

## An Interdisciplinary Approach to High Temperature Chemistry

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In the field of high temperature chemistry, and especially as it pertains to the effluent of plasma jet devices, there has always been substantial uncertainty about the nature of the chemistry that one should expect when the initial high temperature stream is cooled to more conventional temperatures, often in the presence of an admixed cold reagent or spectator gas. As a first example, we may cite the cracking of methane in a plasma jet to make acetylene. For this reaction, as is generally the case, one must postulate some sort of "freezing temperature" because, of course, acetylene is unstable with respect to decomposition to the elements at room temperature. Now, three groups of workers have carefully regarded this reaction. One group<sup>1</sup> has established that chemical equilibrium at their mixed mean temperature determines the yield. (They say nothing about what happens at the intervening temperatures.) A second group<sup>2</sup> concluded that not equilibrium, but rather reaction kinetics controls the extent of reaction until the mixture becomes so cold the reaction "freezes;" while the third group<sup>3</sup> showed that the reaction was very fast and that the kinetics of mixing controlled the reaction rate. Again a "freezing" temperature was invoked. Reed<sup>5</sup> has opined that each group was correct but that the conflicting results stemmed from the different reaction conditions and geometries involved.

To cite further examples, consider the well-known fixation of up to 3 or 4% of the nitrogen when a nitrogen-oxygen mixture is passed through a streaming plasma device and the stream rapidly quenched. When Ammann and Timmins<sup>6</sup> withdrew product from a stationary cascade arc through a fine water-cooled probe they obtained an unheard of 12% yield. This must almost certainly be associated with the high cooling rate attributed to such probes. Again, consider the rather substantial body of information that has been accumulated for the reaction of methane with a nitrogen plasma to make HCN.<sup>1</sup> Attempts to interpret these data<sup>7,8</sup> have resulted in two plausible but contradictory mechanisms each of which accounts for the observed results very well indeed. On the one hand,<sup>7</sup> the yield is exactly what one might expect if each N<sup>+</sup> ion in the jet results ultimately in two molecules of HCN. To explain how this can happen, one must disregard considerations of chemical equilibrium and say that somehow the high temperature molecular and ionic fragments 'fall together' in the proper way in the very rapid quenching that results from the mixing process. The equally attractive alternative<sup>8</sup> is that the methane mixes in a quite ordinary way with the nitrogen jet and that the mixture is always in local thermodynamic equilibrium. At some point one has to postulate a "freezing temperature" below which all of the HCN precursors (assumed to be cyano, CN) proceed as before along some inevitable reaction path to the final product. The rather sophisticated computer program has never been made available for critical appraisal, but assuming it to be a straightforward result, one must ask whether it shouldn't be possible to differentiate between such diametrically opposed concepts by a consideration of the relevant time scales. Indeed one might suppose this would be standard operating procedure.

In the face of such evident need, it is interesting to ask why so little has been accomplished along these lines. Or to rephrase the question, what factors conspire to place such an analysis outside the accepted purview of "chemistry" or "chemical engineering?" The first factor that comes to mind is the real paucity of information about any of the characteristics, but especially the characteristic times of such strongly cooled fluid flow. Is it reasonable to even think about meaningful quenching rates? Another factor is that the whole concept of "freezing" a reaction has always been a bit nebulous to the chemist. Although the transition from frozen flow to equilibrium flow is of vital importance, the chemist has always been pragmatically interested in forcing the situation one way or the other and has had little interest

in systematic study of the compromise situation. Similarly experimental purists and theoretical chemists have generally tried to avoid non-isothermal situations in view of their general analytical intractability. It is in fact only with the advent of streaming thermal plasma devices (and of reentry) that velocities and residence times have achieved such extreme values that one might expect elementary reaction steps to be spatially resolved and temperature changes to be so abrupt that atomic, ionic, and free radical reactions may not proceed along their anticipated course (c.f. the inexplicable inactivity of N atoms in HCN synthesis).

The purpose of the present work is to attempt to formulate a framework for examining these questions and to try the formulation out on a nitrogen plasma configuration. In the next part we formulate an expression for a critical quenching rate vs temperature. In the following section we examine the cooling sequences of a few plasma jet devices under various conditions and establish that "frozen flow" is probably the rule for both ionic and atomic recombination. Finally, we speculate a little on where one might expect this to lead, introducing the concept of characteristic reaction times so as to facilitate choosing between alternatives in the frozen flow regime.

### Threshold Frozen Flow

The problem starts with a fully equilibrated high temperature flow system. The concentration of some species, thought to be chemically relevant, emerges from, say, a free energy minimization program<sup>9</sup> or, in some cases, a simple equilibrium calculation.<sup>3</sup> In either case, we represent the concentration of the interesting species (in moles cm<sup>-3</sup>) by  $(\Gamma)$ :

$$(\Gamma) = f(N_A, N_B, \dots; P, T), \quad (1)$$

where P and T have their usual significance and  $N_A, N_B, \dots$  represent the component molar composition of the mixture (as opposed to the species composition). If we now cause the temperature of this mixture to decrease we may formally write for the time rate change of  $(\Gamma)$ :

$$d(\Gamma)/dt = \partial(\Gamma)/\partial T \partial T/\partial t = \partial f/\partial T \cdot \partial T/\partial t, \quad (2)$$

where t represents time. The equilibrium value at temperature T of the concentration of the species of interest,  $(\Gamma)$ , is the result of a balance between a set of rapid forward and reverse reactions:

$$d(\Gamma)/dt \Big|_{\text{equil}} = \sum_i \left\{ -k_f i (\Gamma)(A_i)(B_i) + k_r i (A_i)(E_i)(Z_i) \right\}. \quad (3)$$

At equilibrium at constant temperature both sides of Equation 3 are equal to zero by definition of the equilibrium process. As long as the temperature change is sufficiently slow that

$$d(\Gamma)/dt \Big|_{\text{equil}} \ll (\Gamma) \sum_i \left( -k_f i (A_i)(B_i) \right) \approx \sum_i k_r i (A_i)(E_i)(Z_i), \quad (4)$$

where the left-hand side of Equation 4 is determined from Equation 2, we say that we have equilibrium flow. If on the other hand, the absolute value of the left-hand side, calculated again from Equation 2, is much larger than that of either of the right-hand terms in Equation 4, then kinetic considerations preclude maintaining any semblance of an equilibrium composition; and we say we have frozen flow. In a classic work, Bray<sup>10</sup> performed suitable calculations for air expanded through a hypersonic nozzle and showed that this cross over from fully equilibrated to fully frozen flow is very abrupt. The results of his detailed calculation indicate in fact that the transition may be considered discontinuous, and he suggested modeling it in this way. He went

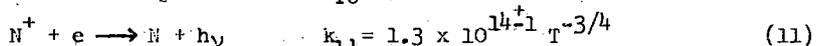
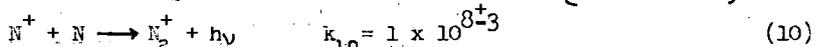
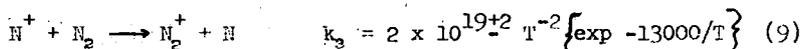
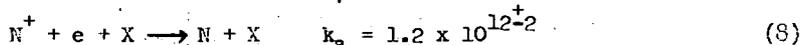
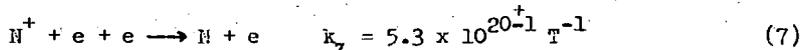
on to argue (though indirectly) that any criterion guaranteed to lie well within this transition region could therefore be used to establish the freezing condition. In his case the condition would be a particular expansion ratio, say; in the present somewhat more general argument the condition will be the result of any or several of many different temperature changing mechanisms, adiabatic expansion, reaction heat, thermal conduction, addition of a cold gas or liquid spray diluent, etc. The criterion suggested by Bray is:

$$\frac{d(T)}{dt} \Big|_{\text{equil}} \approx (\tau) \sum_i \left\{ -k_f (A_i) (E_i) \right\} \approx \sum_i \left\{ k_r (A_i) (E_i) (Z_i) \right\} = \text{URR}(T), \quad (5)$$

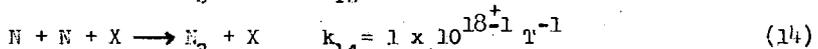
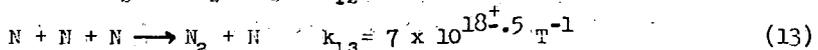
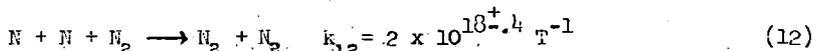
where  $\text{URR}(T)$  represents the total unidirectional reaction rate. Combining Equations 2 and 5 we obtain for the cooling rate required for frozen flow:

$$\delta T / \delta t \Big|_{\text{freezing}} \approx \frac{\text{URR}(T)}{\frac{\partial}{\partial T} \{ f(N_A, N_B, \dots; P, T) \}} \quad (6)$$

Numerical Example. To implement Equation 6, we introduce now the nitrogen system. Curves of the equilibrium particle densities for nitrogen at 1 atm are shown in Figure 1. It is immediately clear by inspection that one need consider but one equilibrium at a time, for at no temperature available to chemists are more than two species present in chemically significant amounts; however, for the moment we use Figure 1 itself. Nearly every reaction rate of interest for this system may be found in a compendium by Bortner.<sup>12</sup> We consider first the principle reactions destroying the  $N^+$  species.



Reaction 11, radiative recombination, dominates at temperatures of 10,000°K and above, while reaction 9, charge exchange, dominates at lower temperatures. Perfectly straightforward numerical application of these rate expressions together with equilibrium values of species concentrations and their derivatives obtained from Figure 1, yields a curve demarcating the cooling rate regime in Figure 2 within which we expect equilibrated ion flow (right-hand shaded region). The calculation was stopped at 12,500°K on the one hand because this corresponds to a good jet center temperature, while it was stopped at 9500°K on the left because below this temperature the number of ions is uninteresting. Similarly the left-hand shaded region shows the cooling rate regime in which we expect equilibration between atoms and molecules. This regime is calculated from the following (again from Bortner<sup>12</sup>):



Above 8000°K, molecular nitrogen has disappeared completely, while below 4000°K there is no atom population of consequence.

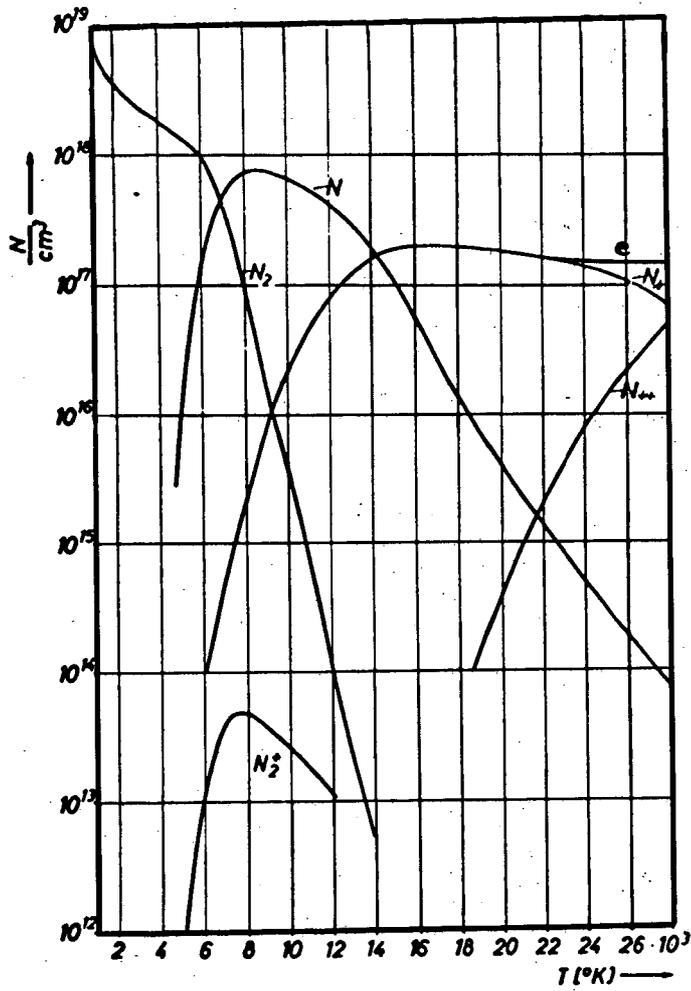


Figure 1: Particle densities of nitrogen at 1 atm total pressure as a function of temperature.

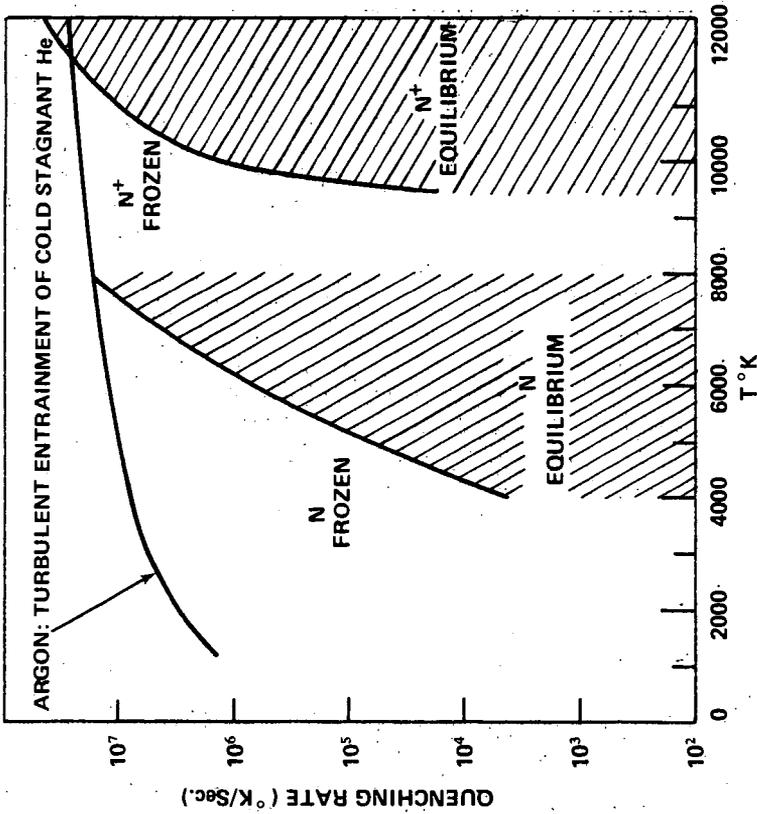


Figure 2: Shaded regions showing for nitrogen at 1 atm cooling rate regimes in which we might expect equilibrated atom-molecule flow (left-hand region); and ion-atom flow (right-hand region). The line shows cooling rates typical of turbulent entrainment by a laboratory scale plasma jet.

Characteristic Reaction Time. It is instructive at this point to examine characteristic times for these reaction rates so as to gain more appreciation for the speed at which significant chemical events occur from a more conventional viewpoint. Considering now just the rate expressions, at any temperature the reciprocal of  $1/N \, dN/dt = d \ln(N)/dt$  will give the time required (by extrapolation of a tangent to the curve) for the concentration of the species of interest to decrease to  $1/e$  of its value. At  $12,500^\circ\text{K}$  and  $10,000^\circ\text{K}$  the characteristic times are 64 and 320  $\mu\text{sec}$ , respectively. Similarly defined atom/molecule relaxation times at  $8000^\circ\text{K}$  and  $5000^\circ\text{K}$  are 413  $\mu\text{sec}$  and 13.4 msec, respectively. To place these numbers in perspective, it has previously been estimated<sup>4</sup> that under typical laboratory conditions for a tube confined flow at  $\frac{1}{2}$  atm, a peripherally added reagent has a characteristic mixing time of about 60  $\mu\text{sec}$  which requires about 1 cm of jet travel.

### Characteristic Quenching Rates

As of the present time, the actual quenching rates achieved in various high temperature flow configurations are not at all well known; however, it is necessary to make some estimate of these rates for comparison with the critical freezing rate of the preceding section. We will, therefore, do the "best we can" for two very important situations, turbulent entrainment of a cold stagnant gas on the one hand and simple cold-walled tube confined flow on the other. There are, of course, other familiar quenching situations: cold liquid quenching, cold doorknob impingement, peripherally pumped coolant added to a tube confined jet, and many others which have not yet yielded to analysis, but which almost certainly lie between the two extreme methods analyzed here.

Thanks to the experimental work of Grey and his co-workers<sup>13,14,15</sup> we have experimental results for the very important situation where a  $3/4$ " diam argon jet (350scfh) is allowed to turbulently entrain a surrounding essentially stagnant cold helium sheath. This should provide a lower bound to the quenching rate for practical purposes; certainly nitrogen entraining methane would have at least a comparable cooling rate. A curve derived from their data is shown in Figure 2 and clearly demonstrates the characteristic high cooling rate that is nearly independent of temperature. Frozen flow must clearly be expected for this quenching method. The second flow situation that has been experimentally characterized is for cold-wall contained plasma flows. In Figure 3 "tube average" curves are presented for various initial conditions.<sup>16</sup> The curves come from the relation

$$\frac{dT}{dt} = \frac{\frac{\partial h(T)}{\partial z} \frac{\partial z}{\partial t}}{\frac{\partial h(T)}{\partial T}} \quad (15)$$

where  $h(T) = H(T) - H(298)$  and is related to the axial coordinate  $z$  by the relation<sup>16</sup>

$$\frac{h(T)}{h(T_0)} = \left( \frac{s}{z + s} \right)^{2/3} \quad (16)$$

In this expression  $s$  is a characteristic flow development length and is experimentally on the order of 10 diameters (to within a factor of 2). Using the continuity equation for the velocity term we obtain:

$$\frac{dT}{dt} = \frac{-\frac{2}{3} \frac{G}{As} \left( \frac{h(T)}{h(T_0)} \right)^{3/2}}{\rho(T) \frac{\partial \ln[h(T)]}{\partial T}} \quad (17)$$

For the curves shown,  $G/A$  is taken as  $0.07 \text{ moles cm}^{-2} \text{ sec}^{-1}$ ,  $s$  as 5 cm and  $\rho(T)$  and  $h(T)$  are taken from the extensive tables for nitrogen published by Hilsenrath and

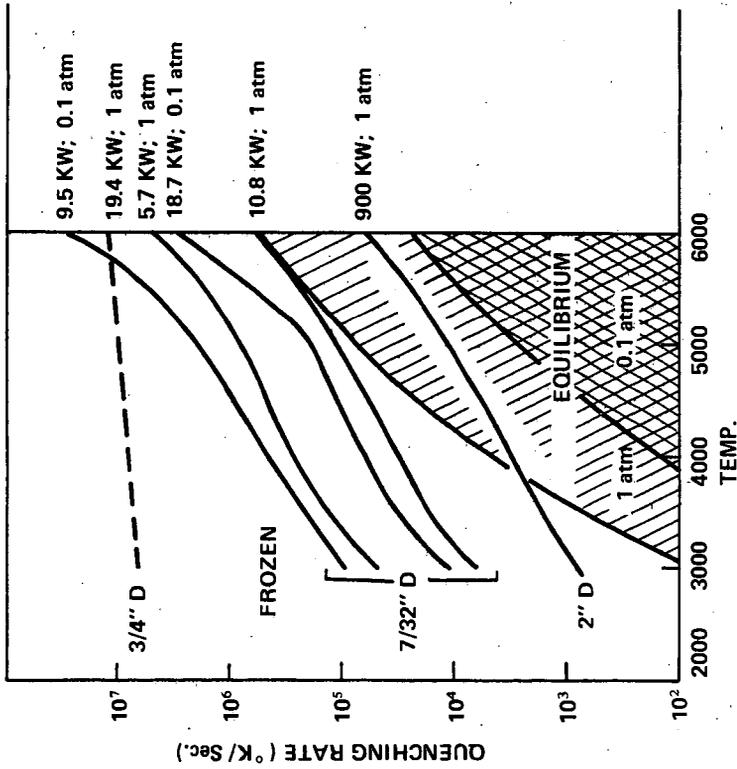


Figure 3: Characteristic quenching rates for various "tube average" flow configurations and entry conditions. The dashed line is again the curve representing turbulent entrainment of stagnant cold helium by an argon jet (Figure 2). Equilibrium flow regimes are shown for nitrogen at 0.1 atm and 1 atm, respectively.

and Klein.<sup>17</sup> The values of  $T_0$  shown, much lower than actual entrant centerline temperatures, were chosen to correspond to easily attainable net entrant power levels for gas flows of .017 g mole sec<sup>-1</sup>. Note that all else equal, a quenching rate a factor of 10 higher would be obtained with a .020" quenching probe.<sup>6</sup>

On the same figure equilibrium flow regimes are shown for the nitrogen atom/molecule reaction at 0.1 atm and 1 atm, respectively. To the extent the "tube average" curves may be believed, we can draw the conclusions that equilibrium flow is possible in a tube. It is favored by

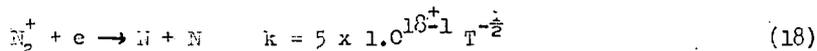
- . larger diameters (quenching rate is inversely proportional)
- . higher pressures
- . higher power levels.

One may equally well infer that frozen flow is also possible in tubes. In particular, a .020" diam tube might very well be used to "freeze" a flow with very nearly the same efficiency as turbulent entrainment.

The "tube average" curves may drastically understate the quenching in a tube, of course. Figure 4 illustrates, in a very exaggerated way, that while the "tube average" model takes a flow from 7000 to sub-thousand temperatures in a few milliseconds, in actual fact nearly one-fourth the total flow is at 12,000°K and goes to sub-thousand temperatures in (probably) comparable times. Calculations are currently in progress to see if any great discrepancy is encountered; however, Figure 3 agrees so well with the writer's experience that it seems unlikely that any surprises will arise in this area.

### Discussion

Frozen flow is generally necessary at some point for the recovery of useful products. It is clear from the trends displayed in the preceding sections that freezing is generally inevitable and in fact generally to be expected at fairly high temperatures in laboratory scale units (but not necessarily at such high temperatures for the larger production units, such as the Westinghouse unit described at this meeting). Once the fact of frozen flow has been established, one may examine relative characteristic reaction times (such as defined above) to test the feasibility of proposed reaction mechanisms (or alternatively by rearrangement of Equation 6 to establish a limiting value on reaction rates when the information is unavailable). Just by way of illustration, consider one interpretation of the HCN experiments cited above that involves an  $N_2^+$  intermediate (a specie not favored by equilibrium). It is now clear that under the reaction conditions the composition of the flow freezes long enough to intermix well with the carbon-containing species while still several per cent ionized. That is, the quenching rate is 20 to 30°K ( $\mu\text{sec}$ )<sup>-1</sup> while the characteristic reaction time (see above) for the radiative recombination of  $N^+$  and  $e^-$  lengthens from 64  $\mu\text{sec}$  at 12,500°K to 320  $\mu\text{sec}$  at 10,000°K. Thus, we arrive with most of our ions intact at a temperature where formation of  $N_2^+$  by charge exchange (Equation 11) is the fastest available  $N^+$  ion removing reaction (characteristic time = 150  $\mu\text{sec}$ ). However,  $N_2^+$  has virtually no chance of participating directly in bulk chemistry because of the extremely fast dissociative neutralization reaction



which clearly has a characteristic time of about  $10^{-10}$  seconds. Thus, if the ions do participate in this reaction, it must be through carbon-containing moieties as intermediates. By the same token, however, the alternative explanation, that of fully equilibrated flow, seems equally untenable in light of the present considerations.

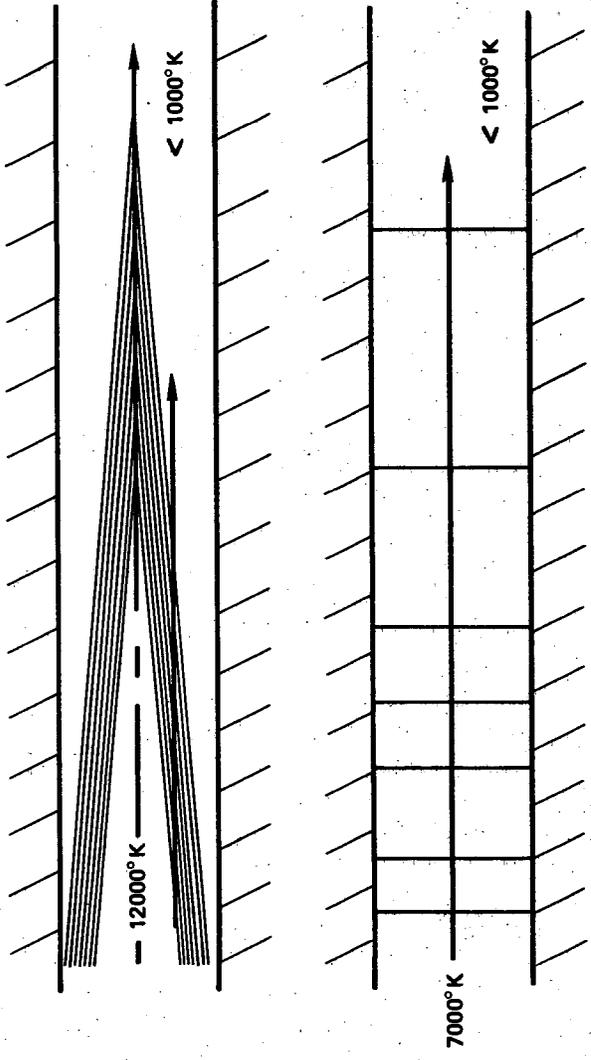


Figure 4: Isotherms for the "tube average" model (bottom) compared to the highly exaggerated decay of the more realistic isotherms of the hot center jet.

### Conclusions

By taking a freezing criterion from aerodynamics and quenching and chemical kinetic rate data from whatever sources available, it is clear that it is possible to bring new light to bear, however poorly in focus, on the subject of high temperature chemistry, particularly that of streaming thermal plasmas. Especially for tube confined plasmas, the trends with changes in total pressure, tube diameter and input power density are seen to be straight forward. Turbulent entrainment of a stagnant cold gas is seen to be fast enough to freeze even the simplest reactions in the nitrogen plasma system (excepting the dissociative neutralization of  $N_2^+$ ) while fine probes are seen to be nearly as good. Finally, the concept of "characteristic reaction time" has been invoked to help examine illustratively the plausibility of a particular reaction mechanism in a frozen flow regime.

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