with the heat flowing out of the system into the environment to lead to long thermally runaway times. With the first order system the slice of parameter space which lead to long thermal runaway times was so small that the probability that a chemical system would have the parameters necessary was minuscule. As with the first order system, an arbitrary order kinetic system would have to balance the heat flow out of the system with the heat generated by the chemistry and, in a similar fashion, the multidimensional slice of parameter space which would lead to long thermal runaway times would be excessively small.

As an example of the sensitivity of the thermal runaway times to the kinetic parameters, consider a drum which differs from the 3:1 pet litter to nitrate salt ratio by 1 milligram. That is, for an entire drum filled with the pet litter/salt mixture, one extra mg of the pet litter is added above the necessary amount of pet litter to reach the 3:1 ratio. This will result in an increase of enthalpy of $\sim 10^{-8}$ cal/g, which for values of the kinetic parameters near the go/no-go boundary, can mean a change in thermal runaway times of ~ 100 days. This is an extraordinary dependence in runaway times on the kinetic parameters and illustrates how unlikely it is to have the particular combination of kinetic parameters which can lead to runaway times of ~ 300 days, let alone of greater than 675 days.

Another caveat included not subjecting the drums to any additional thermal insult. Consider, for example, a drum was filled with material, which followed first order kinetics, with a set of Arrhenius parameters which did not result in thermal runaway but were close to the thermal runaway boundary. If this system was aged and then subjected to further thermal insult – say an increase of environment temperature of 10°C – then there is a possibility of thermal runaway occurring, depending on the exact kinetic parameters and the length time the drum was aged. ***Therefore, it is recommended that the current LANL nitrate drums be protected from any additional increases in temperature.*** A complete analysis of the temperature response after aging is beyond the scope of this report.

However, cooling the drums will drop the already extremely low probability of thermal runaway to absurdly low values. For example, if the LANL nitrate drums which have been stored at 20 or 25°C , are then cooled to 10°C , any drums which would have undergone thermal runaway at 10°C already would have undergone thermal runaway and any drums which could still undergo thermal runaway, despite the extremely low probability of it occurring, would now be quite firmly placed in the no-go region of parameter space. Figure 8 illustrates this quite clearly. ***It is very strongly recommended that any processing of the LANL nitrate drums take place with the drums cooled to at least 10°C .***

The caveat that the material in the drums is well-mixed is another condition which could possibly fail. It is possible to imagine a scenario where previously unmixed material can become mixed after agitation and activate exothermic chemistry. This makes a diagnostic for detecting active chemistry, which can lead to thermal runaway highly desirable.

The most obvious diagnostic for detecting active exothermic chemistry is, of course, measuring the temperature of the drums. However, measuring the internal temperature of the current configuration of the LANL nitrate salt drums would be impractical and while the computational work done shows that the temperature of the surface of the drum would be noticeably higher than the environmental temperature in the days leading to thermal runaway, the computational work assumed the drum were completely filled with the reacting mixture. In the real drums this would not likely be the case and it would be more likely that exothermic reactions would be occurring in isolated pockets in the drums. This means that temperature measurement of the surface of the drums might not detect the presence of active exothermic chemistry.

As discussed in the chemistry section, the exothermic chemistry, which becomes active at low temperatures involves various gases. The monitoring of these gases would be a useful diagnostic for detecting the presence of active exothermic reactions. Specifically, measuring the concentration of O_2 , NO , N_2O and CO_2 in the head space of the drums would be the most useful as a diagnostic.

In the mechanism proposed in the chemistry section, the free oxygen oxidizes NO to NO_2 , which in turn oxidizes HNO to HNO_2 , which oxidizes the pet litter. This means as the reaction proceeds, the concentration of the free oxygen in the head space of the drum will decrease. This would occur before an increase of concentration of the NO and N_2O , since the NO reacts with the oxygen and significant quantities of N_2O will not form until the concentration of HNO becomes significant. The HNO concentrations will not build up until the free oxygen becomes depleted since it is oxidized by NO_2 . While it is possible for the nitric acid to oxidize the NO , it will occur at slower rate than the reaction with oxygen, which will allow detectable quantities of NO and N_2O to form.

While measuring the concentration of the free oxygen could be a useful diagnostic, it would require sampling from the head space of the drums, which might not be practical. This means measuring NO and N_2O might be a more practical diagnostic, specifically, the concentration of N_2O . While it is expected that the reaction will produce large quantities of NO when nearing thermal runaway, NO will oxidize rapidly to NO_2 in the presence of oxygen, which is harder to measure. If the sampling does not take place from the head space of the drum, there would be excess oxygen present for this reaction, making the measurements of NO unreliable.

Another gas, which could provide a useful diagnostics, would be CO_2 , which is expected to be produced during any exothermic oxidation reactions of the organic pet litter. While biological activity would produce CO_2 as well, it is expected to see an exponential increase in production both the CO_2 and N_2O as thermal runaway is approached.

Conclusions

In order to quantify the risk involved with the handling and processing of the existing LANL Nitrate Salt drums it is desirable to calculate the likelihood of another violent thermal runaway happening as occurred with the drum #68660 breach event. In order for long time thermal runaway events to occur the heat production by the exothermic chemistry occurring in the drum must be very finely balanced by the heat flowing out of the system into the environment. It was hypothesized that the particular combination of thermal parameters which lead to thermal runaway after long term storage would be so rare the probability of another thermal runaway occurring in the existing drums would be beyond extremely unlikely.

This hypothesis was presented with several caveats. Namely, that the chemical system in the drum was well-mixed and homogeneous, that the chemistry occurring in the drum obeyed Arrhenius kinetics, specifically, first order kinetics and the drum would not undergo any additional thermal insults.

In order to test this hypothesis a computational model of the drum was built and tested for a range of first order Arrhenius parameters to determine the dependence of thermal runaway times on the parameters. It was shown, given the caveats above, that the slice of parameter space which led to thermal runaways times of interest was so small that the probability of another thermal runaway occurring in the LANL Nitrate Salt drums is beyond extremely unlikely.

The computational work done also strongly suggest that the LANL Nitrate Salt drums should be

cooled to 10° C or lower before they are processed, which will increase safety in several ways. First, if there still exists even a remote possibility for thermal runaway, cooling will pull the set of kinetic parameters away from the go/no-go boundary in parameter space, reducing the likelihood of runaway even further. Second, if the agitation associated with processing the drum activates temperature chemistry, which was not active before, the cooling will slow the reaction rate of the chemistry down significantly.

It is also possible that the well-mixed caveat of the hypothesis could fail. This makes a useful diagnostic for detecting the active exothermic chemistry highly desirable. While temperature is an obvious diagnostic, measuring the internal temperature of the current configuration of the LANL Nitrate Salt drums is not practical and measuring the temperature of the surface of the drums might not detect the presence of active chemistry. However, measuring the concentration of the gases involved in the exothermic reactions would be a useful diagnostic. As mentioned in the chemistry and discussion sections of this report, any significant increases in the concentration of NO, N₂O or CO₂, as well as a decrease in the free oxygen, can be taken as an indicator that this reaction is proceeding at a significant rate. If the gas is being sampled from the head space of the drum, then these gases can be used as a diagnostic. However, if the gases are sampled from outside the head space of the drums then the concentrations N₂O and CO₂ would likely be the most useful as a diagnostic.

Assuming the caveats presented with the hypothesis are true, then the remaining LANL Nitrate Salt drums are beyond very unlikely to undergo thermal runaway and a repeat of the drum #68660 breach event is very improbable. In order to assure the caveats remain true the existing drum should be protected from additional thermal insults and avoid agitation. When processing of the drums occurs, they should be cooled to at least 10 °C and diagnosed as suggested above to insure no exothermic reactions are occurring to increase the safety of the workers.

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