Chemical Reactions During Rapid Quenching of Oxygen-Nitrogen Mixtures from Very High Temperatures

P. R. AMMANN and R. S. TIMMINS
Avco Corporation, Wilmington, Massachusetts

A model has been developed to study chemical reactions which occur in oxygen-nitrogen mixtures during very rapid cooling in small-diameter tubes. The system considers both homogeneous gas phase reactions and surface reactions based upon a simplified mass transfer mechanism. With an energy balance used to determine the rate of quenching, the mole fractions of nitrogen, oxygen, nitric oxide, atomic nitrogen, and atomic oxygen were calculated as a function of temperature. In these studies, air and an equimolal oxygen-nitrogen mixture were cooled from temperatures which ranged between 3,000° and 7,000°K. The calculations showed that when the gases were cooled at rates exceeding ten million degrees per second, the species did not follow a chemical equilibrium path during the quenching process. In cooling from 4,000° to 7,000°K. the computations show that consideration of surface reactions predicts greater nitric oxide yields in the quenched gas than for homogeneous reactions alone. In fact, the heterogeneous reactions must contribute to the overall chemistry of quenching air. The composition of the quenched gas is strongly dependent upon the temperature-time history of the gas in the probe and upon the composition of the hot gas before it is quenched.

Research and development on the production of chemicals from very high temperature gases or plasmas have created an interest in the effects of rapid cooling on the products obtained. Often in this type of work it is desirable to preserve a chemical composition which is more favorable at high temperatures than at low temperatures. The manufacture of acetylene by the partial oxidation of hydrocarbons or by pyrolysis of hydrocarbons in an electric arc is an example of this type of system. As another illustration, during the past sixty years a number of investigations have been undertaken on the fixation of nitrogen from air in which the maximum equilibrium nitric oxide concentration occurs at approximately 3,500°K.

In the course of an experimental investigation on the preparation of nitric oxide in an arc (*1*), mixtures of oxygen and nitrogen were heated to temperatures that ranged between 3,000° and 10,000°K. To obtain the fixed nitrogen, the hot reactants were quenched very rapidly in small-diameter, water-cooled probes. The final yields of nitric oxide varied from 2 to 7%, as compared with a 5.2% maximum that is attainable under equilibrium conditions at 3,500°K. and at 1 atm. During this work, it was decided to pursue a related analytical study on the kinetics of quenching oxygen-nitrogen mixtures from very high temperature. Fortunately, there was a wealth of published rate data on chemical reactions in air at high temperature. A model for energy transfer in small-diameter tube was devised, and in combination with the rate equations, it was used to calculate the yield of nitric oxide as a function of initial gas temperature, the rate of quenching, total pressure, and the diameter of the tube. The study included both homogeneous gas phase reactions and reactions at the tube surface. The results are related to chemical mechanisms of collecting high-temperature gas samples through probes, as well as consideration of high-temperature, direct nitrogen fixation processes. This paper describes some theoretical aspects of rapid quenching from very high temperatures.

CHEMISTRY OF THE OXYGEN–NITROGEN SYSTEM

Chemical Equilibrium

The major chemical species in this system up to 8,000°K. are molecular nitrogen, oxygen, and nitric oxide, and atomic nitrogen and oxygen. Equilibrium compositions have been computed from data from the JANAF Tables for air and an equimolal mixture of nitrogen and oxygen at 1 atm. and over a temperature range of 300° to 8,000°K. A diagram of the equilibrium composition of air as a function of temperature appears in Figure 1 and provides useful information for the kinetic work. The important aspects of the equilibrium data are: (1) the maximum nitric oxide concentration is obtained at approxi-

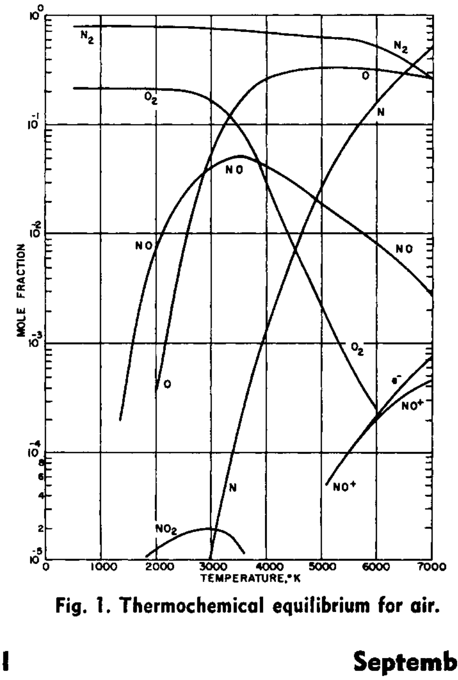

Fig. 1. Thermochemical equilibrium for air.

mately 3,500°K., (2) the dissociation of molecular oxygen into the atomic species is extensive above 3,000°K., and (3) the dissociation of nitrogen becomes important above 6,500°K. For the equimolal nitrogen–oxygen system, the maximum equilibrium concentration is 6.6% nitric oxide as compared with 5.2% for air.

Subatmospheric pressures lead to greater dissociation of nitrogen and oxygen at a given temperature. In addition, the maximum concentrations of nitric oxide also decrease. Thus, at 0.01 atm. the maximum nitric oxide, which is 2.2%, occurs at 3,000°K.

Chemical Reaction Kinetics

Of the many reactions that can occur in an oxygen–nitrogen system in the temperature range of interest, the six most important ones are listed in Table 1. The first two are simply the dissociation-recombination reactions of nitrogen and oxygen. The next two are the so-called *exchange reactions*, which, being bimolecular, occur rapidly. The last two equations give expressions for the formation of nitric oxide directly from molecular and atomic oxygen and nitrogen, respectively.

Reaction rate constants have been determined for the forward and reverse reactions listed in Table 1 by a number of investigators (3 to 5). Wray (3) reviewed much of the research in the field and recommended rate constants which appear in Table 1. In the termolecular reactions, M is any third body, and researchers have determined that the value of the rate constant is sensitive to the nature of the third body. To employ a rate constant according to the nature of the third body would severely complicate any kinetic calculations; consequently, mean values were used.

The fastest reactions given in Table 1 are

$$N + NO \rightleftarrows N_2 + O \quad E = 0 \qquad (6, 5)$$

$$N + O_2 \rightleftarrows NO + O \quad E = -7{,}080 \text{ cal./mole} \qquad (7, 8)$$

and even at cooling rates of 10^9 °K./sec., equilibrium is maintained among the species involved in these equations. The rate constants of the reverse reactions are at least an order of magnitude lower than the forward rates at 6,000° to 8,000°K., but because of the high activation energies for the back reactions, these rate constants decrease rapidly with decreasing temperature. The rate constants for the recombination of nitrogen and oxygen atoms are high in value and essentially constant over the temperature range of interest, but because they are termolecular reactions, the overall rates are low. The dissociations of nitrogen and oxygen are highly activated, and the rates are low except at the very high temperatures, but these reactions are relatively unimportant in the quenching of nitrogen–oxygen mixtures from high temperature.

TABLE 1. RATE CONSTANTS FOR THE OXYGEN-NITROGEN SYSTEM (3 TO 5)

	Reaction	k_f	k_r
1, 2	$O_2 + M = 2O + M$	$1.9 \times 10^{13} T^{1/2} \left\{\frac{118{,}000}{RT}\right\} \exp \left\{\frac{-118{,}000}{RT}\right\} \frac{\text{cc.}}{\text{mole/sec.}}$	$1.58 \times 10^{10} T \left\{\frac{118{,}000}{RT}\right\} \frac{\text{cc.}^2}{\text{mole}^2\text{/sec.}}$
3, 4	$N_2 + M = 2N + M$	$1.7 \times 10^{12} T^{1/2} \left\{\frac{224{,}900}{RT}\right\} \exp \left\{\frac{-224{,}900}{RT}\right\} \frac{\text{cc.}}{\text{mole/sec.}}$	$9.44 \times 10^{11} T^{1/2} \left\{\frac{224{,}900}{RT}\right\} \frac{\text{cc.}^2}{\text{mole}^2\text{/sec.}}$
5, 6	$O + N_2 = NO + N$	$7 \times 10^{13} \exp \left\{\frac{-75{,}500}{RT}\right\} \frac{\text{cc.}}{\text{mole/sec.}}$	$1.55 \times 10^{13} \frac{\text{cc.}}{\text{mole/sec.}}$
7, 8	$N + O_2 = NO + O$	$13.3 \times 10^9 T \exp \left\{\frac{-7{,}080}{RT}\right\} \frac{\text{cc.}}{\text{mole/sec.}}$	$3.2 \times 10^9 T \exp \left\{\frac{-39{,}100}{RT}\right\} \frac{\text{cc.}}{\text{mole/sec.}}$
9, 10	$N_2 + O_2 = 2NO$	$9.1 \times 10^{24} T^{-5/2} \exp \left\{\frac{-128{,}500}{RT}\right\} \frac{\text{cc.}}{\text{mole/sec.}}$	$4.79 \times 10^{23} T^{-5/2} \exp \left\{\frac{-85{,}520}{RT}\right\} \frac{\text{cc.}}{\text{mole/sec.}}$
11, 12	$NO + M = N + O + M$	$7 \times 10^{10} T^{1/2} \left\{\frac{150{,}000}{RT}\right\} \exp \left\{\frac{-150{,}000}{RT}\right\} \frac{\text{cc.}}{\text{mole/sec.}}$	$1.75 \times 10^{10} T^{1/2} \left\{\frac{150{,}000}{RT}\right\} \frac{\text{cc.}^2}{\text{mole}^2\text{/sec.}}$

THE MODEL FOR THE QUENCHING KINETICS

At the high temperatures under consideration, the flow in small-diameter tubes is laminar. For the analysis however a one-dimensional model was employed, and plug type of flow was assumed. A gas containing several reactive species enters a small-diameter, cold-wall probe at very high temperature. It is assumed that the gas is in chemical equilibrium at the initial temperature, and as the gas is cooled in passing through the tube, reactions occur both in the gas phase and at the surface of the tube.

Material Balance

The material balance for any component i is given by Equation (1), in which the rate of change in the number of moles of any species is set equal to the rate of formation or loss by homogeneous reactions and by heterogeneous reactions taking place at the tube wall:

$$-G\frac{d\left(\frac{y_i}{M}\right)}{dx}=\left\{W_{i-G}+\frac{4}{D}W_{i-S}\right\}\frac{\text{moles } i}{\text{cc./sec.}} \qquad (1)$$

Expressions for the homogeneous and heterogeneous reaction rates are developed later.

Since distance and time are related by the velocity

$$\frac{dx}{d\theta}=V=\frac{G}{\rho M} \qquad (2)$$

Equation (1) may be expanded and rewritten as

$$-\frac{dy_i}{d\theta}+y_i\left\{\sum_{i=1}^{S}\left(\frac{M_i}{M}\right)\frac{dy_i}{d\theta}\right\}=\frac{1}{\rho}\left\{W_{i-G}+\frac{4}{D}W_{i-S}\right\} \qquad (3)$$

If the equations for all species i are summed together, the second term on the left-hand side of Equation (3) is determined:

$$\sum_{i=1}^{S}\left(\frac{M_i}{M}\right)\frac{dy_i}{d\theta}=\frac{1}{\rho}\sum_{i=1}^{S}\left(W_{i-G}+\frac{4}{D}W_{i-S}\right) \qquad (4)$$

The general equation then becomes

$$-\frac{dy_i}{d\theta}=\frac{1}{\rho}\left\{\left[W_{i-G}-y_i\sum_{i=1}^{S}W_{i-G}\right]+\frac{4}{D}\left[W_{i-S}-y_i\sum_{i=1}^{S}W_{i-S}\right]\right\} \qquad (5)$$

From Equation (5) the rate of change of the molal composition of the i^{th} component is a function of the rate expressions W_{i-G} and W_{i-S} and the molal gas density. Both the density and rates are strong functions of temperature, and the mole fractions y_i are dependent upon time and temperature. Consequently

$$\frac{dy_i}{dT}=\frac{dy_i}{d\theta}\Bigg/\frac{dT}{d\theta} \qquad (6)$$

and by substitution of Equation (6) into Equation (5), a new expression results:

$$-\frac{dy_i}{dT}=\frac{1}{\rho\left(\frac{dT}{d\theta}\right)}\left\{\left[W_{i-G}-y_i\sum_{i=1}^{S}W_{i-G}\right]+\frac{4}{D}\left[W_{i-S}-y_i\sum_{i=1}^{S}W_{i-S}\right]\right\} \qquad (7)$$

If $dT/d\theta$ is defined as a function of temperature alone, then in Equation (7) temperature is the only independent variable, and the problem is amenable to solution. The derivative of temperature with time is determined by an energy balance, as described in the next section.

In Equation (7), certain influences on the change in any y_i with temperature are delineated. It is shown in the next section that the heterogeneous reactions, that is, $\left(\frac{dT}{d\theta}\right)^{-1}\left[W_{i-S}-y_i\sum_{i=1}^{S}W_{i-S}\right]$, are functions of y_N, y_O alone, and thus are independent of quench rate, while the homogeneous reactions are inversely proportional to the quench rate. Equation (7) shows, then, that at very low quench rates the homogeneous reactions will dominate the kinetics, whereas at very high $dT/d\theta$ the surface reactions will be most important.

Energy Balance

The energy balance is described by Equation (8). The energy lost from the gas is equal to the energy convected to the tube walls and to the energy associated with the chemical reactions that occur at the tube surface:

$$-\frac{GD}{4}\frac{dH}{dx}=\left[h\,(T-T_w)+\sum_{i=1}^{S}\lambda_i W_{i-S}\right] \qquad (8)$$

Equation (8) is modified by replacing the enthalpy with a product of a fictitious specific heat and temperature and also by changing from a distance to time variable:

$$-\frac{d(CT)}{d\theta}=\frac{4h(T-T_w)}{\rho DM}\left\{1+\frac{\sum_{i=1}^{S}\lambda_i W_{i-S}}{h(T-T_w)}\right\} \qquad (9)$$

In Equation (9), the specific heat C includes both a sensible heat term and a term based on the energy associated with the homogeneous chemical reactions. Thus, C is a function of the change in both composition and temperature, but in the calculations it turned out to be fairly constant [varying from 8 to 20 cal./(g.-mole) (°K.)].

The solution of Equation (9) provides a time-temperature history which is employed for the solution of the material balance. In this equation, h, ρ, M, and W_{i-S} are functions of temperature.

For the solution of Equation (9) the heat transfer coefficient was obtained from the work of Kays (6), in which heat transfer from laminar flow in a circular tube, including the entrance region, was analyzed. In the correlation, the heat transfer coefficient which is based on a mean temperature over the cross section of the tube is directly proportional to the thermal conductivity and $N_{Re}\,N_{Pr}/\frac{x}{D}$ and inversely proportional to the diameter. The thermal conductivity, Reynolds number, and Prandtl number are functions of temperature, and so the heat transfer coefficient as applied to the energy balance, Equation (9), is only a function of temperature and distance x (time θ).

Homogeneous Chemical Reactions

Expressions for the rates of change of each of the five species considered have been derived directly from the six reversible reactions presented in Table 1. The volumetric rate of loss of molecular nitrogen is, for example

$$W_{N_2-G}=\rho^2\{k_3 y_{N_2}+k_5 y_{N_2} y_O+k_9 y_{N_2} y_{O_2} - k_4 y_N{}^2\rho-k_6 y_{NO} y_O-k_{10} y_{NO}{}^2\} \qquad (10)$$

According to this expression, the absolute rate of reaction is approximately proportional to the square of the pressure, with the exception of the termolecular nitrogen atom recombination, which is a function of the cube of the pressure.

Heterogeneous Chemical Reactions

Although the high-temperature chemical reactions have been studied extensively and are well characterized, reactions occurring among nitrogen, oxygen, nitric oxide, and atomic nitrogen and oxygen at cold surfaces are more difficult to describe. For this work only reactions involving the recombination of atomic species were considered:

$$N + N \xrightarrow{\text{Wall}} N_2 \qquad (11a)$$

$$O + O \xrightarrow{\text{Wall}} O_2 \qquad (11b)$$

$$N + O \xrightarrow{\text{Wall}} NO \qquad (11c)$$

It was further assumed that the rates were extremely rapid with respect to mass transfer rates. The rates of formation of nitrogen, oxygen, and nitric oxide are equal to the rate of mass transfer of reactants to the wall times the probability of recombination of the atomic reactants. Thus

$$W_{N_2-S} = K_G P\,(y_N - y_{N,\,\text{wall}}) \cdot f_i' \quad \text{g.-moles/(sq.cm.)(sec.)} \qquad (12)$$

An example of the probability function is given by Equation (13):

$$f'_{N_2} = \frac{1}{2}\,\frac{y_N}{y_N + y_O} \qquad (13)$$

Heat and mass transfer are approximately related by

$$K_G P M \cong \frac{h}{C} \qquad (14)$$

and therefore Equation (12) may be rewritten as

$$W_{i-S} = \frac{h}{CM} \cdot y_i f_i' \qquad (15)$$

For use in Equation (9) to solve the energy relationship, Equation (15) is rewritten as

$$\frac{W_{i-S}}{h(T-T_w)} = \frac{1}{MC}\,\frac{y_i \cdot f_i'}{(T-T_w)} = \frac{1}{MC}\,\frac{f_i}{(T-T_w)} \qquad (16)$$

In the solution of the material balance, Equation (7), the terms $W_{i-S}/\dfrac{dT}{d\theta}$ are required. By the substitution of Equation (9), with only the convective heat transfer used, into Equation (16), this term is evaluated as

$$\frac{4}{\rho D}\,\frac{W_{i-S}}{\left(\dfrac{dT}{d\theta}\right)} = \frac{f_i}{(T-T_w)} \qquad (17)$$

Thus, in accordance with the model, the effects of the heterogeneous chemical reactions on dy_i/dT are independent of the quench rate.

Method of Calculation

Calculations were performed for the two general cases, as stated previously: homogeneous gas phase reactions only, and homogeneous and surface catalyzed reactions. The general procedure was to determine a time-temperature history for the quenched gas, by the appropriate expression in Table 2, and then to use this information in the solution of the material balance equations. An advantage of this sequence of calculations is that any time-temperature history, such as those found in the literature, could be used.

The energy balance was integrated numerically by using property data and by computing the Nusselt number as a function of time (distance along the probe) and temperature.

From the calculated time-temperature relationship, the function $dT/d\theta$ was determined as a function of temperature. This tabulated information was employed along with the suitable rate expressions W_{i-G} to solve the material balance equations. Since the variation in composition with temperature, as calculated, would affect the properties in the energy Equation (9), the properties were adjusted. If the newer properties differed significantly from those used in the first approximation, the sequence of calculations was repeated.

COMPUTED RESULTS AND DISCUSSION

Results of computations are grouped into two general categories: homogeneous chemical reactions considered only, and homogeneous plus heterogeneous reactions. Effects of several variables, such as probe diameter, pressure, rate of cooling, and oxygen–nitrogen stoichiometry, are discussed in subsequent sections.

A set of reference conditions, upon which the calculations were based, was chosen: probe diameter: 0.050 in., pressure: 1.0 atm., probe wall temperature: 27°C., mass flow rate: 0.881 lb._m/(sq.ft.)(sec.), initial gas temperature: 3,000° to 7,000°K., and chemical composition of the gas: 21% oxygen, 79% nitrogen.

Quenching with Homogeneous Chemical Reactions

Temperature-time relationships that were determined by the energy balance are presented in Figure 2 for several cases in which the initial temperature ranged between 3,000° and 7,000°K. The calculated initial quench rates were on the order of 10^8 to 10^9°K./sec. and decaying approximately three orders of magnitude by the end of the cooling process. The plot of quench rate in Figure 3 gives an idea of the cooling rate as a function of gas temperature. At the entrance of the probe, the heat transfer coefficient is approximately 0.2 B.t.u./(sq.ft.)(sec.)(°F.), and by 20 to 30 diam. downstream the value decreases to less than 0.01 B.t.u./(sq.ft.)(sec.)(°F.).

The mole fractions of the several species have been calculated as a function of temperature (for the given quench curves), and some of the results are presented in Figures 4 and 5. The calculations show that contrary to chemical equilibrium (Figure 1), in quenching very rapidly from 7,000°K. the oxygen and nitric oxide mole fractions de-

TABLE 2. SUMMARY OF THE GENERAL MATERIAL AND ENERGY BALANCE EQUATIONS

	Homogeneous chemical reactions	Homogeneous and surface chemical reactions
$\dfrac{d(CT)}{d\theta}$	$\dfrac{4h}{\rho DM}(T-T_w)$	$\dfrac{4h\left[1+\dfrac{1}{MC}\sum_{i=1}^{S}\lambda_i f_i(y_O,y_N)\right](T-T_w)}{\rho MD}$
$-\dfrac{dy_i}{dT}$	$\dfrac{1}{\rho\left(\dfrac{dT}{d\theta}\right)}\left\{-y_i\sum_{i=1}^{S}(W_{i-G}) + W_{i-G}\right\}$	$\dfrac{1}{\rho\left(\dfrac{dT}{d\theta}\right)}\left\{\left[W_{i-G} - y_i\sum_{i=1}^{S}W_{i-G}\right] + \dfrac{4}{D}\left[W_{i-S} - y_i\sum_{i=1}^{S}W_{i-S}\right]\right\}$

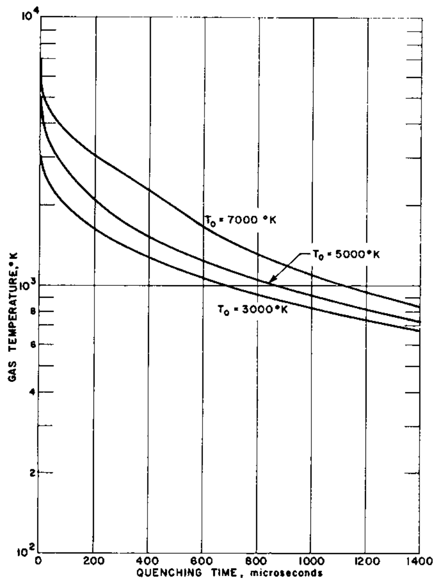

Fig. 2. Computed temperature-time histories for quenching air from several temperatures.

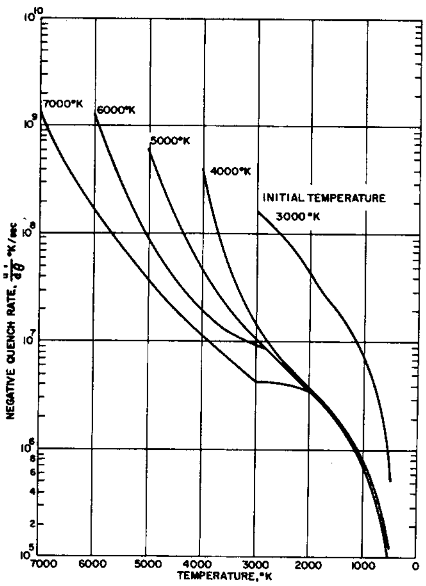

Fig. 3. Computed quench rates as a function of temperature for several starting temperatures.

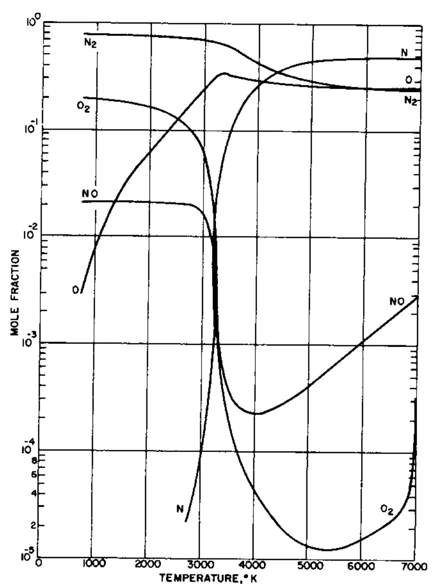

Fig. 4. Rapid quenching of air from 7,000°K. Homogeneous reactions.

crease initially. This behavior is determined by the very rapid exchange reactions, which are (6, 5) and (7, 8).

The forward and reverse rates for Equation (6, 5) are very high, and consequently the species in this reaction are in equilibrium throughout the quenching process. Since the mole fractions of atomic nitrogen, nitrogen and atomic oxygen are approximately constant down to 5,000°K. (because of the extremely rapid rate of cooling, the recombinations of the atomic species are frozen), the mole fraction of nitric oxide is determined by the equilibrium constant for the Equation (6, 5). As the temperature drops from 7,000°K., equilibrium for the (6, 5) reaction shifts to the right resulting in a decrease in nitric oxide. The forward rate of the second equation (7, 8) is somewhat slower than either rate of the first reaction, but it is an order of magnitude higher than the reverse rate. Consequently, oxygen is depleted by reaction with nitrogen atoms in accordance with Equation (7, 8), and then nitric oxide is destroyed by reaction (6, 5). Below 5,500°K., as the cooling rate falls off, atom recombinations begin to be important as oxygen and nitrogen mole fractions increase. As the temperature goes below 4,000°K., the mole fraction of atomic nitrogen decreases rapidly, and a shift in the equilibrium of the reaction (6, 5) causes a marked increase in nitric oxide; at 3,000°K., where atomic nitrogen is essentially depleted, the nitric oxide fraction levels off very nearly to its final value. Recombination of the oxygen atoms is largely accomplished in the final cooling from 3,000°K.

The interesting aspect of these data is the change in nitric oxide content of the gas as it is quenched, and that during the early part of the cooling nitric oxide is in fact destroyed. The calculated final concentration is about 2%, which is greater than the equilibrium value at 7,000°K. but still less than the maximum attainable equilibrium mole fraction.

The characteristics for quenching from 5,000°K. are similar to those from 7,000°K. except that the changes are less pronounced. The initial nitric oxide mole fraction, which is about 0.018 and six times greater than that at 7,000°K., decreases relatively little during the onset of quenching. At 4,000°K. the nitric oxide fraction begins to increase, and by 3,000°K. the final value of 2.2% is nearly achieved. The nitrogen atom concentration is only slightly greater than the chemical equilibrium value down to about 3,000°K., and the oxygen atom fraction behaves similar to the previous case.

During quenching from temperatures between 4,000°K. (Figure 5) and 3,000°K. the chemical reactions take on a new complexion. The initial mole percentage of nitric

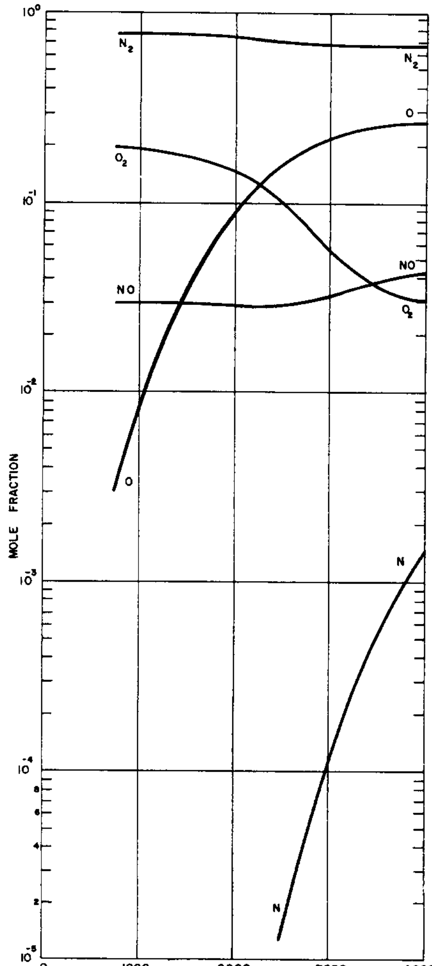

Fig. 5. Rapid quenching of air from 4,000°K. Homogeneous reactions.

oxide ranges from 4 to 5.2%, and the nitrogen atom percentage is less than 0.15. Thus, the exchange reactions involving nitrogen atoms become unimportant, and the two significant net reactions are: the recombination of atomic into molecular oxygen, and some slight decomposition of nitric oxide. The final nitric oxide composition, for an initial temperature of 4,000°K., is 3%, which is less than the starting value but more than the final values after quenching from higher temperatures.

In quenching from about 3,500°K. and below, the final nitric oxide concentration is only slightly below the initial equilibrium value. This is because the decomposition of nitric oxide is suppressed at the computed high quench rates.

Quenching with Heterogeneous and Homogeneous Chemical Reactions

In considering reactions at the tube surface, both slightly higher quench rates and faster recombination rates are obtained. The calculated quench rates are about one and a half to two times greater than for the homogeneous case. With the exception of considering the surface reactions, the conditions are otherwise the same as those described in the previous discussion.

In quenching rapidly from 7,000°K. (Figure 6), the calculations show that the nitrogen atoms recombine more rapidly than in the homogeneous case. The oxygen mole fraction increases slightly, as quenching commences, before decreasing to a minimum value at 4,800°K. The nitric oxide mole fraction increases more markedly than the oxygen initially, but it too drops to a minimum at approximately 4,200°K. These increases of these species are explained by the initial wall reactions (11*c*) and (11*b*). When the cooling process begins, the quench rate is about 10^9 °K./sec. and nitric oxide is produced about twice as fast as it is destroyed by the exchange reactions in the gas phase. However, by 6,700°K. the cooling rate has decreased by a factor of a little more than 2, and the homogeneous reactions start to dominate the kinetics. Other than these particular trends, the paths of chemical change during quenching from 7,000°K. are generally the same both with and without the surface reactions. Including the surface reactions, however, the final nitric oxide concentration is about 2.6% as compared with 2.1% for the homogeneous reactions alone.

For quenching from 5,000°K. the profiles for the change in species concentrations are distinct from those for quenching from 7,000°K., when one considers homogeneous and heterogeneous reactions. The nitrogen and oxygen atom fractions decrease rapidly during the course of cooling. The nitric oxide fraction increases between 5,000° and 3,600°K. and then falls off slightly to a final value of about 3%. The oxygen mole fraction increases to its final value throughout the cooling process.

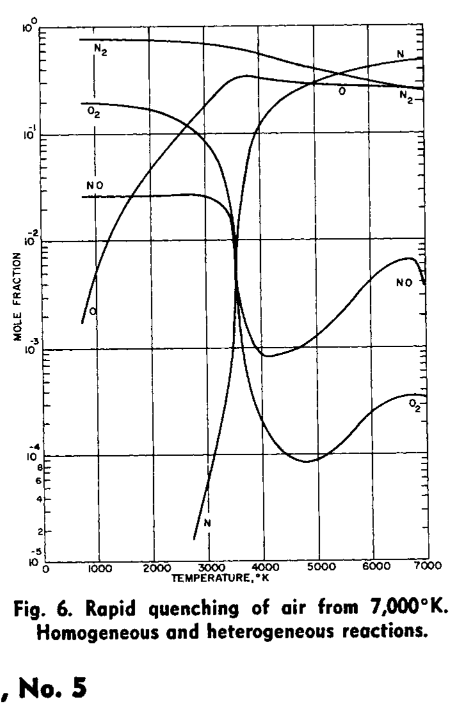

Fig. 6. Rapid quenching of air from 7,000°K. Homogeneous and heterogeneous reactions.

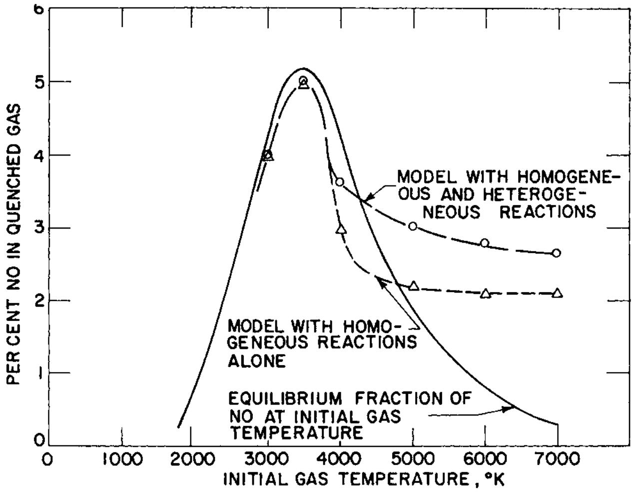

Fig. 7. Comparison of computed nitric oxide in quenched gas according to the quench model (air).

When the initial gas temperatures are in the neighborhood of 3,500°K., the profiles for the two cases, namely homogeneous reaction and homogeneous and heterogeneous reactions, become identical because the nitrogen atom concentration is negligible and the oxygen atoms, whose fraction is modestly small, can only combine with themselves in accordance with the model.

Comparison of Quenching With and Without Heterogeneous Reactions

In the two previous sections, the computed data showed that the composition of a quenched gas was dependent upon the initial gas temperature and its composition. The concentration of nitric oxide in the quenched gas is higher when heterogeneous reactions are included in the model. A comparison of the final mole fraction of nitric oxide is presented as a function of the initial gas temperature in Figure 7. Briefly, the calculations show that a maximum yield of nitric oxide is obtained when the air is quenched rapidly from approximately 3,500°K. and is independent of the proposed model of reactions at the tube wall. For air quenched from temperatures greater than 4,200°K., the model which includes recombination reactions at the tube surface predicts a higher mole fraction of nitric oxide in the cooled gas.

Effect of Oxygen–Nitrogen Stoichiometry

The quenching of an equimolal mixture of nitrogen and oxygen from very high temperatures was also examined. Composition profiles of the five species are very similar to those for air with the two quenching models used. The only differences are that the nitrogen atom concentration approaches the equilibrium value at a higher temperature and that the nitric oxide mole fraction in the quenched gas is higher, as would be expected.

A comparison of the nitric oxide in the quenched gas predicted by both models is shown in Figure 8. At initial temperatures greater than 4,000°K., the calculated percent nitric oxide in the quenched gas is significantly larger than the chemical equilibrium value at the starting temperature. However, consideration of surface reactions does not increase the nitric oxide yield as it did for air. The expla-

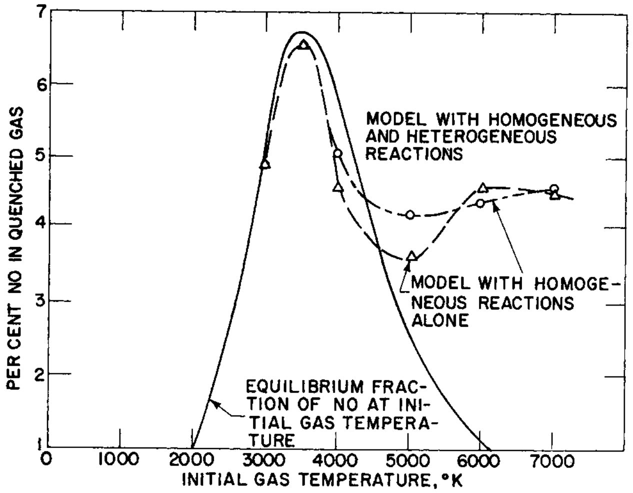

Fig. 8. Comparison of computed nitric oxide in quenched gas according to the quench model (50-50 oxygen-nitrogen mixture).

nation for these results lies in the relative rates for the formation of nitric oxide and nitrogen by surface reactions and the decomposition of nitric oxide by the gas phase shuttle reactions.

Effect of Quench Rate

In cooling high temperature reactive oxygen–nitrogen gases, there are two extremes to the effect of quench rate of chemical reactions. First, at very slow cooling rates, chemical equilibrium is obtained throughout the cooling process. In general, rates of less than 10^6 to 10^7 °K./sec. are required to follow equilibrium from above 3,500°K. and less than 10^5 to 10^6 °K./sec. below 3,500°K. Under these conditions the homogeneous reactions control the reaction chemistry.

At the very opposite extreme are extremely high quench rates, which may be considered as greater than 10^{10} °K./sec. In this case, the homogeneous chemical reactions can be frozen, and the heterogeneous reactions dominate the overall chemical reactions. These two regimes are seen from Equation (18) which is obtained by substitution of Equation (17) into Equation (7):

$$-\frac{dy_i}{dT} = \underbrace{\frac{1}{\rho\left(\dfrac{dT}{d\theta}\right)}\left[W_{i-G} - y_i \sum_{i=1}^{s} W_{i-G}\right]}_{\text{Homogeneous Reactions}}$$

$$+ \underbrace{\frac{1}{(T - T_w)}\left[f_i(y_N, y_O) - y_i \sum_{i=1}^{S} f_i(y_N, y_O)\right]}_{\text{Heterogeneous Reactions}} \qquad (18)$$

The calculations on chemical reactions during quenching were performed for three temperature-time histories of the gas which were different from those presented in Figure 2. The purpose of these calculations was to examine the effect of the quench rate on the final composition of the cooled gas. In Figure 9 the rate of quench is presented as a function of temperature. In contrast to the quenching curves determined by the energy balance, these curves are arbitrary and each curve applies to all initial gas temperatures. Also, the rate of cooling changes much more gradually than the data in Figure 3.

The computed percent of nitric oxide in quench gas is presented in Figure 10 as a function of starting temperature for the three quench rates. For the condition of the largest rate of cooling (curve I) the yield of nitric oxide is below 1% for initial temperatures above 5,000°K. based upon gas phase reactions alone. When the surface reactions are included in the model, substantially higher concentrations of nitric oxide are calculated. The product nitric oxide fractions for starting gas temperatures above 4,000°K. are significantly different from those presented in Figure 7. The generally lower nitric oxide yields in Figure 10 are attributed to the nature of the rate of cooling as a function of gas temperature. Therefore, it may be concluded that prediction of the ultimate nitric oxide in the quenched gas requires a precise description of the time-temperature history of the gas during cooling.

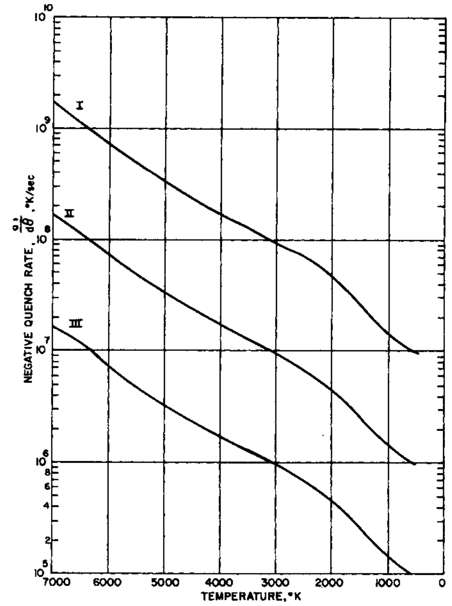

Fig. 9. Computed quench rates as a function of temperature for three quench histories.

If the rate of quenching is lowered by a factor of 10 (curve II in Figure 9), then higher concentrations are obtained in the quenched gas, still with higher nitric oxide yields with the surface reactions than without. As the rate of quenching is decreased, the nitric oxide percentage in the cooled gas approaches the maximum equilibrium value of 5.2% at 3,500°K.; that is, the gases cool along an equilibrium path down to 3,500°K. and then quench without much decomposition of the nitric oxide present at that temperature.

As might be expected, the quenched gas contains approximately the chemical equilibrium value when the gas

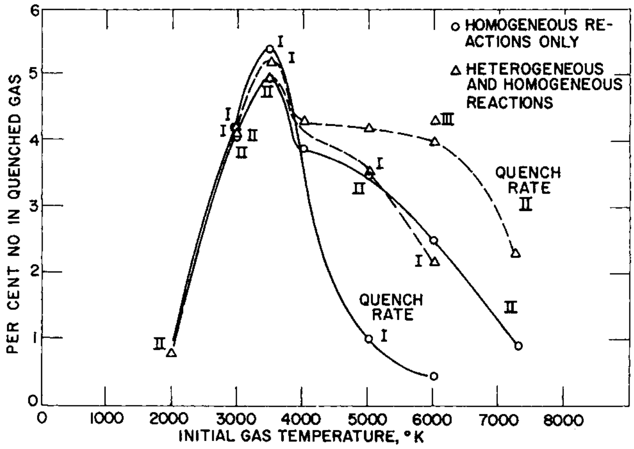

Fig. 10. Computed percent nitric oxide in quenched gas for three quench rates.

is cooled from 3,500°K. or below, and the quench rate is on the order of one million degrees per second or greater.

The most important aspect of these data is the demonstrated effect of the proposed surface reactions on the nitric oxide yield when air is cooled rapidly from above 4,000°K.

Effect of Pressure

Pressure influences the quenching reactions in two ways: the rate of cooling of the gas, and the absolute rates of the several chemical reactions. How pressure affects the quench rate may be obtained from Equation (9). When one assumes that the initial gas velocity is constant for all pressures (that is, the mass flow rate is proportional to the pressure), then the convective heat transfer coefficient is fixed and the rate of cooling is inversely proportional to pressure. As the pressure is decreased, therefore, the quench rate is increased.

Recombination of oxygen and nitrogen (reactions 2 and 4 in Table 1) occurs by three-body collisions, and thus these rates are proportional to the third power of the pressure. The shuttle reactions (5, 6, 7, and 8 in Table 1) are bimolecular, and therefore the rates are related to the square of the pressure. Consequently, the termolecular recombinations are slowed down relative to the shuttle reactions, as the pressure is lowered, but all reaction rates are decreased. The bimolecular reactions (9, 10, and 11 in Table 1) involving nitrogen, oxygen, and nitric oxide are similarly affected.

The net effect of decreasing the pressure is to increase the rate of quenching while at the same time decreasing the homogeneous reaction rates. As long as the quench rate is sustained above 10^9 °K./sec., the atomic nitrogen and atomic oxygen recombinations are frozen, and above about 10^{10} °K./sec. the shuttle reactions are frozen. At low pressures, then, surface reactions tend to dominate the reaction kinetics. This is in agreement with experimental work of other investigators in which concentrations of up to 10 to 12% nitric oxide are obtained from dissociated air at very low pressures (7, 8).

Effect of Probe Diameter

The effect of the probe diameter on the yield of nitric oxide in the quenched gas has been considered only qualitatively. The rate of quenching is inversely proportional to the tube diameter and directly related to the heat transfer coefficient. The latter is, through the Nusselt relationship, also inversely proportional to the diameter. At the onset of quenching, that is, very small distances down the probe, the quench rate is, by approximation, inversely proportional to the square of the diameter. Enlargement of the diameter tends to decrease the quench rate, and the effect of changing this rate has been shown in previous sections.

Conclusions

1. The one-dimensional model contributes to an understanding of chemical behavior of gases during very rapid quenching from very high temperature.
2. The chemical reaction mechanisms which occur during very rapid quenching of high-temperature air are quite complicated. The compositions of the quenched gases are determined jointly by a number of factors including (1) the initial temperature and composition, (2) the time-temperature history of the gas, (3) probe diameter, (4) pressure, and (5) reactivity of the probe surface.
3. The product compositions of oxygen–nitrogen gases which are quenched rapidly from very high temperature are not directly related to the equilibrium composition at the initial temperature.
4. In small-diameter probes, the tube surface can contribute significantly to the chemical reactions during quenching.

NOTATION

C = specific heat ($\equiv dH/dT$), cal./(g.)(°K.)
C_i = specific heat of ith species, cal./(g.)(sec.)
D = diameter of quench tube, cm.
E = activation energy, cal./g.-mole
f_i' = probability function for heterogeneous recombination [Equation (13)]
f_i = $y_i f_i'$ [Equation (16)]
G = mass flux, g./(sq.cm.)(sec.)
H = enthalpy $\left[\equiv \sum_{i=1}^{s} \frac{y_i M_i}{M}(C_i T + \Delta H^\circ_{f,i})\right]$ cal./g.
h = convective heat transfer coefficient, cal./(sq.cm.)(°K.)(sec.)
$\Delta H^\circ_{f,i}$ = heat of formation of ith component from elements at 298°K., cal./g.-mole
k = reaction rate constant, g.-mole, cc., sec.
k_f = forward reaction rate constant, g.-mole, cc., sec.
k_r = reverse reaction rate constant, g.-mole, cc., sec.
K = thermal conductivity of gas, cal./(sq.cm.)(sec.)(°K.)
K_G = mass transfer coefficient [Equation (14)]
M = molecular weight $\left(\equiv \sum_{i=1}^{s} y_i M_i\right)$, g./g.-mole
M_i = molecular weight of ith species, g./g.-mole
N_{Nu} = Nusselt number, hD/K, dimensionless
N_{Re} = Reynolds number, DG/μ, dimensionless
P = pressure, atm.
R = ideal gas constant, cal./(g.-mole)(°K.)
T = gas temperature, °K.
T_w = quench tube surface temperature, °K.
V = gas velocity, cm./sec.
W_{i-G} = homogeneous rate of loss of ith species, g.-moles/(cc.)(sec.)
W_{i-S} = heterogeneous rate of loss of ith species, g.-moles/(cc.)(sec.)
x = length, cm.
y_i = mole fraction of ith species

Greek Letters

λ = energy of surface reactions, cal./g.-mole
ρ = molar gas density (P/RT), g.-mole/cc.
θ = time, sec.

Subscripts

i = ith species
s = number of terms in summation

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