NEW JERSEY DEPARTMENT OF ENVIRONMENTAL PROTECTION

BUREAU OF RELEASE PREVENTION

Guidance for Determining the Applicability of the TCPA Program Rules

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Introduction

TCPA Program rules apply when a threshold quantity of an Extraordinarily Hazardous Substance (EHS) is first present at a facility. The EHSs covered by the TCPA program and the respective threshold quantities are listed at N.J.A.C 7:31-6.1 et seq. The guidance provided in the following sections is to help facilities that use, manufacture, store, or produce an EHS to determine the quantity of EHS present at the facility. This guidance document covers the threshold quantity (TQ) applicability for toxic, flammable, and Reactive Hazardous Substance (RHS)/RHS mixture EHSs. Part I of this guidance discusses applicability for toxic and flammable EHSs, and Part II discusses applicability for RHSs and RHS mixtures.

Reactive substances are those that can cause a dangerous release of heat, energy, toxic vapors, or gases when exposed to conditions that may occur in either normal or abnormal situations. The Department considered the circumstances under which a reactive hazard substance could be classified as an EHS and cause a catastrophic accident and created two groups of reactive substances that are included in the EHS list. The first group includes individually listed substances that could be involved in unintentional reactions caused by the inherent properties of the chemical itself. These chemicals may be unstable or self-reacting or may react if they are unintentionally exposed to air or water. These chemicals are included in the List of Individual Reactive Hazardous Substances at N.J.A.C. 7:31-6.3(a), Table I, Part D, Group I. The second group includes substances that could be involved in an accident when they are mixed with one or more other substances in a process vessel. If any of the chemicals in this combination of substances includes one of the Reactive Hazard Substances Mixture Functional Groups listed at N.J.A.C. 7:31-6.3(a), Table I, Part D, Group II, the heat of reaction and corresponding threshold quantity must be determined for applicability to the TCPA rules.

The TCPA rule requirements cited in this guidance may be found in the document entitled "N.J.A.C. 7:31 Consolidated Rule Document," available at the TCPA web site at http://www.nj.gov/dep/enforcement/tcpa/tcpadown.htm. (Please note that the N.J.A.C 7:31 Consolidated Rule Document should be used as a guidance document only. All of the Department's rules are compiled in Title 7 of the New Jersey Administrative Code. Should there be any discrepancies between the Consolidated Rule Document text and the official version of the rules, the official version will govern.)

I. Determining the Applicability to the TCPA Rules for Toxic and Flammable Extraordinarily Hazardous Substances

A. TCPA Program Provisions Regarding Applicability

The following provisions of TCPA Program rules must be read prior to reading the remaining sections of this guidance document:

1- 40 CFR 68.10(a) as incorporated by reference with specified changes at N.J.A.C. 7:31-1.1(c)3.
2- The definition of threshold quantity and covered process at 40 CFR 68.3 as incorporated by reference with specified changes at N.J.A.C. 7:31 – 1.1 (c)2.
3- The definitions of extraordinarily hazardous substance (EHS), facility, inventory and process at N.J.A.C. 7:31-1.5.
4- 40 CFR 68.115 as incorporated by reference with specified changes at N.J.A.C. 7:31-6.1 (c).
5- N.J.A.C. 7:31-6.2.

B. Procedure for Determining the Quantity of EHS at the Facility

Identify all the processes that may have an EHS present.

For each process in which an EHS may be present, determine the following as applicable:
1- The maximum instantaneous static inventory that may be contained in the process,
2- The maximum hourly generation rate of the EHS in the process,
3- The maximum amount of the EHS that can be released in one hour from the process.
Select the highest value determined above for each process.

Sum all the highest values selected above for all the processes to determine the maximum total amount of EHS that can be released at the facility.

Compare the total amount of EHS that can be released at the facility with the threshold quantity of the EHS listed at N.J.A.C. 7:31-6.3. If this total amount equals or exceeds the threshold quantity (TQ), the facility is subject to the TCPA rules and must submit a Risk Management Plan (RMP).

C. Records to Use to Determine Facility Inventory

An owner/operator (o/o) of a facility may have to use and review various records to determine the quantity of EHS present at the facility. The types of records needed may vary depending on the type of EHS inventory (i.e. instantaneous static inventory, generation rate, or amount that can be released in an hour).

Inventory in Shipping Containers or Storage Vessels.

At many facilities, the maximum inventory is the instantaneous static amount of the EHS contained in shipping containers (e.g. drums, cylinders, or rail cars) or in storage tanks that are connected to the process. This static inventory will fluctuate as the facility receives deliveries of the EHS or ships the EHS. The facility should use records to determine the maximum instantaneous inventory at any time. The facility should review records showing EHS inventory transactions in and out of the facility such as invoices, receipts, and bills of lading. The resulting inventory balance following a transaction should be reviewed. Facilities typically record the static inventory of shipping containers and storage tanks on a daily basis. The inventory of shipping containers can be recorded on logsheets and typically is put into spreadsheets to tabulate the information. The inventory in storage tanks can be kept with logsheets and spreadsheets or by recording the inventory with the process control system.

Inventory in an Ammonia Refrigeration System.

A different example of instantaneous static inventory determination and the inventory records needed to determine applicability involves ammonia refrigeration. An ammonia refrigeration system is a closed loop system. Once the refrigeration system has taken on its initial charge, it becomes a closed loop system provided there are no leaks in the system. For a new refrigeration system, the o/o can simply provide the invoice or an engineering document from the equipment provider or the refrigerant seller which indicates the amount of ammonia in the system. The only time that the inventory changes in the refrigeration system is when the system must take on an additional charge of anhydrous ammonia or when ammonia is removed from the system. In this case, a daily record of inventory is not practical since the levels of ammonia in the equipment are constantly fluctuating. For an existing refrigeration system, the o/o first should conduct an initial calculation of the maximum design capacity of the static inventory of the system. To do this, the o/o should determine the equipment that is in service and online and estimate the liquid and vapor volume and mass taking into account the operating parameters of pressure and temperature. The o/o should use a means to update the initial calculated inventory to ensure that it is current. The o/o should update the calculated inventory whenever changes are made to the process by adding or deleting equipment after the time of the initial inventory calculation. Also, the o/o should review receipt records along with the calculated inventory records whenever additional ammonia charges are made to the system.

Inventory that is Generated or Capable of Being Released in an Hour.

The same types of records should be used to determine the inventory for both an EHS that is generated and an EHS capable of being released in an hour. The o/o should have a calculated estimate of the static inventory. This estimate should be based on the maximum process operating conditions and the equipment design records.

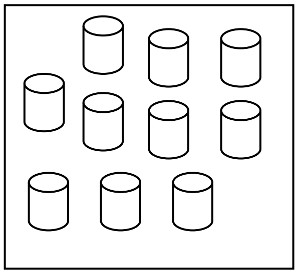
The o/o also should review records based on the maximum process operating conditions showing the EHS generation rate and the EHS amount capable of being released in an hour. Both of these types of inventory relate to the mass flow rate of the EHS through the equipment. This information may be found in documents such as the process design records, process chemistry, process flow diagrams, and standard operating procedures. Also, data on the EHS flow rate for EHS equipment and piping often is recorded in the process control system. The inventory amount to be used for threshold quantity applicability is the actual maximum operating rate, not the maximum design capacity. For example, a water treatment system may have two ozone generators, each generating 20 pounds/hour of ozone. However, the facility only operates one of the generators at a time. Therefore, 20 pounds/hour is the inventory to be used as the inventory for threshold quantity determination.

The o/o must review the records for the static inventory, generation rate, and amount capable of being released in one hour and select the inventory amount that yields the greatest value to determine TQ applicability.

D. Examples of Threshold Quantity Applicability Determination

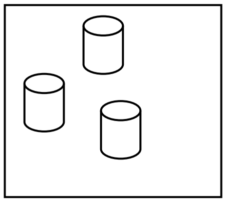
Example 1

Assume: EHS A with a 5,000-pound threshold quantity.



Storage Area 1

EHS A drum storage pad area,
Each drum holds 400 pounds.
Maximum instantaneous
inventory of
EHS A is 4,000 pounds.



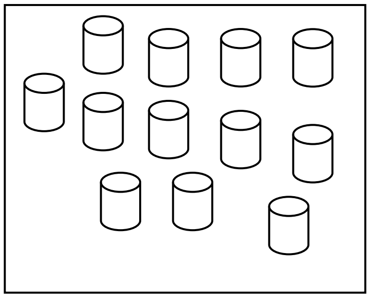
Storage Area 2

Second drum storage area of
EHS A. Maximum
instantaneous inventory is 1,200
pounds.

The total inventory at the facility is 5,200 pounds. Therefore, the facility is subject to the TCPA rules.

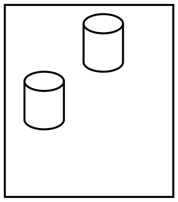
Example 2

Assume: EHS A with a 5,000-pound threshold quantity.



Storage Area 1

EHS A drum storage pad area. Each drum holds 400 pounds. Maximum instantaneous inventory of EHS A is 4,800 pounds.



Process Building

Reactor process area. Two drums (800 pounds) of EHS A are taken from Storage Area 1 and are used in the reaction process and are not replaced in Storage Area 1 until the 800 pounds is consumed.

The maximum amount that is present at the facility at any time is 4,800 pounds; this is the total inventory. Therefore, the facility is not subject to the TCPA rules.

Example 3

Assume: EHS B with a 1,000-pound threshold quantity.

Process 1

EHS B generated at 700 pounds/hour.
Maximum instantaneous static inventory is 100 pounds.

Process 2

EHS B is not generated.
Maximum instantaneous static inventory is 500 pounds.

For threshold quantity determination, the total inventory is the sum of the maximum inventories of each process. The sum of the maximum inventories of each process is 1,200 pounds (700 pounds/hour from Process 1 and 500 pounds from Process 2). Therefore, the facility is subject to the TCPA rules.

Example 4

Facility ABC receives an EHS by pipeline from adjacent Facility XYZ at a rate of 2,000 pounds per hour. The calculated instantaneous static inventory of EHS in this pipeline is 50 pounds.

The EHS has a threshold quantity of 1,000 pounds. The EHS is consumed in a continuous process at Facility ABC.

Facility ABC is subject to the TCPA rules for the EHS because an amount exceeding the threshold quantity, 2,000 pounds, can be released in one hour from a failure of the EHS pipeline.

Example 5

A petroleum refinery generates hydrogen sulfide in five of the petroleum refining process units at a rate of 500 pounds/hour at each unit. The instantaneous maximum inventory of the hydrogen sulfide in each of the refining units is 50 pounds. The total hydrogen sulfide flow rate of 2,500 pounds per hour is fed to the sulfur recovery unit, where it is consumed. The threshold quantity of hydrogen sulfide is 1,000 pounds/hour.

The refinery is subject to the TCPA rules because the total generation inventory of 2,500 pounds exceeds the threshold quantity.

II. Special Consideration for Substances Listed as Solutions or Mixtures

In this section, NJDEP refers to the TCPA regulation only. Facilities in New Jersey that have both federally listed and state-only listed chemicals in more than threshold quantities must fill out two RMPs: one to be sent to USEPA and one to be sent to NJDEP. The RMP to be sent to USEPA should include only information relating to federally listed chemicals (this applies to chemicals and threshold quantities specified at 40 CFR 68.130). The RMP sent to NJDEP should include information on both federally regulated and state-only regulated chemicals since both are subject to the TCPA rules and are equally enforced since USEPA delegates implementation of the federal accidental release prevention program to NJDEP.

A. Aqueous Ammonia, Hydrochloric Acid, Hydrofluoric Acid, and Nitric Acid

Some chemicals regulated by NJDEP and USEPA are specified as solutions or mixtures with different concentration cutoffs. These include aqueous ammonia, hydrochloric acid, hydrofluoric acid, and nitric acid. See the tables below for a summary of the concentrations and threshold quantities (TQ) for NJDEP and USEPA.

Table 1: NJDEP Concentration and TQ

Chemical	CAS #	TCPA Concentration (%)	TCPA TQ* (lbs of solution)
Aqueous Ammonia	1336-21-6	28%	19,000
Hydrochloric Acid	7647-01-0	36%	5,600
Hydrofluoric Acid	7664-39-3	70%	700
Nitric Acid	7697-37-2	94%	450
Oleum	8014-95-7	94%	450

Table 2: USEPA Concentration and TQ

Chemical	CAS #	USEPA Concentration (%)	USEPA TQ* (lbs of solute)
Aqueous Ammonia	7664-41-7	20%	20,000
Hydrochloric Acid	7647-01-0	37%	5,600
Hydrofluoric Acid	7664-39-3	50%	1,000
Nitric Acid	7697-37-2	80%	15,000
Oleum	8014-95-7	-	15,000

If a regulated substance has a specific concentration listed, the o/o needs to only consider solutions/mixtures with concentrations of the regulated substance that are at or above this concentration. The o/o does not need to consider solutions/mixtures with concentrations of a regulated substance below the listed concentration when you determine threshold quantities.

*For NJDEP, the TQ is the weight of the entire solution. For USEPA, the TQ is the weight of the regulated substance (solute) in the solution/mixture.

If the concentration and threshold quantity is exceeded for only one agency, further evaluation must be conducted to determine which RMP substance and quantity should be registered (see Examples 1 and 2 for further clarification). If an o/o has one of these EHSs that is above both the NJDEP and USEPA concentration level and threshold quantity, the o/o must register the EHS with NJ under the NJDEP concentration and quantity as well as with EPA under the USEPA concentration and quantity (see Example 3 below for further clarification). The following examples use aqueous ammonia as the EHS but apply to hydrochloric acid, hydrofluoric acid, and nitric acid as well:

Example 1
An o/o has 90,000 lb inventory of a 25% aqueous ammonia solution.

USEPA:
The aqueous ammonia solution is above the 20% concentration and therefore this solution potentially falls under the USEPA regulation. Now, the weight of the solute must be calculated to determine if this solution should be registered with USEPA.

90,000 lbs of solution * 0.25 = 22,500 lbs of solute (ammonia)

Since this amount is above the USEPA TQ of 20,000 lbs, the o/o would need to submit an RMP to USEPA for 20% aqueous ammonia as the regulated substance with a 22,500 lb. registration amount.

NJDEP:
The aqueous ammonia solution is below the 28% concentration required by NJDEP and is not subject to the TCPA rule due to the concentration. However, as stated above, USEPA delegates implementation of the federal accidental release prevention program to NJDEP. Therefore, the o/o must submit an RMP to NJDEP as well for 20% aqueous ammonia as the regulated substance with a 22,500 lb. registration amount.

Example 2
An o/o has 50,000 lb inventory of a 30% aqueous ammonia solution.

USEPA:
The aqueous ammonia solution is above the 20% concentration and therefore this solution potentially falls under the USEPA regulation. Now, the weight of the solute must be calculated to determine if this solution should be registered with USEPA.

50,000 lbs of solution * 0.30 = 15,000 lbs of solute (ammonia)

Since this amount is below the USEPA TQ of 20,000 lbs, the o/o would not need to submit an RMP to USEPA.

NJDEP:
The aqueous ammonia solution is above the 28% concentration required by NJDEP and the total solution quantity is above the 19,000 NJDEP TQ. Therefore, the o/o must submit an RMP to NJDEP only for 28% aqueous ammonia as the regulated substance with a 50,000 lb. registration amount.

Example 3
An o/o has 75,000 lb inventory of a 30% aqueous ammonia solution.

USEPA:
The aqueous ammonia solution is above the 20% concentration and therefore this solution potentially falls under the USEPA regulation. Now, the weight of the solute must be calculated to determine if this solution should be registered with USEPA.

75,000 lbs of solution * 0.30 = 22,500 lbs of solute (ammonia)

Since this amount is above the USEPA TQ of 20,000 lbs, the o/o must submit an RMP to USEPA for 20% aqueous ammonia as the regulated substance with a 22,500 lb. registration amount.

NJDEP:
The aqueous ammonia solution is above the 28% concentration required by NJDEP and the total solution quantity is above the 19,000 NJDEP TQ. Therefore, the o/o must submit an RMP to NJDEP as well for 28% aqueous ammonia as the regulated substance with a 75,000 lb. registration amount.

B. Formaldehyde

Formaldehyde (gas) is listed in N.J.A.C. 7:31-6.3 Table 1 Part A – EHS List. O/o of stationary sources who handle pure formaldehyde (gas) that is not in an aqueous solution in a quantity greater than or equal to 175 lbs must submit an RMP to NJDEP.

Formaldehyde (solution) is listed in 40 CFR 68.130 Table 1. Formaldehyde is listed with the qualifier “solution” because pure formaldehyde has a tendency to polymerize and it is usually handled as an aqueous solution (commercially, 40% formaldehyde, 15% methanol, water). Although the listing refers to aqueous solutions of formaldehyde, other solutions or mixtures may be covered, as well. If formaldehyde is handled, at any concentration, so that the amount of the pure formaldehyde in the solution (the solute) exceeds the 15,000-pound threshold listed by the USEPA, the o/o should submit an RMP to the USEPA and NJDEP. (Note: There is a mixture exemption which states the amount of any listed toxic substance present in a mixture at a concentration greater than 1% does not need to be included in a threshold quantity determination if it can be shown that the partial vapor pressure is less than 10 mm Hg. This mixture exemption does not apply to oleum, toluene, 2,4-diisocyanate, and toluene diisocyanate.)

C. Oleum

Oleum with 65% free SO_3 is listed on the NJDEP’s list of chemicals. If a facility has oleum with 65% or greater free SO_3 in a quantity greater than or equal to 800 lbs of total solution, an RMP must be submitted to NJDEP.

Oleum (Fuming Sulfuric acid), which is a mixture of sulfuric acid and sulfur trioxide, is listed on the USEPA’s list of chemicals. If the o/o is handling oleum in quantities greater than or equal to 10,000 lbs, an RMP must be submitted to USEPA. As mentioned above in the formaldehyde section, the mixture exemption does not apply to oleum.

III. Determining the Applicability to the TCPA Rules for Reactive Hazard Substances (RHS) and RHS Mixtures

40 CFR 68.10(a) incorporated with changes at N.J.A.C. 7:31-1.1(c)3i requires an o/o of a facility that has at least the threshold quantity of an RHS or RHS mixture as determined under N.J.A.C. 7:31-6, to comply with TCPA requirements. The simplified flow chart of Attachment A plus the steps presented in this guidance are expected to help an o/o determine whether his facility is subject to the TCPA rules for RHSs or RHS mixtures.

A. Group I Individual Reactive Hazard Substances

1. Determine whether any of the RHSs listed in Table I, Part D, Group I, from N.J.A.C. 7:31-6.3(a), are at the facility.

2. Determine the maximum inventory of the Group I RHS at the facility in the same way as maximum inventory applicability is determined for toxic and flammable EHSs, as described in Part I of this guidance. If the maximum inventory of the Group I RHS at the facility equals or exceeds the threshold quantity, the facility is subject to the TCPA rules. (Note: No exemption from applicability is provided for any use of inhibitors [see NJAC 7:31-6.3(b)1].)

3. If the inventory of the Group I RHS evaluated in A.2. above is less than the threshold quantity, then determine if the Group I RHS is handled in a combination of substances intentionally mixed in a process vessel at the facility. (All Group I RHSs have a functional group specified in the list at N.J.A.C. 7:31-6.3(a), Part D, Group II.) Process vessels include, but are not limited to, equipment such as reactors, mixers, extractors, heat exchangers, and distillation columns. If the Group I RHS is handled in a combination with other substances in a process vessel, the o/o must determine applicability for an RHS mixture following the procedure described in Part B below.

B. RHS Mixtures

Use the following procedure to determine whether the facility is subject to the TCPA rules for handling an RHS mixture in a process vessel in an amount that equals or exceeds the threshold quantity.

1. Determine the substances with functional groups in process vessels at the facility using the listing in N.J.A.C.7:31-6.3(a), Table I, Part D, Group II.

   A Safety Data Sheet (SDS) provided by the supplier of the substance, Bretherick Handbook of Reactive Chemical Hazards, (6th Edition, 1999), Volumes 1 and 2, and other appropriate sources may be used to determine whether the substances at the facility contain the subject functional groups.

   Applicability for an RHS mixture must be determined if the substance with the Group II functional group is handled in a combination of substances intentionally mixed in a process vessel at the facility. Process vessels include, but are not limited to, equipment such as reactors, mixers, extractors, heat exchangers, and distillation columns. The RHS mixture applicability determination is not limited only to a reactor vessel in a process. For example, in some processes, reactants with a Group II functional group are first combined in a pre-mix tank prior to being fed to a reactor vessel where the reaction is intended to take place. The pre-mix tank must be evaluated for RHS mixture applicability in addition to the reactor. Other vessels such as mixers which contain a substance with a Group II functional group must be evaluated for RHS mixture applicability. A catastrophic incident involving a blending vessel occurred at the Napp Technologies facility in Lodi, New Jersey, on April 21, 1995, resulting in deaths, injuries, public evacuations, and serious damage both on and off site. In this incident, sodium dithionite was being mixed with other substances in a blender vessel. Water inadvertently entered the vessel through a faulty seal and initiated an extreme exothermic reaction and subsequent explosion and fire.

2. Determine the maximum weight capacity <u>including any non-reacting substances such as solvents</u> of each individual reaction or mixing vessel that will handle the identified RHS mixtures with functional groups. This is required even if the vessel normally is charged with an amount of the RHS that is less than the full capacity of the vessel. Administrative controls to limit the amount of RHS mixture in the vessel <u>cannot</u> be taken into account for the purpose of determining the maximum capacity. For example, if the vessel normally is run at 50 percent of its capacity, the contents must be “scaled up” to calculate the weight capacity of the RHS mixture if the vessel is filled to capacity. To do this:

   a. First, calculate the density of the RHS mixture that is normally charged to the vessel. You can obtain the RHS mixture density by determining the total mass of the RHS mixture and dividing by the total volume of the RHS mixture. Alternatively, you may estimate the RHS mixture density for an ideal solution using the following equation:

   $1/\rho_n = \Sigma\ (x_i/\rho_i)$
   where:
   ρ_n is the density of the RHS mixture;
   x_i is the mass fraction of component i in the RHS mixture; and
   ρ_i is the density of component i in the RHS mixture.

   b. Multiply the RHS mixture density by the maximum volume capacity of the vessel to obtain the maximum weight capacity of the RHS mixture in the vessel.

   If it is determined that the RHS mixture weight capacity of the vessel is less than 2,400 pounds, the RHS mixture amount is below the lowest threshold quantity (TQ) of an RHS mixture as specified at N.J.A.C. 7:31-6.3(c), Table II; no further analysis for TQ applicability is needed, and the RHS mixture amount for the vessel is not counted towards applicability determination. If the RHS mixture weight capacity is equal to or greater than 2,400 pounds, the heat of reaction of the RHS mixture must be determined.

3. Determine the heat of reaction, ΔH_R, of the RHS mixture in calories per gram of mixture not including any non-reacting substances for each process vessel handling any RHS mixture (see discussion in Part C of this guidance for a more detailed description of determining the heat of reaction). If the ΔH_R is less than 100 calories per gram of the RHS mixture, the mixture does not meet the criteria of an RHS mixture specified at N.J.A.C. 7:31-6.3(b)2, and the process vessel is not counted towards the RHS mixture applicability determination.

4. If the ΔH_R is greater than or equal to 100 calories per gram of the RHS mixture, identify the applicable threshold quantity corresponding to the ΔH_R of the RHS mixture in a process vessel from Table II at N.J.A.C.7:31-6.3(c). If more than one product is made in a particular vessel on a campaign basis and functional groups are present in those different products, determine the ΔH_R for each distinct RHS mixture in that vessel and identify the corresponding TQs.

   Compare the maximum weight capacity of each process vessel with an RHS mixture with the TQ derived from Table II at N.J.A.C. 7:31-6.3(c). If the maximum weight capacity of an RHS mixture in the process vessel meets or exceeds the TQ determined for that vessel, the facility is subject to the TCPA rules. (Note: The ΔH_R/TQ/maximum weight capacity comparison and applicability determination must be made for each individual product made in a particular vessel if more than one product is made on a campaign basis and functional groups are present in those different products, as described in 4 above. Each product meeting the ΔH_R/TQ/maximum weight capacity applicability criteria is subject to the TCPA rules.) However, pursuant to N.J.A.C. 7:31-6.2(h), if the total quantity of all the ingredients charged to the vessel, including components such as reactants, catalysts, and solvents, used in the RHS mixture present at the facility is less than the amount of the vessel capacity, that total quantity may be used for threshold quantity determination. (Note: In order to utilize this limitation of the total quantity of the RHS mixture ingredients, the o/o must implement administrative controls to ensure that the total quantity of all the RHS mixture ingredients present at the facility at all times is below the stated maximum amount and that this amount will never be exceeded.)

C. Heat of Reaction (ΔH_R) Determination for RHS Mixtures

N.J.A.C. 7:31-6.3(b)5 requires the o/o to determine and document the heat of reaction either by calorimetry testing or by another generally accepted practice such as literature review or engineering calculations. The heat of reaction must be determined using the intended combination over the lower temperature of 400º C or the maximum achievable temperature (MAT). The rule states that the heat of reaction determination is based on the intended combination. If the o/o chooses to determine the heat of reaction for the intended combination, then using 400º C as the temperature value for the calorimetry testing, calculation, or literature review is acceptable. However, if the o/o chooses to go through the MAT analysis, which may result in a lower temperature value, the abnormal conditions specified in the MAT definition must be evaluated.

The maximum achievable temperature is defined at N.J.A.C. 7:31-1.5 as the highest temperature that can be attained during abnormal conditions in the process vessel taking into consideration the vessel design, the heating and cooling systems connected to the vessel, and the potential chemical reactions involving the vessel's contents. Examples of abnormal conditions include: 1) a vessel having a steam heating system where maximum heating is applied to the vessel; 2) a vessel having a cooling system where there is a total loss of cooling; 3) an exothermic reaction generating heat that takes place inside the vessel; 4) contamination to the normal vessel contents causing an exothermic reaction; 5) external fire; and 6) unintended ratio or amounts of reaction ingredients. Abnormal conditions (4) and (6) above need further clarification.

Abnormal condition (4) requires evaluation of contamination to the vessel. There may be many substances in the vicinity of the process vessel that can potentially contaminate the vessel. The o/o should screen the substances in the vicinity of the process vessel to determine which ones have a reasonable possibility to enter the vessel and which may cause an unintended reaction if inadvertently mixed with the reactants in the process vessel.

Abnormal condition (6) requires evaluation of the effects of adding unintended ratios or amounts of reaction ingredients. Common examples of this include:

1. Adding more catalyst. A standard practice for this in relief system design using the DIERS methodology is to assume that 100% additional catalyst is charged.
2. Decreased amount of solvent. A standard practice for this in relief system design using the DIERS methodology is to assume that 50% of the normal amount of solvent is charged.

In order to determine the MAT for the process vessel, the o/o should first estimate the maximum temperature rise by conducting a brief hazard analysis, such as a what-if or hazard and operability (HAZOP) study, to consider all possible abnormal condition scenarios that could occur. Next, all possible side reactions, including the decomposition reaction, have to be considered to determine if an unintended exothermic reaction other than the primary intended reaction can occur to cause a temperature rise. When analyzing the MAT, the o/o does not have to analyze combinations of the six abnormal conditions listed in the MAT definition or other abnormal conditions beyond the six that are listed. The maximum temperature rise determined from the analysis of all these abnormal condition scenarios then should be added to the process vessel's maximum operating temperature to obtain the MAT.

Next, the o/o should compare the maximum achievable temperature to 400 degrees C to determine the lower temperature. Determine the heat of reaction to this lower temperature either by calorimetry testing or by another generally accepted practice such as literature review or engineering calculations. If the calorimetric test gives a heat of reaction value lower than 100 cal/g because the test had to be aborted prematurely due to an excessive pressure/temperature rise, the o/o should check the value of the heat of reaction through literature search or by engineering calculation.

When determining the heat of reaction, the o/o must express the final heat of reaction value for the RHS mixture in units of calories per gram of RHS mixture <u>not including any non-reacting substances</u>. The heat of reaction commonly is expressed in units of calories per mole or calories per gram of one of the reactants. This value must be converted to calories per gram of the total RHS mixture contents in the process vessel <u>not including the non-reacting substances</u>. To calculate the heat of reaction excluding the non-reacting substances, use the following equation:

$\Delta H_{R,\text{ excluding non-reacting substances}} = \Delta H_{R\text{ with non-reacting substances}}$ X $1/(1-x_{\text{non-reacting substances}})$
where:
$x_{\text{non-reacting substances}}$ is the mass fraction of the non-reacting substance of the total mixture contents of the vessel.

An example of calculating the heat of reaction excluding the non-reacting substances is illustrated in Section D, Example 2, step 3 below.

1. Calorimetry Testing

   N.J.A.C. 7:31-6.3(b)5i states that calorimetry testing performed to determine the heat of reaction must be performed to the lower of the specified temperature ranges. Screening tests are available and may be used to make the heat of reaction determination for RHS mixture applicability to the TCPA rules. One commonly used screening test is the Differential Scanning Calorimeter (DSC). In the DSC, a small sample size of about a few milligrams is used. The DSC provides limited reaction data such as the heat of reaction, the reaction onset temperature, and the maximum temperature achieved.

   The calorimetry test should be performed with the RHS mixture including the solvent since in some reactions the solvent acts as a vehicle for the reactants to take part in the reaction, with the solvent remaining unreacted. However, the heat of reaction value must be calculated excluding the amount of the solvent and other non-reacted substances from the mixture. The o/o must maintain printouts of the calorimetry tests to be available for review by the Department.

2. Literature Search

   The heat of reaction may be obtained from various reference sources. A heat of reaction value found in the literature must apply to the specific process chemistry for the RHS mixture. Also, the heat of reaction value must meet the temperature criteria requirements specified at N.J.A.C. 7:31-6.3(b)5 (i.e. to the lower of 400 degrees Celsius or the maximum achievable temperature in the process vessel). For example, a literature search may show that the heat of polymerization (heat of reaction) for a particular polymerization reaction is X calories per gram at 25º C. The o/o must first verify whether this value is valid over the lower of the rule's temperature criteria: up to 400º C, or the maximum achievable temperature. If other reactions such as side reactions or decomposition take place at these higher temperatures, the heat of reaction of those reactions must also be determined to determine the total heat generated over the temperature range. Also, the heat of reaction value must be converted to the units of calories per gram of the RHS mixture, excluding the amount of the solvent and other non-reacting substances from the mixture. The o/o must maintain copies of the reference documentation to be available for review by the Department.

3. Engineering Calculations

The rule allows the o/o to determine the heat of reaction by making engineering calculations. The o/o can complete this using computer software models or by hand calculations. One known computer model that is available is the Chemical Thermodynamics and Energy Release (CHETAH) program sold by ASTM International. To obtain the heat of reaction using the CHETAH program or by hand calculation, the o/o must have the balanced chemical reaction equation(s) for all the reactions that take place over the lower of the temperature criteria specified at N.J.A.C. 7:31-6.3(b)5. The o/o must determine the total heat generated for all reactions that occur over the required temperature range and calculate the heat of reaction in units of calories per gram of the RHS mixture excluding the amount of the solvent and other non-reacted substances from the mixture. The o/o must maintain documentation of the heat of reaction calculations to be available for review by the Department.

4. Determination of Heat of Reaction in Batch, Semi-batch, and Continuous Reactions

a. Batch Reaction

In a batch reaction, a reaction vessel is filled in various steps with a charge of reactants and possibly solvents and catalysts, which comprise the RHS mixture, and this “batch” is allowed to react over a set period of time. Heating or cooling may be applied to the reactor at various stages of the reaction. The heat of reaction for this case is the total heat generated in calories divided by the total aggregated weight of material fed excluding the amount of the solvent and other non-reacted substances from the mixture.

b. Semi-batch Reaction

In a semi-batch reaction, typically the reactor is charged with one or more reactants and possibly solvents or catalysts. One or more other reactants are then slowly fed over a period of time to control the temperature and amount of heat generated. Pursuant to N.J.A.C. 7:31-6.3(b)6, to determine the heat of reaction in the case of a semi-batch reaction, the o/o must assume that the total amount of all the reactor ingredients are charged together as in a batch reaction. The heat of reaction for this case is the total heat generated in calories divided by the total aggregated weight of material fed excluding the amount of the solvent and other non-reacting substances from the mixture.

c. Continuous Reaction

In a continuous reaction, reactants, solvents and catalyst are fed continuously to a reaction vessel, mixed or plug flow, and a stream containing the product is discharged continuously. The heat of reaction must still be expressed as calories per gram of RHS mixture, which would equal the total heat generated per unit time (for example, calories per hour) divided by the total mass flow rate of all the RHS mixture components fed through the reactor (grams per hour) excluding the amount of the solvent and other non-reacting substances from the mixture.

To determine the amount of RHS mixture for threshold quantity determination, assume that the reactor is filled to capacity and determine the instantaneous, or "snapshot," inventory of the reactor contents including the solvent and other non-reacting substances.

D. Examples of RHS and RHS Mixture Covered Process Applicability Determination

Example 1:

A facility stores eight drums of tert-butyl hydroperoxide (inhibited with 30 percent water), which is a Group I RHS, in a storage shed, and another drum is stored in a blending room.

To determine applicability for a Group I RHS, calculate the total net weight of the tert-butyl hydroperoxide at the facility.
The net weight of each drum is 410 pounds. The percentage of tert-butyl hydroperoxide in each drum is 70 percent (100 percent minus 30 percent water). The amount of tert-butyl hydroperoxide in each drum is 287 pounds (410 pounds times 70 percent).
The total quantity of tert-butyl hydroperoxide at the facility is 2,583 pounds (9 drums times 287 pounds). Therefore, the facility is subject to the TCPA rules.

Example 2:

The following product is made in a 2,000 gallon batch reactor vessel:

Product 1:
Substances charged to the reactor specified by the batch recipe:

Substance	*Charge amount (weight, pounds)*	*Charge amount (volume, gallons)*	*Density (pounds/gallon)*
Solvent A, liquid	*4,000*	*500*	*8*
Reactant B, liquid	*4,000*	*400*	*10*
Reactant C, liquid	*3,000*	*400*	*7.5*
Total	*11,000*	*1,300*	

To determine applicability for an RHS mixture, complete the following:

1. Determine whether any of the substances being charged to the vessel include one of the functional groups specified in N.J.A.C. 7:31-6.3(a), Part D, Group II. You determine that Reactants B and C are monomers being used in an alkene (vinyl) polymerization reaction, which is functional group number 40. Therefore, applicability for an RHS mixture must be evaluated.

2. Determine the maximum weight capacity of the reactor vessel.

First, the density of the RHS mixture must be determined. Divide the total weight of the RHS mixture by the total volume: 11,000 pounds divided by 1,300 gallons = 8.46 pounds per gallon
(If all the components are liquids forming an ideal solution, you could also obtain the density by using the equation, $1/\rho_n = \Sigma (x_i/\rho_i)$, described at section II.B.2.a. above.)

Next, "scale up" to the full 2,000-gallon capacity of the reactor:
2,000 gallons X 8.46 pounds per gallon = 16,920 pounds.
Since 16,920 pounds is greater than 2,400 pounds, the lowest threshold quantity from Table II at N.J.A.C. 7:31-6.3(c), the heat of reaction must be determined.

3. Determine the heat of reaction of the RHS mixture.
   Assume that literature data is not available, and the o/o decides to obtain the heat of reaction by calorimetry testing. The o/o provides a sample of the batch ingredients to a laboratory experienced in reactive hazard calorimetry testing. The results of the calorimetry test show that the heat of reaction for all the ingredients (including the Solvent A) is 50 calories per gram. However, the heat of reaction value must be determined excluding the amount of solvent. In this example, the solvent is 36.3 percent by weight of the total amount (4,000 pounds of Solvent A divided by 11,000 pounds total reactor contents). Calculate the heat of reaction excluding the solvent:
   50 cal/g X 1/(1-0.363) = 78 cal/g

Since the heat of reaction is less than the 100 calories per gram minimum value at N.J.A.C. 7:31-6.3(c), Table II, Product 1 is not subject to the TCPA rules as an RHS mixture.

<u>Example 3:</u>

Product 1 is made in the 2,000 gallon reactor described in Example 2. Also, another product, Product 2, is made in this reactor on a campaign basis with Product 1 during the year.

Assume that the weight capacity of the reactor and heat of reaction for Product 2 are determined using the same procedure illustrated in Example 2 and the following results are obtained:

Product 2 results:
Reactor weight capacity = 11,500 pounds
$\Delta H_{R,2}$ = 210 cal./g of RHS mixture

From Table II at N.J.A.C. 7:31-6.3(c), the corresponding threshold quantity for the heat of reaction range of 200 to 300 calories per gram is 8,700 pounds.

The RHS mixture for Product 2 is subject to the TCPA rules.

Example 4:

An o/o has a batch reaction process where 500 gallons of a mixture consisting of a peroxide, which has a Group II functional group, and a solvent are first charged to a 2,500 gallon batch reactor vessel. A monomer is then charged and the first step of the reaction takes place to form an intermediate product. Next, another reactant is charged, and the second stage of the reaction takes place to form the final product.

To determine applicability, the o/o should determine the ΔH_R of the mixture for each step:

1. The 500-gallon mixture consisting of the peroxide and the solvent;
2. The stage 1 reaction consisting of the addition of the monomer to peroxide and solvent to form the intermediate; and
3. The stage 2 reaction consisting of the addition of the other reactant to the intermediate formed in the stage 1 reaction to form the final product.

The o/o must evaluate the ΔH_R/TQ/maximum weight capacity for each of the three steps to determine if any meet the RHS mixture applicability requirements of the rules. If any do meet the RHS mixture applicability criteria, the vessel and process are subject to the TCPA rules.

Example 5:

An o/o runs a batch reaction in a 2,000-gallon vessel where the final contents of an RHS mixture in the vessel at the completion of the reaction amount to 1,500 gallons. Following the completion of the reaction, another 200 gallons of a solvent are added to the reactor.

If the final products in the reactor include a substance that contains a Group II functional group, the final step of the process in which the final products are combined with a solvent would have to be evaluated for RHS mixture applicability. This would include evaluating the ΔH_R, maximum weight capacity, and TQ for the mixture to determine if it meets the RHS mixture applicability requirements of the rules. This is similar to the required analysis for each step of process described in Example 4 above.

If the final product contents of the reactor do not contain a substance with a Group II functional group, no further evaluation to determine RHS mixture applicability would be required. However, please note that the earlier steps of the production process in which substances containing a Group II functional group were used to make the final product would have to be evaluated for RHS mixture applicability.

Example 6:

An o/o runs a batch reaction normally in a 2,000-gallon reactor. Occasionally during the year, the o/o runs the same reaction (the same contents and amounts) in a 5,000-gallon reactor.

In this example, the o/o must evaluate both reactors for RHS mixture applicability.

Attachment A – Reactive Hazard Substance Applicability Flowchart