THERMAL RUNAWAY IN TUBULAR REACTOR SYSTEMS WITH n-th ORDER KINETICS

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ABSTRACT

This paper addresses the problem of predicting the critical parameters that characterize thermal runaway in a tubular reactor with wall cooling, introducing a new view of the n-th order kinetics reactions. The paper describes the trajectories of the system in the temperature-(concentration)^n plane, and deduces the conditions for the thermal risk.

1. INTRODUCTION

Substances that can react exothermically represent always a potential hazard. This risk can appear both in the storage of substances that can react by themselves and in chemical reactors in which exothermic processes are carried out under supposedly controlled conditions due to an incorrect operation.

Barkelew (Barkelew 1959) established design criteria that give the safety conditions for various types of reaction kinetics. The Barkelew criteria are based on the examination of a great number of cases in which the heat and mass balance equations were solved numerically. Further elaboration of the runaway conditions is due to (Dente 1964; Van Welsenaere 1970; Morbidelli and Varma 1982) between others.

Most sensitivity criteria treat only the case where the kinetics of the reaction is first order, and only a few papers have been found treating different kinetics. For example (Velo, Bosch et al. 1996) treat the general second order kinetics. Recently, a state estimation method based on extended Kalman filter (EKF) was presented for nonlinear dynamical systems that are characterized by complex dynamic phenomena such as multiple steady state behavior(Karri 2011).

In the present work, a new view of the n-th order kinetics reactions is presented and analyzed, describing the trajectories of the system in the temperature-(concentration)^n plane. The initial concentrations conducing to the thermal instability are also computed by means of an algorithm. In essence, the paper interprets the first-order findings of (Van Welsenaere 1970) to the n-th order space.

2. MATHEMATICAL MODEL OF AN IDEAL TUBULAR REACTOR

The continuity equation for one of the reacting components and the energy equation of a "one dimensional" tubular reactor with constant wall temperature, for a single reaction, constant fluid density and no difference in temperature between solid and fluid, may be written:

$$\left(-r_A\right) = -u\frac{dC_A}{dL} \tag{1}$$

$$u\rho c_P \frac{dT}{dL} = \left(-r_A\right)\left(-\Delta H_R\right) + U\left(T_h - T\right)\frac{A}{V} \tag{2}$$

U may be an overall coefficient, accounting for the resistance to convective heat transfer at the inner and outer wall and to conduction through the wall itself or only an inner convection coefficient. T_h represents the coolant temperature, assumed to be equal to the wall temperature. In what follows, 'wall' temperature will be used without really distinguishing both cases.

The following discussion will be based on an irreversible reaction with a n-th order rate equation:

$$\left(-r_A\right) = k_0\, e^{-E/RT}\, C_A^n \tag{3}$$

the following definitions will also be used:

$$N_h = \frac{U\left(A/V\right)}{k_h\, \rho\, c_P} \tag{4}$$

$$N_{ad} = \frac{E \, \Delta T_{ad}}{RT_h^2} \qquad (5)$$

$$\Delta v = \frac{E}{RT_h^2}(T - T_h) \qquad (6)$$

where k_h is the kinetic constant at the coolant temperature (T_h).

The parameter ΔT_{ad} in eq. (5) represents the change in temperature that would present an adiabatic system where the complete reaction takes place (until C_A equals zero), and is not a function of the kinetics. Is easy to check that:

$$\Delta T_{ad} = \frac{C_{A0}(-\Delta H_R)}{\rho C_P} \qquad (7)$$

Note that the dimensionless N_{ad} is directly proportional to C_{A0}. In some parts of the paper $N_{ad}'=N_{ad}/C_{A0}$ (m³/kmol in S.I. units) will be used, in order to remark that some curves will not depend on C_{A0}.

The relationship of the kinetic constant with k_h may be expressed as:

$$k = k_0 \, e^{-E/RT} = k_0 \, e^{-E/RT_h} e^{E(T-T_h)/RT_h T} \approx k_h \, e^{E(T-T_h)/RT_h^2} = k_h \, e^{\Delta v} \qquad (8a)$$

so $\qquad (-r_A) = k_h \, e^{\Delta v} \, C_A^n \qquad (8b)$

3. THE REACTOR BEHAVIOUR REPRESENTED IN THE C_A^n-Δv PLANE.
Dividing eq. (2) by eq. (1) and making use of the preceding definitions, we can write:

$$-\frac{d(\Delta v)}{dC_A} = N_{ad}' - \frac{N_h \, \Delta v \exp(-\Delta v)}{C_A^n} \qquad (9)$$

Let us develop the former equation in terms of $d(\Delta v)/dC_A^n$. For this purpose, assume a function of the type:

$$\frac{df(x)}{dx} = H + J \, x^{-n} \qquad H, J = constants \qquad \text{for n≠1 (10)}$$

If the last expression is integrated:

$$f(x) = Hx + \frac{J \, x^{1-n}}{1-n} \qquad (11)$$

let Z=x^n, so

$$\frac{df(x)}{dZ} = \frac{df(x)}{dx^n} = \frac{d}{dZ}\left(HZ^{\frac{1}{n}} + \frac{JZ^{\frac{1}{n}-1}}{1-n}\right) = \frac{1}{n}HZ^{\frac{1}{n}-1} + \left(\frac{1}{n}-1\right)\frac{J}{1-n}Z^{\frac{1}{n}-2} = \frac{1}{n}\left[Hx^{1-n} + Jx^{1-2n}\right] \quad (12)$$

Applying this rule to eq. (8) we obtain:

$$\frac{d(\Delta v)}{dC_A^n} = \frac{1}{n}\left[N_{ad}' C_A^{1-n} - N_h \Delta v \exp(-\Delta v)C_A^{1-2n}\right] \quad (13)$$

that is also valid for n=1. To obtain an idea of the form of this equation and of the phenomenon of parametric sensitivity and runaway, Figure 1 presents various dotted curves (these curves are what will be called 'trajectories' in the C_A^n-Δv plane) obtained by integration of eq. (13) with different values of N_{ad} but maintaining, as an example, the quotient N_h/N_{ad}=2. Other parameters fixed in this example were n=2 and C_{A0}=1. The boundary condition for the integration has been $C_A^n=C_{A0}^n$ when $\Delta v=\Delta v_0$=0 in this case. This Figure is completely equivalent for that presented in the case of first order reaction in the conversion-temperature plane (Westerterp 1984). Figure 1 also shows different arrows that represent the value and direction of the derivative eq. (13). In the Figure we see that, particularly above a certain value of N_{ad} (between 42 and 52 in the figure), the curve completely misses the lower part of the locus with the results that the maximum of this trajectory will become very high and close to the value obtained for adiabatic operation, so runaway can be expected. We shall return later to this great sensitivity of the maximum to a variation in parameters.
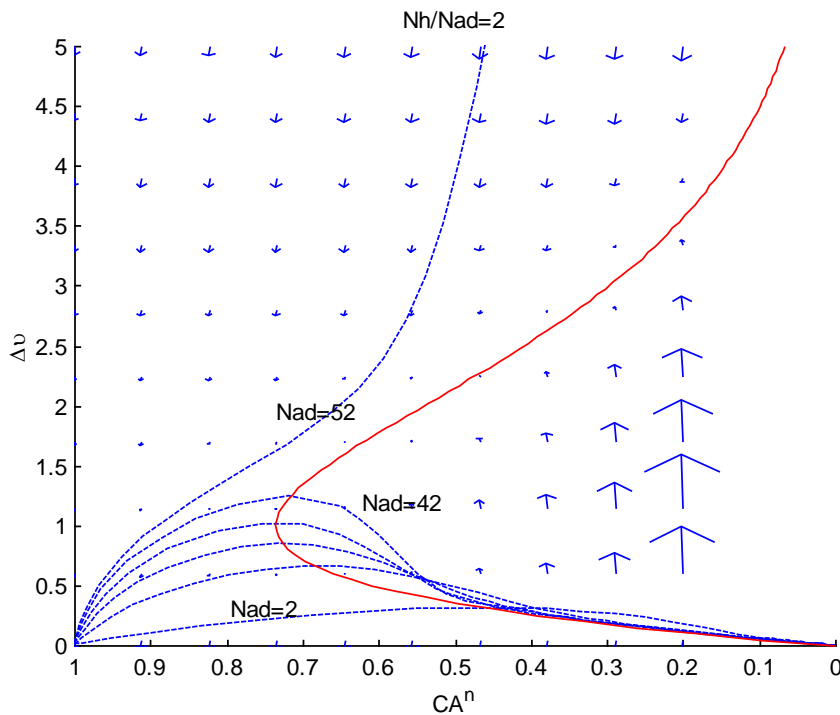
[Figure 1] Temperature increase and locus of maxima temperatures for second order exothermic reactions in cooled tubular reactors.

The loci of the maxima and the inflexion points in the reactor temperature profile, when represented in the C_A^n-Δv plane, will now be discussed in detail.
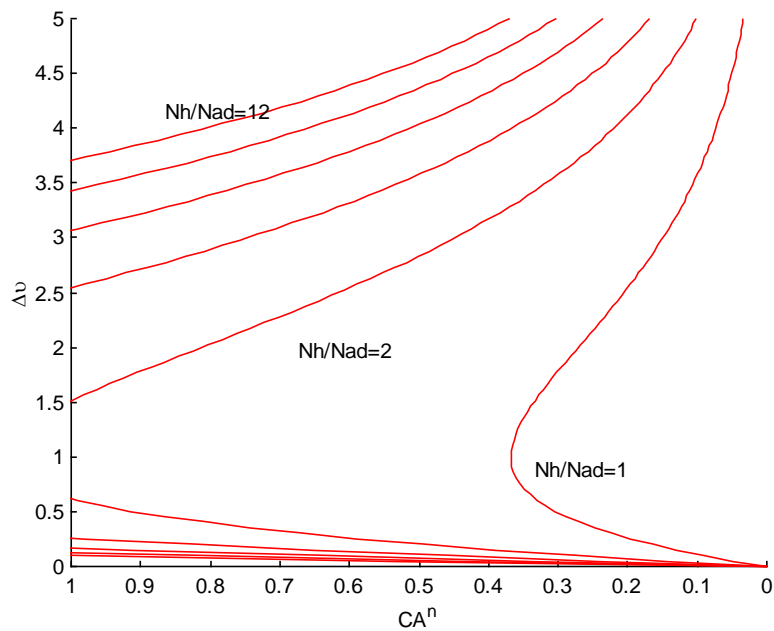
The locus of the maxima

In the maximum of the reactor temperature profile, the derivative eq. (13) equals zero and the following equation is easily obtained:

$$\left(C_A^n\right)_m = \frac{N_h}{N_{ad}'} \Delta v_m \exp(-\Delta v_m) \qquad (14)$$

where the subindex 'm' would mean 'loci of the maxima'. An important fact is that *this loci does not depend on the order of reaction*, the quotient N_h/N_{ad}' being the most important parameter for the curve position. This equation can also be derived by setting $dT/dL=0$ in eq. (2), so it represents also the loci of the maxima in the T-L plane.

Figure 1 presents the loci of the maxima (continuous line) for the case considered. Figure 2 presents the curve for different values of the quotient N_h/N_{ad}', and for n=2. In the same way that has been described for first order reaction in the T-L plane (Westerterp et al, 1984), when the cooling capacity is relatively small (say $N_h/N_{ad}<2$), the locus lies very much to the right and the chance that, at constant N_{ad}', Δv_m will exceed a certain value is increased. On the other hand, if N_h/N_{ad}' is large, a large reagion exists where $d(\Delta v)/dC_A^n$ must be negative. Thus for $N_h/N_{ad}'=12$ (see Figure 2) and a value of Δv_0 between 0.16 and 3.7 no maximum in Δv will occur; accordingly Δv will be consistently lower than Δv_0. In case Δv_0 lies below 0.16, the reaction temperature will remain the value of 0.16. Finally, if the feed temperature corresponds to $\Delta v_0>3.7$, the reaction temperature will raise to a high value.

[Figure 2] Locus of maximum temperatures for n=2 reactions- The influence of N_h/N_{ad}'.

By setting $d\left(C_A^n\right)_m / d(\Delta v) = 0$, we found:

$$\frac{d\left(C_A^n\right)_m}{d(\Delta v)} = \frac{N_h}{N_{ad}'}\left[\exp(-\Delta v_{mm}) - \Delta v_{mm}\exp(-\Delta v_{mm})\right] = 0 \qquad (15)$$

The solution of this equation is the temperature corresponding to the maximum of a 'maxima curve', Δv_{mm}, given by:

$$\Delta v_{mm} = 1 \qquad (16a)$$

The position of this point 'mm' does not depend neither on N_h, N_{ad} nor n, and it could be perfectly observed in Figure 2 (also in Figure 1). The corresponding concentration is

$$\left(C_A^n\right)_{mm} = \frac{N_h}{eN_{ad}'} \qquad (16b)$$

Figure 1 shows how the trajectories corresponding to stable systems (systems not presenting runaway condition) does intersect the loci of the maximum before its maximum (before the point 'mm'). A particular importance may be adscribed to the trajectory that intersects the 'maxima curve' in its maximum. According to the criterion established by (Van Welsenaere 1970) for first order reactions, it is proposed as a first objective criterion for runaway be based upon the point 'mm'. The new criterion for n-th order reactions would then state:

"*The trajectory going through the maximum of the maxima curve is considered as critical, and therefore as locus of the critical inlet conditions for C_A^n and Δv*".

This is a criterion for runaway based on an intrinsic property of the system, not on an arbitrarily limited temperature increase.

Locus of inflexion points of the reactor temperature profiles
The T(L)-curves shown in the work of (Van Welsenaere 1970) revealed that the hot spot became important when inflexion points occur before the temperature maximum in the T-L plane.

From eq. (2) and (3), and using L'=L/u:

$$\rho c_P \frac{dT}{dL'} = k_0 \exp\left(-\frac{E}{RT}\right)C_A^n(-\Delta H_R) + U(T_h - T)\frac{A}{V} \qquad (17)$$

that using the notation presented, becomes:

$$\frac{d(\Delta v)}{dL'} = N_{ad}' k_h \exp(\Delta v)C_A^n - k_h N_h \Delta v \qquad (18)$$

Let us now calculate $d^2(\Delta v)\big/ dL'^2$:

$$\frac{d^2(\Delta v)}{dL'^2} = N'_{ad} k_h \exp(\Delta v)\frac{dC_A^n}{dL'} + N'_{ad} k_h \exp(\Delta v)C_A^n \frac{d(\Delta v)}{dL'} - k_h N_h \frac{d(\Delta v)}{dL'} \tag{19}$$

In this equation, $d(\Delta v)\big/ dL'$ is given by eq. (18). On the other hand, in order to calculate $dC_A^n \big/ dL'$, we see from eq. (8b) that

$$\frac{dC_A}{dL'} = (+r_A) = -k_h \exp(\Delta v)C_A^n \tag{20}$$

so,

$$\frac{dL'}{dC_A} = -\frac{1}{k_h}\exp(-\Delta v)C_A^{-n} \tag{21}$$

applying the rule obtained in eq. (12), we found:

$$\frac{dL'}{dC_A^n} = -\frac{1}{n}\frac{1}{k_h}\exp(-\Delta v)C_A^{1-2n} \tag{22}$$

and then,

$$\frac{dC_A^n}{dL'} = -n k_h \exp(\Delta v)C_A^{2n-1} \tag{23}$$

Inserting eqs. (23) and (18) into (19), equating to zero and rearranging we found the loci of the inflexion points:

$$\exp(2\Delta v_i)\left(\left(C_A^{2n}\right)_i N'_{ad} - n\left(C_A^{2n-1}\right)_i\right) - \exp(\Delta v_i)\left(C_A^n\right)_i N_h (1+\Delta v_i) + \frac{N_h^2 \Delta v_i}{N'_{ad}} = 0 \tag{24}$$

being the subindex 'i' referred to the inflexion points. The following groups will be introduced to simplify the notation:

$$A = -n\left(C_A^{2n-1}\right)_i + \left(C_A^{2n}\right)_i N'_{ad} \qquad (25a)$$
$$B = \left(C_A^n\right)_i N_h \qquad (25b)$$
$$C = \frac{N_h^2}{N'_{ad}} \qquad (25c)$$

in this way, (24) reduces to:

$$A\exp(2\Delta v_i) - B\exp(\Delta v_i)(1+\Delta v_i) + C\Delta v_i = 0 \tag{26}$$

This equation has no analytical solution. The complexity of the former mathematical expression makes difficult to work with it, and there is no possibility to obtain an explicit equation on Δv_i. In the case of first order

reactions (Van Welsenaere 1970), an explicit equation was derived, with two solutions. The investigation of the sign of d^2T/dL'^2 in that simple case suggested a second objective criterion for runaway, derived from the occurrence of inflexion points before the maximum.

4. CRITICAL INLET CONDITIONS

The most important fact when working with possibilities of runaway is to find the inlet conditions that lead to the critical situations. Rigorously, this requires back integration. However, approximate values for the critical inlet conditions may be obtained by simple extrapolations. Several ways of extrapolation are possible. Two ways will be presented, so as to define an upper and a lower limit for the approximated critical inlet conditions.

The lower limit is based upon the property of the trajectories to start in the $C_A{}^n$-Δv plane with adiabatic slope for $T_0=T_h$, and to bend under this line due to heat transfer with the surroundings. Therefore, an adiabatic line starting from a point on a critical trajectory (critical according to one of the criteria) leads to a lower limit for the critical inlet conditions. The following relationship is then derived:

$$\left(C_{A0}\right)^n_{lower} = \left(C_A\right)^n_{critical} - \frac{1}{\left(slope\ adiabatic\ line\right)}\left(\Delta v_{critical} - \Delta v_0\right) \qquad (27)$$

Let us calculate then the slope of an adiabatic line in the $C_A{}^n$-Δv plane. From eq. (13), if we make $N_h=0$, then

$$\frac{d(\Delta v)}{dC_A^n} = \frac{1}{n} N_{ad}^{'} C_A^{1-n} \qquad \text{for an adiabatic system} \qquad (28)$$

and combining with eq. (27) we finally obtain:

$$\left(C_{A0}\right)^n_{lower} = \left(C_A\right)^n_{critical} - \frac{n}{N_{ad}^{'}\left(C_A\right)^{1-n}_{critical}}\left(\Delta v_{critical} - \Delta v_0\right) \qquad (29)$$

The critical point according to the first criterion is the maximum of the "maxima-curve", but as such it is also a point of the loci of inflection points, upon which the modified second criterion is based. This means that for the calculus of $(C_A)^n_{critical}$ we can use eq. (14) with $\Delta v=\Delta v_{critical}$ (i.e. $\Delta v=\Delta v_{mm}=1$) or eq. (26) with $\Delta v_i=\Delta v_{critical}$. Due to the complexity of eq. (14) we will use first criterion.

Upper limits are based on the observation made by (Van Welsenaere 1970). As has been pointed out, the first order reaction system represented in the conversion-temperature plane is totally equivalent to a n-th order reaction represented in the $C_A{}^n$-Δv plane. Following the reasoning, and considering the tangents through the points $\Delta v=\Delta v_{critical}$ and $C_A{}^n=C_A{}^n_{critical}$, the value of $C_{A0}{}^n$ found is:

$$\left(C_{A0}\right)^n = \left(C_A\right)^n_{critical} - \frac{\left(\Delta v_{critical} - \Delta v_h\right)}{\left(\dfrac{d\Delta v}{dC_A^n}\right)_{\Delta v=\Delta v_{critical}}} \qquad (30)$$

The value of $\Delta\nu_h$ is zero by definition. The value of the slope at the critical conditions is calculated from eq. (13). In this way:

$$\left(C_{A0}\right)^n = \left(C_A\right)^n_{critical} - \frac{\Delta\nu_{critical}}{\frac{1}{n}\left[N'_{ad}\left(C_A\right)^{1-n}_{critical} - N_c\,\Delta\nu_{critical}\exp\left(-\Delta\nu_{critical}\right)\left(C_A\right)^{1-2n}_{critical}\right]} \qquad (31)$$

The lowest $\left(C_{A0}\right)^n$ is obtained for $d\left(C_{A0}\right)^n \big/ d\left(C_A\right)^n_{critical} = 0$. After substituting and rearranging the resulting equation, we finally found that:

$$\left(N'_{ad} - \frac{\gamma}{\left(C_A\right)^n_{critical}}\right)^2 - \left(1-\frac{1}{n}\right)\frac{\alpha}{\left(C_A\right)_{critical}}\left(N'_{ad} - \frac{\gamma}{\left(C_A\right)^n_{critical}}\right) + \frac{\gamma\alpha}{\left(C_A\right)^{n+1}_{critical}} = 0 \qquad (32)$$

with

$$\alpha = n\Delta\nu_{critical}$$
$$\gamma = N_c\Delta\nu_{critical}\exp\left(-\Delta\nu_{critical}\right) \qquad (33)$$

The solution of this equation in $\left(C_A\right)^n_{critical}$ and substitution in eq. (31) would give the wanted $\left(C_{A0}\right)^n_{upper}$.

Application to different kinetics

The former equations have been applied to different cases, in order to test their usefulness. The first example has been extracted from the book of (Westerterp 1984). Let a *first order* system be defined by the following parameters:

$k=7.4e8*exp(-13600./T)\ s^{-1}$ $U=100\ W/m^2{\cdot}K$

$\rho{\cdot}C_P=1300\ J/m^3{\cdot}K$ $(-\Delta H_R)=1300000\ J/mol$

$A/V=4/(25e\text{-}3)\ m^{-1}$ $E/R=13600\ K^{-1}$

Suppose we are interested in calculate the initial concentration provoking the thermal risk for T_h between 635 and 735 K. If so, we then make $\Delta\nu_{critical}=1$, and calculate $(C_A)^n_{critical}$ from eq. (16b) for each value of T_h considered (in this case, n=1); these values of critical concentration are used in eq. (29) to evaluate $(C_{A0})^n_{lower}$. On the other hand, the condition $\Delta\nu_{critical}=1$ is introduced in eq. (32) to find the $(C_A)^n_{critical}$ for this second condition (trial and error), and $(C_{A0})^n_{higher}$ is calculated using eq. (31). The result of this calculus is presented in Figure 3. The Figure also presents the average value between upper and lower limit for the input concentration. For $T_h=635$ K, the average is 0.55 mol/L (correct value as indicated in (Westerterp 1984)). This means that an initial concentration higher than 0.55 mol/L may provoke thermal instability. The average value between the two limits is close to the critical points predicted, as remarked in the original work of (Van Welsenaere 1970). It could be also observed that the average is closer to critical trajectories at higher values of T_h (more problematic situations).
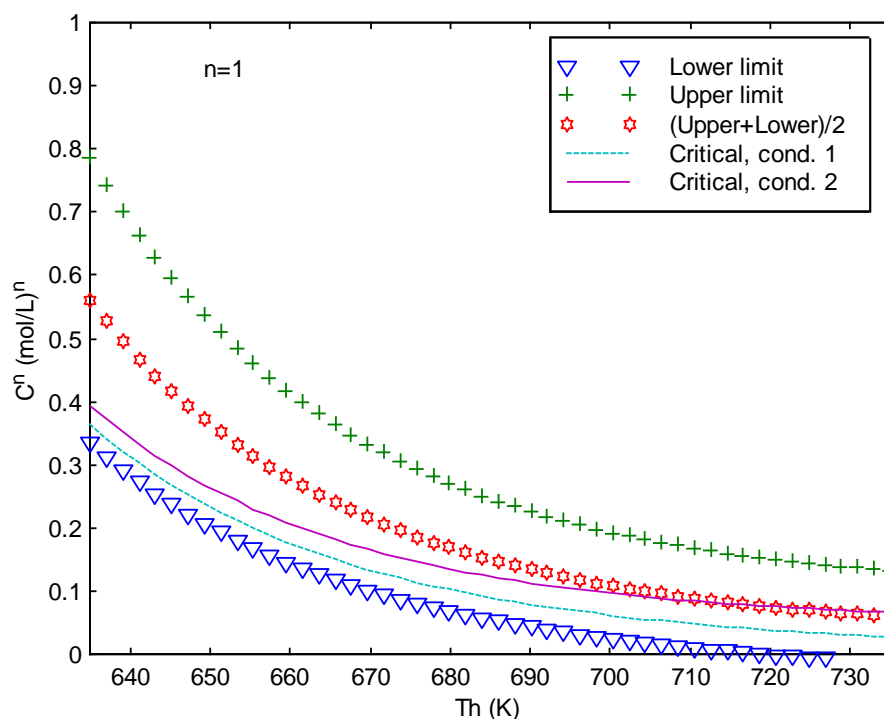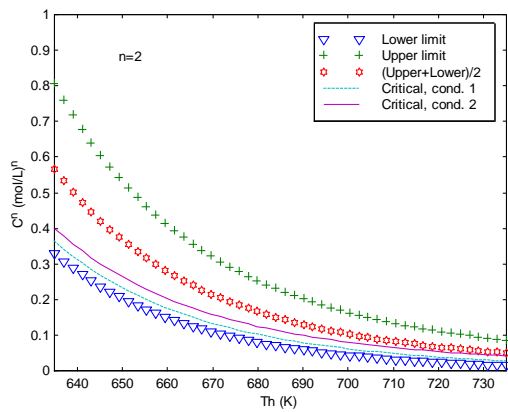
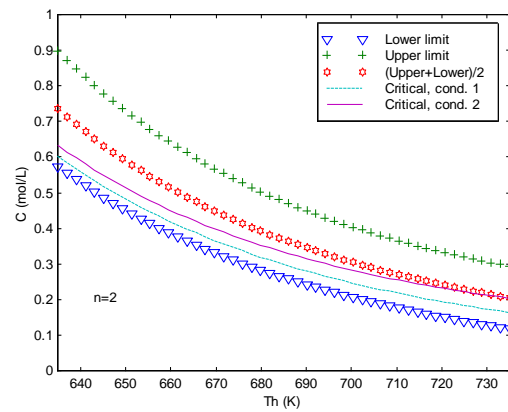[Figure 3] Calculation of maximum initial concentration for n=1 and different Th. Cn vs. Th.

Let the order be 2, 5 and 10, maintaining the others values of constants. The corresponding graphs are shown in Figures 4, 5 and 6. These Figures have two parts. In part (A) the C^n-T_h graph is presented, and in part (B) the exponent of the concentration has been eliminated (i.e. C-T_h is presented). Concerning to Figures 3, 4(A), 5(A) and 6(A) several facts may be remarked:

- As commented above, the position of the critical points does not depend on the order of reaction.

- The approximation (critical point) $\approx$ (average upper and lower) is as valid as for first order kinetics.

- All the curves corresponding to different orders are quite similar, and an average curve may be proposed accounting for all the cases.
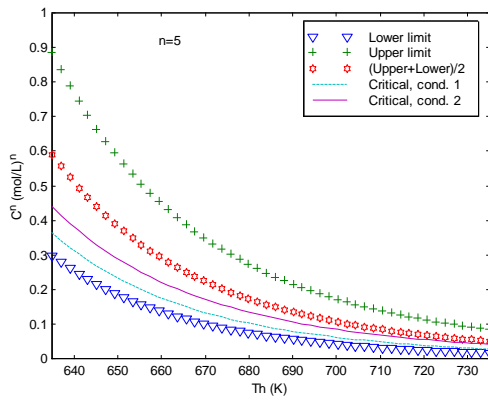
Comparing Figures 3, 4(B), 5(B) and 6(B), the approximation continues being valid, but the position of the critical point does depend on the order and the curves corresponding to different orders are quite different.
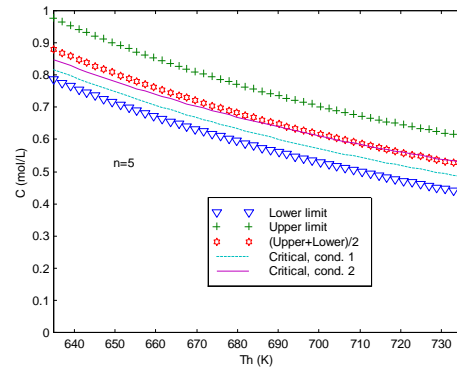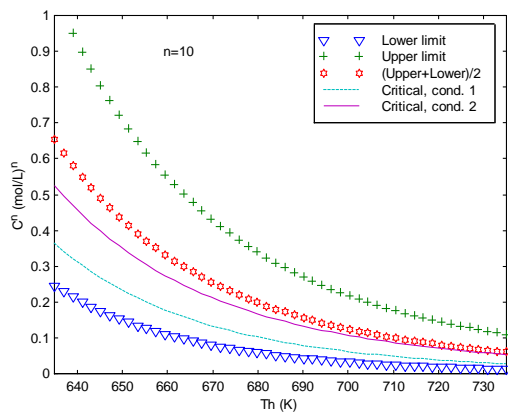
(A)   (B)

Figure 4. Calculation of maximum initial concentration for n=2 and different Th. (A) Cn vs. Th. (B) C vs. Th.
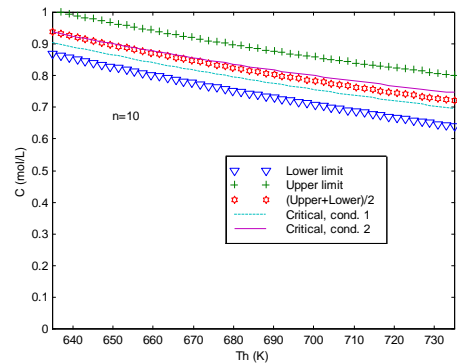

(A)

(B)

Figure 5. Calculation of maximum initial concentration for n=5 and different Th. (A) Cn vs. Th. (B) C vs. Th.

(A)

(B)

Figure 6. Calculation of maximum initial concentration for n=10 and different Th. (A) Cn vs. Th. (B) C vs. Th.

5. CONCLUSIONS

A new view of the runaway for n-th order reactions has been presented. The trajectories of the curves in the (concentration)^n-temperature plane have been introduced and compared to the curves conversion-temperature for first order reactions.

The translation of the criterion already accepted for thermal safety in first order processes, to the case of n-th order reactions has been done, and the steps in the calculation of the initial concentration provoking thermal risks have been also introduced.

The procedure has been applied to a model system, for different orders of reaction, concluding that the ap-proximation (critical point) $\approx$ (average upper and lower limits) is valid for all kinetics, and that all the curves corresponding to different orders are quite similar.

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