

Review on hazard classification methodology

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Executive summary

Stoessel classification system is commonly used in the pharmaceutical industry to categorize reaction hazards. In this project, we first read some papers and textbook to understand what is Stoessel classification system, what key parameters are selected and used to describe reaction thermal risk and how the risk classes are determined based on the relationship of key parameters. We then applied Stoessel classification to one specific example in which T2 laboratories explosion. Then we did a literature review to learn some other applications of Stoessel classification methodology in real industry and also study some limitations of traditional Stoessel classification. Some modifications add more temperature related parameters and some focus on extending Stoessel classification to two or multiple reaction steps. We noticed that none of the literature (according to our knowledge) attempts to including pressure together with temperature into thermal risk classification. So, in this study, we also spent some efforts on figuring out how and where pressure affects the thermal risk and whether it is necessary/possible to include pressure into thermal risk classification. We first studied whether the change of pressure will affect the enthalpy of formation and Gibbs free energy and further increase/decrease the heat release. After implementing so-called group additivity approximation and some example calculation we concluded that the change of both temperature and pressure just have a tiny effect on heat release. Finally, we focused on the relationship between Maximum temperature for technical reasons (MTT) and pressure and pointed out the relationship between temperature and pressure can be quite complex for gas releasing reactions. For such situations, pressure might be needed to classify reaction risks.

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Introduction

Stoessel classification system was developed to categorize reaction hazards for the cooling failure scenario of process in case of exothermal chemical reactions.[1] To systematically analyze the thermal risk linked to a chemical reaction, which is the risk of loss of control of the reaction and associated consequences, the worst scenario must be considered. For thermal risks, the worst case is that the reactor loses cooling, or in general, considering that the reaction is performed under adiabatic conditions. Such scenario is called cooling failure scenario. During the cooling failure scenario analyze, four temperature levels are crucial and need to be assessed, which are the process temperature (T_p), maximum temperature of synthesis reaction (MTSR), temperature at which TMRad is 24 h (TD24) and maximum temperature for technical reasons (MTT).

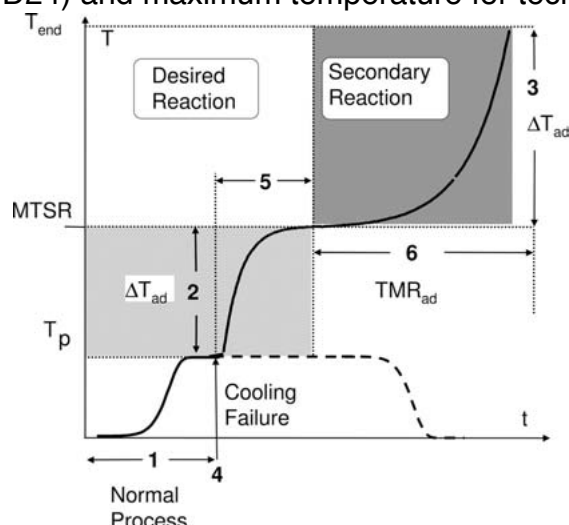


Figure 1: Cooling Failure Scenario: After a cooling failure, the temperature rises from process temperature to the maximum temperature of synthesis reaction. At this temperature, a secondary decomposition reaction may be triggered. The left-hand part of the scheme is devoted to the desired reaction and the temperature increase to the MTSR in case of a failure. In the right-hand part, the temperature increases due to a secondary exothermic reaction is shown, with its characteristic time to maximum rate.[1]

One scenario developed by R. Gyax et. al [2] will help illustrate these temperature levels. This scenario assumes that the reactor is at the reaction temperature (T_p) and a cooling failure happens (point 4 in Figure 1). If unconverted material is still present in the reactor when cooling failure happens, the temperature will increase due to the completion of the reaction. When the temperature reaches a level called the Maximum Temperature of the Synthesis Reaction (MTSR), where a secondary decomposition reaction may be initiated. The temperature will continually increase to a pretty high final temperature. The duration of the secondary decomposition reaction (main reaction runaway) is called TMR_{ad} which is also shown in Figure 1 and can be estimated using:

$$\text{TMR}_{\text{ad}} = \frac{C_p R T_p^2}{q_{Tn} E}$$

Temperature at which TMRad is 24 h (TD24) can be obtained by solving this equation. Finally, Maximum temperature for technical reasons (MTT) is the boiling point in an open

system. Based on the calculation/estimation of these four temperature levels, five different criticality classes have then been proposed. (Figure 2)

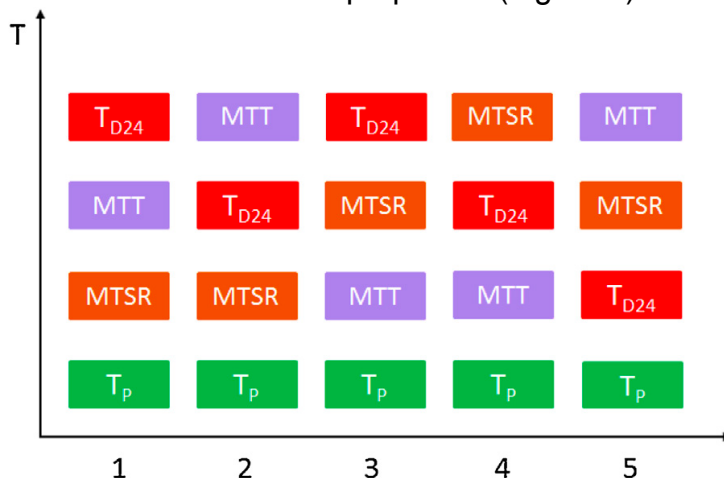


Figure 2: Criticality classes of scenario, obtained by combining the four temperature levels: T_p , MTSR, T_{D24} and MTT [3]

As the critical index changes from 1 to 5, the thermal risk of exothermic reactions increases. This diagram, which is called Stoessel criticality diagram, contains the thermodynamic information which defines the behavior of a reaction mass during the starting stage of a runaway. Because of this, Stoessel classification system are widely used to assess the probability of interrupting a runaway situation and to design of protection measures.

Literature review

Basic concept of Stoessel classification system is introduced in reference [1], which is the major reference for this project. Chapter 3 “Assessment of Thermal Risks” in this book gives an introduction to basic concepts of temperature levels and how 5 criticality classes are classified. Some specific applications of Stoessel classification method is offered by reference [4].

Some modifications made based on traditional Stoessel criticality diagram is introduced in reference [1]. In addition to four temperature levels used in Stoessel classification, the final temperature is introduced into the classification and 7 criticality classes are developed. Some other limitations of Stoessel classification are pointed out by reference [5], such as Stoessel risk assessment methods are aimed at single step reactions which will miss the influence of the correlation between the two(multi) reaction steps on the thermal runaway risk of the synthetic process.

Reference [6] summarizes the state-of-art thermal hazardous assessment in industry. In this paper the authors point out that for reactive chemicals releasing a large amount of gases, some pressure rated parameters must to be included besides temperature parameters, such as the maximum pressure during overall reaction (P_{max}) and maximum pressure rise ($(dP/dt)_{max}$). Those pressure related parameters are quite important to

estimate explosion potential. One specific example is provided with reference [7], where the thermal risk of dicumyl peroxide (DCPO) is systematically studied by measuring thermokinetic parameters, such as heat of decomposition, exothermic onset temperature, maximum pressure rise, etc. These two papers lead us to think about how pressure affect the thermal risk and should it be included in risk classifications?

Definition of the problem & objective

1. Understand how Stoessel classification system works, what problem it wants to address.
2. Understand how Stoessel criticality diagram are related to four temperature levels and search for some typical examples in each risk class.
3. Study how to use Stoessel classification system to leverage and control reaction risks.
4. Think about some limitations of Stoessel classification system and what improvements can be made based on it. Specifically, think about whether pressure need to be added into risk classification.

Analysis of the problem

- **Reviewing temperature excursions-based hazard classification methodology.**

The classifications for the Stoessel method can be classified in multiple ways to see the severity of the runaway will be, the probability of that runaway even occurring, and risk of the runaway reaction. Each one of these parameters are crucial to the Stoessel Method and with the severity and probability, a risk matrix can be made so a company can see what the risk is based off those two parameters. With all this a company can set up their facilities accordingly so if a runaway reaction occurs, it can be stopped or mitigated so the severity will be less.

Severity

The severity of Stoessel Classification is based on the adiabatic temperature rise which can be found by the energy of the reaction divided by the specific heat capacity of the reaction using:

$$T_{ad} = \frac{Q'}{C'p}$$

The Q' is the specific energy of the reaction or the undesired reaction as the cooling system fails. As the energy increases the temperature will also increase because heat capacity is constant. The severity depends on how high the final temperature is as the final temperature is low, the severity will be low or negligible but as the final temperature is high, the severity will be worse.[8] The Table 1 below shows different severities based off temperature range and specific energy range.

Simplified	Extended	ΔT_{ad}	Q' (kJ/kg)
High	Catastrophic	>400	>800
	Critical	200-400	400-800
Medium	Medium	50-100	100-400
Low	Negligible	<50	<100

Table 1: Classification of severity for the Stoessel [1,8]

Probability

The probability can also be evaluated and classified for the possibility of a runaway reactions. The probability is based off time and how long it takes the reaction to happens. The simplest way to show this is to compare temperature to time. If the cooling system fails and the temperature slowly increases of a long period of time then there a low probability of a runaway reaction but if the temperature spikes in a short amount of time then the probability of a runaway reaction is high.[8] In figure 3 below, 2 cases are shown by using the using the method above.

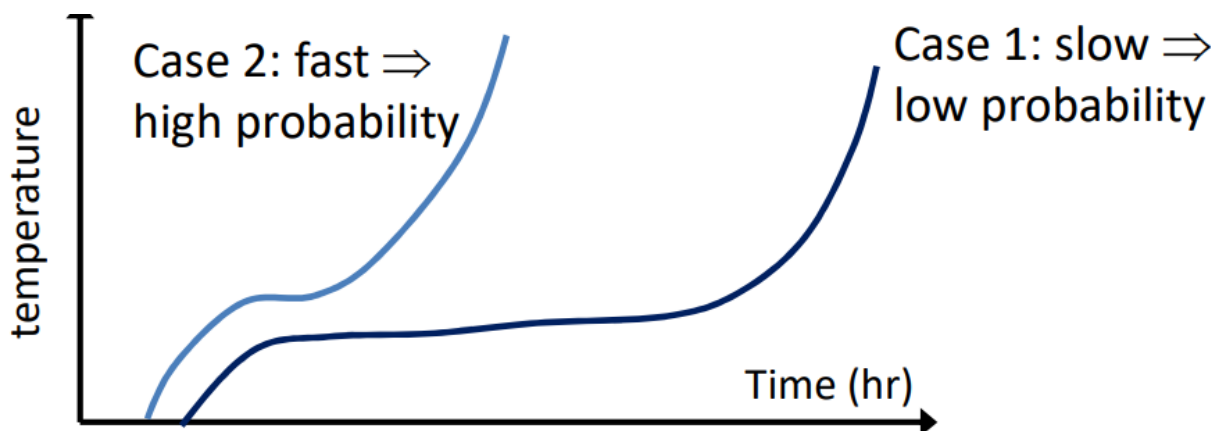


Figure 3: Temperature vs Time graph of the probability of a runaway reaction.[6]

The probability can be broken down into three different categories High, medium, and low. Each of these three categories have subcategories showing the likeliness of a runaway reaction happening based off time of TMR_{ad} . [8] Table 2 shows the different categories and subcategories based off time for the possibility off a runaway reaction.

Simplified	Extended	TMR _{ad} (hr)
High	Frequent	<1
	Probable	1-8
Medium	Occasional	8-24
Low	Seldom	24-50
	Remote	50-100
	Almost impossible	>100

Table 2: Probability categories of a runaway reaction. [1,8]

Risk Matrix

A risk matrix can be set off based off the severity and probability classification. With the matrix, a company can see the severity of a runaway reaction and the probability of that reaction. When the severity is low, at all probability levels, the risk is not a problem, and no measures are required.

Severity	High	$\Delta T_{ad} > 200K$			
	Medium	$50K < \Delta T_{ad} < 200K$			
	Low	$\Delta T_{ad} < 50K$ no pressure increase			
			TMR _{ad} • 24h	8h < TMR _{ad} < 24	TMR _{ad} • 8h
			Low	Medium	High
			Probability		

Figure 4: Risk Matrix for A runaway reaction based of the severity and probability. [8]

When the severity is at as medium level, and the probability is low or medium, the risk is at a level where there can be an incident and there should be designed technical measure in the process. When the severity is at a medium level and probability at a high level then the risk is high, the process should be redesigned. When the severity is at as high level, and the probability is low, the risk is at a level where there can be an incident and there should be designed technical measure in the process. When the severity is high and the probability is medium or high, the risk is high, and the process should be redesigned. [8]

Stoessel Criticality Classification

The risk can be classified in a criticality index from 1 to 5 with 1 being low and 5 being high. As shown in figure 2 above, the criticality index and where MTT and MTSR happen based off temperature. Red dotted zones are the boiling points or above T_{D24} .

Criticality Classification 1 is the lowest risk on the index and the process is a low thermal risk. The MTSR is less than the MTT so decomposition is not triggered. This classification has no need for special measures as long as the mass of the reaction is not held under heat accumulation for a long period. An emergency pressure relief valve on the tank would be good to have on the tank for a safety barrier. Criticality Classification 2 is similar to classification 1 but the MTT is at a higher temperature and it is in the boiling point zone. Decomposition is not triggered but if the temperature reached the MTT then decomposition could be triggered. No special measure is required for classification 2 as long as heat accumulation is avoided. An emergency pressure relief valve on the tank would be good to have on the tank for a safety barrier. Criticality Classification 3 is the process starts getting into the medium risk level where reducing measures are required. The MTT is smaller than the MTSR and the MTSR is smaller than the T_{D24} . Decomposition is not triggered and for safety systems that should be used are evaporative cooling, controlled depressurization, backup cooling, dumping of the reaction mass or quenching. Criticality Classification 4 is the higher end of the medium risk level where reducing measures are required. The MTT is smaller than the MTSR but the MTSR is greater than the T_{D24} . Decomposition could be triggered and for safety systems that should be used are evaporative cooling, controlled depressurization, backup cooling, dumping of the reaction mass or quenching. If controls fail, secondary reaction will be triggered. Criticality Classification 5 is the highest risk and worst-case scenario. Both MTSR and MTT are greater than T_{D24} with MTT being greater than MTSR. Decomposition is triggered and during the runaway, the technical limit will be reached by the secondary reaction. The heat release of the secondary reaction may be too great, and it might result in a critical pressure increase. Neither an evaporite cooling or pressure relief valve can serve as a safety measure so the only dumping or quenching can be used as a safety measure. If the risk level is at classification 5, it would be good to redesign the process so its not at the highest risk level. [8]

- Application of Stoessel classification

The T2 incident happened on December 19, 2007, in Jaskonville, Florida. This incident ended up killing 4 people and injuring 28 civilians. At the laboratories, they were making methylcyclopentadienyl manganese tricarbonyl (MCMT) in a 2450 gallon batched reactor. The temperature of the first reaction 300 °F. As the first reaction of sodium and the MCPD started to process, the temperature raised to the T_p . The T_p of the process was 360 °F and the cooling system was supposed to turn

on. At 1:23 p.m., The cooling system did not start up and the temperature raised up to the MTSR at 390 °F in less than 10 mins of the cooling system failure. The T_{D24} was at 380 °F so when the temperature of the runaway reaction reached the MTSR, it triggered decomposition and instantly setting off the second reaction hitting the MTT within seconds of decomposition. At 1:33 p.m. the reactor exploded with an equivalent of 1400 lbs. of TNT. The secondary reaction's heat release was so great, and it resulted in a critical pressure increase and this reaction was between the sodium and the diglyme solvent. The pressure and temperature rise during this secondary reaction is 32,000 psig/minute and 2340 °F/minute. The CSB tested this reaction in multiple sealed test cells, the reaction was so powerful, it burst the test cells completely open. [11] The classification of this incident is a Criticality Index 5 because The MSTR and MTT are greater than the T_{D24} and decomposition happened right when the temperature reached the MSTR. Looking at the risk matrix, The TMR_{ad} was less than 1 so the probability of the reaction running away was high which puts the process on the far right side of the risks matrix and either the process is a Criticality index 1 or it's a 5. The severity when the reaction started to run off was high which places the incident as a criticality index 5. What also added to the severity also was the size of the reaction.

- How pressure affects the thermal risk.

As pointed out by professor, Stoessel hazard classification methodology is mainly based on temperature excursions, we want to study how pressure will affect the thermal risk and whether it's possible/necessary to include pressure into the classification methodology.

First of all, since both the enthalpy and free energy are related to the pressure, and will change the heat release (enthalpy will change the heat of reaction while free energy will change the activation barrier), we want to study whether the change of pressure will dramatically affect these two parameters. Take enthalpy for example, starting from the enthalpy of reaction at standard condition, which is denoted as ΔH_r° , the enthalpy change at different temperature and pressure can be calculated as following.

$$\Delta H_{r,P,T} = \Delta H_r^\circ + \int_1^P \left[\left(\frac{\partial H_{\text{prod.}}}{\partial P} \right)_T - \left(\frac{\partial H_{\text{react}}}{\partial P} \right)_T \right] dP \\ + \int_{298}^T \left[\left(\frac{\partial H_{\text{prod.}}}{\partial T} \right)_P - \left(\frac{\partial H_{\text{react}}}{\partial T} \right)_P \right] dT$$

However, calculating the derivative of enthalpy change with respect to temperature / pressure is not straightforward. Quantum chemistry calculation, such as Density functional theory is one of the commonly used tools to calculate the enthalpy of formation at different temperature and pressure. In addition, one approximation method, group increment models can be used as a substitution. For instance, in Benson group increment theory (BGIT),[9] three levels of approximation are given, which are atoms increment, bond increment and group increment. The foundation of such increment theory is that the thermochemistry properties, including enthalpies and free energies, are 'dividable' based on molecule structure. Although we don't know

the exact value of the derivative of enthalpy with respect to temperature / pressure, we know such derivative is much smaller than the enthalpy itself. If we apply atoms increment theory, which can be considered as the first order approximation, $\Delta H_{r,T,P} \approx \Delta H_r^0$, because the number of elements is unchanged. To validate such assumption, the enthalpy change of one reaction at different pressure should be calculated and compared with each other. However, I couldn't find any database/software which can provide enthalpy change at different pressure, I used Chetah to calculate the enthalpy of reaction at different temperature for instead.

Reaction: C3H6O3 (g) ----> C3H6O3 (g)

Temp °K	delHrxn kJ/mol	delGrxn kJ/mol	logK	delCp kJ/(mol-K)	delSrxn kJ/(mol-K)
298.15	-52.467	-7.447	1.305	0.002	-0.151
348.15	-52.456	0.100	-0.015	-0.001	-0.151
400.00	-52.575	7.935	-1.036	-0.003	-0.151

Reaction: C2H5NO2 (g) + CH5N (g) ----> C3H7NO (g) + H3NO (g)

Temp °K	delHrxn kcal/mol	delGrxn kcal/mol	logK	delCp cal/(mol-K)	delSrxn cal/(mol-K)
298.15	-26.380	-24.715	18.117	-1.647	-5.583
348.15	-26.493	-24.428	15.334	-2.880	-5.931
400.00	-26.673	-24.109	13.172	-4.030	-6.412

Figure 5: Enthalpy of reaction at different temperature [10]

From Figure 5 we can see, the enthalpy of reaction just has minor change when temperature increase from 300K to 400K. So, from above discussion, we find that the thermochemistry properties won't be affected a lot when pressure changes.

We then go back to four key parameters in Stoessel classification to find the role of pressure. From the definition of T_p , T_{D24} , MTSR and MTT, only MTT is related to pressure. Maximum temperature for technical reasons (MTT) is defined as the boiling point in an open system and as the temperature at the maximum permissible pressure.[1] In the risk classification, MTT is related to the emergency pressure relief device. When $MTSR / T_{D24}$ is smaller than MTT, the emergency pressure relief device can serve as a safety barrier to reduce the thermal risk. However, simply use temperature to describe the pressure is not an easy task, especially when the chemical reactions release a large amount of gases. For instance, in an open system, MTT is defined as the boiling point because when the temperature reaches the boiling point, the liquid vaporizes into gas which lead to a dramatic increase in pressure and will trigger the pressure relief device. However, if the reaction itself will directly generate gaseous products, MTT should be lower than the boiling point since before the liquid vaporizes into gas, the pressure may already reach

the setting pressure. Similarly, for a closed system, the relationship between temperature and pressure can be quite complex if gaseous products are continually generated and may not even be deterministic. For instance, one real case example shown in reference [3] in Figure 6 illustrates that the relationship between T and P can be quite complex.

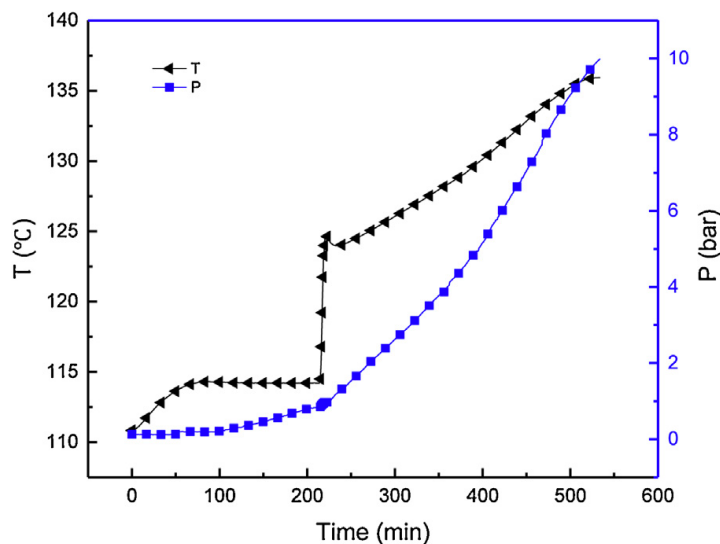


Figure 6: Temperature and pressure vs. time under adiabatic conditions by Phi-TECII. [3]

So, it might be valuable to incorporate pressure onsets to replace the MTT in risk classification. For instance, replace one-dimensional temperature-based classification figure to a 2D temperature and pressure-based classification figure. Another option is to find some quantity including both temperature and pressure to replace temperature.

Conclusions

1. The classification of the Stoessel method is a powerful and commonly used tool to determine the thermal risk of an exothermic reaction system. T_p , T_{D24} , MTSR and MTT can be determined from the thermochemistry calculation of the reactants and possible products and the system settings.
2. Temperature and pressure effects on thermochemistry properties of reactions are nearly neglectable.
3. Among all key parameters selected in the Stoessel method, only Maximum temperature for technical reasons (MTT) is strongly related to the pressure. For gas releasing reactions, it might be valuable to incorporate pressure onsets to replace the MTT in risk classification.

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