Nonequilibrium Nozzle Expansions of Carbon Dioxide from a High-Enthalpy Reservoir

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Theme

A NUMERICAL study is presented of nonequilibrium nozzle expansions of carbon dioxide from a reservoir at high specific enthalpy h_0 ranging from 3 to 85×10^{10} cm^2 sec^{-2}. The effect of uncertainties in the relevant reaction rates and of assumptions made about the vibrational energy of the molecular components is examined. The results show that the gas composition at large area ratios does not separately depend on reservoir pressure and temperature, but depends only on reservoir specific entropy.

Contents

The nozzle flow problem consists of the solution of the conservation equations for mass, momentum and energy in conjunction with an equation specifying the equilibrium condition of the gas and the reaction rate equations, the boundary streamline being defined by the nozzle shape. With the assumption of quasi-one-dimensional flow the problem is reduced to a set of ordinary differential equations with the nozzle cross-sectional area A as an input. A conical nozzle with 7.5° semiangle is considered. An inviscid, thermally and electrically nonconducting gas is considered, consisting of the species, C, O, CO_2, CO, O_2, CO^+, O^+, C^+ and electrons, in proportions such that the mixture may be totally recombined to CO_2. A conventional equilibrium gas model is used, similar to that of Ref. 1. From calculations allowing for vibrational relaxation of the molecular species it was found that, at the present conditions, the vibrational modes of CO_2 may be considered to be in equilibrium with the translational temperature, while those of O_2 and CO may be described by a sudden freeze criterion. In all cases the effect of vibrational nonequilibrium is quite small. The rate of change of each species concentration with distance along the streamline is given by the sum of the contributions to it over all the reactions considered, as in Ref. 1. Table 1 gives these reactions together with parameters defining the reaction rate according to

$$k_{fi} = A_i T^{\eta_i} \exp(-E_i/RT) \tag{1}$$

k_{fi} is the forward rate of reaction number i in cm^3 mole^{-1} sec^{-1}. E_i is the activation energy (kcal mole^{-1}), R is the universal gas constant (kcal mole^{-1} K^{-1}), η_i and A_i are constants and T is the translational temperature (K).

Table 1 Chemical reactions and rate parameters used

i	Reaction	Third body M	A_i	η_i	E_i
Dissociation					
1	$CO_2 + M \rightarrow CO + O + M$	all species	2.88×10^{11}	0.5	74.8
2	$CO + M \rightarrow C + O + M$	all except CO and O	8.79×10^{29}	−3.52	255.76
3	$CO + CO \rightarrow C + O + CO$	...	1.76×10^{30}	−3.52	255.76
4	$CO + O \rightarrow C + O + O$	...	1.29×10^{31}	−3.52	255.76
5	$O_2 + M \rightarrow 2O + M$	all except O and O_2	2.55×10^{18}	−1.0	118.7
6	$O_2 + O_2 \rightarrow 2O + O_2$	...	2.75×10^{19}	−1.0	118.7
7	$O_2 + O \rightarrow 3O$	...	2.1×10^{18}	−1.0	117.96
Carbon exchange					
8	$CO + CO \rightarrow CO_2 + C$	...	2.33×10^{9}	0.5	130.5
9	$O + CO \rightarrow C + O_2$	...	2.73×10^{11}	0.5	138.1
10	$CO + O_2 \rightarrow CO_2 + O$	...	1.6×10^{13}	0	41.0
Ionization					
11	$CO^+ + e^- \rightarrow C + O$	...	1.7×10^{22}	−1.5	0
12	$C^+ + e^- + e^- \rightarrow C + e^-$	...	2.94×10^{40}	−4.5	0
13	$O^+ + e^- + e^- \rightarrow O + e^-$	...	1.9×10^{40}	−4.5	0
14	$CO + M \rightarrow CO^+ + e^- + M$	all	7.24×10^{12}	0.5	323.18
15	$O + M \rightarrow O^+ + e^- + M$	all	7.34×10^{12}	0.5	314.05
16	$C + M \rightarrow C^+ + e^- + M$	all	7.86×10^{12}	0.5	259.84

Figure 1 exhibits some of the features of a CO_2 expansion from a reservoir at temperature T_0 = 10,000K, pressure p_0 = 200 atm. The initial drop of the O_2 and CO_2 concentrations associated with the equilibrium behavior of CO_2 is followed by departure from equilibrium at an area ratio of about 5

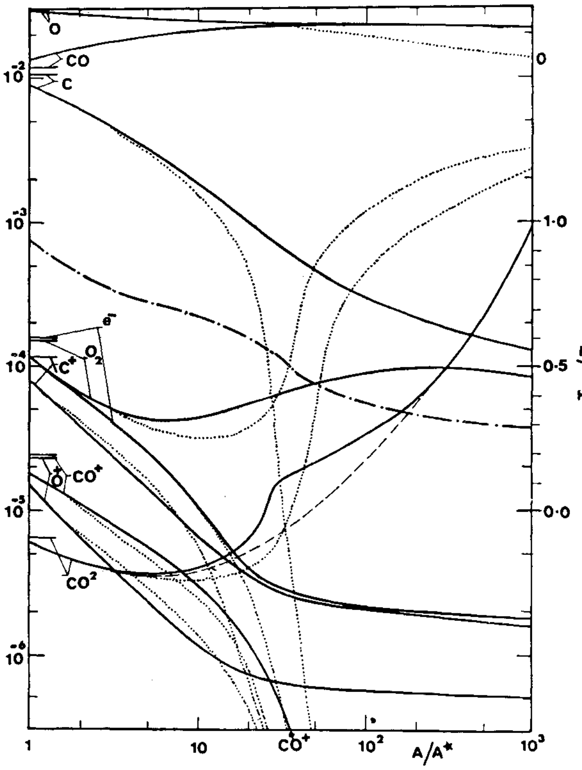

Fig. 1 **Variation of composition and equilibrium temperature in a nozzle expansion from T_0 = 10,000K, p_0 = 200 atm. Bars at left show reservoir composition. .... equilibrium, —— nonequilibrium, – – – – without reaction 10, –.–.–.– equilibrium temperature.**

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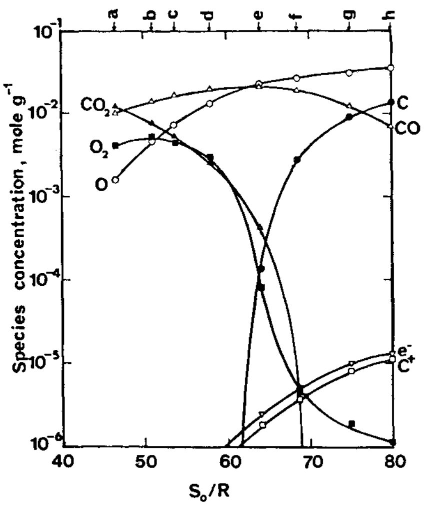

Key	T_0, K	p_0, atm	Key	T_0, K	p_0, atm
a	6000	1200	e	10000	200
b	8000	1200	f	13000	600
c	9000	800	g	19000	600
d	10000	600	h	20000	400

Fig. 2 Species concentration at area ratio = 700 as a function of specific reservoir entropy.

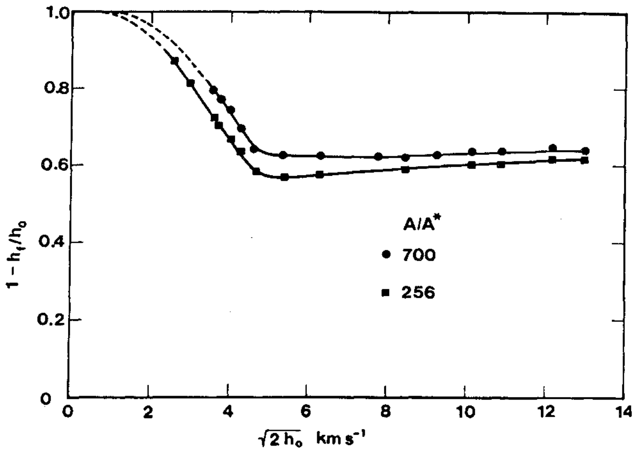

Fig. 3 Nozzle efficiency as measured by recovered specific enthalpy as a function of equivalent flight velocity.

(A^* = throat area). Beyond $A/A^* = 50$ all species except C, O_2, CO_2 are inactive. The continuing rise of the CO_2 concentration is mainly due to reaction 1 in reverse, and the effect of the binary reaction 10 is seen to be unimportant. At lower reservoir enthalpies reaction 10 becomes progressively more important in this respect. The hump in the equilibrium temperature T_{eq} around $A/A^* = 20$ is associated with the behavior of the equilibrium specific heat ratio.

Results from a large number of such calculations (only 8 of which are shown) are plotted in Fig. 2 in the form of species concentration at $A/A^* = 700$ against S_0/R. (S_0 = reservoir entropy/original mole of CO_2). It is seen that the composition of the gas does not separately depend on p_0 and T_0, but is uniquely determined by S_0, as has been found previously for air.[2,3] Figure 2 shows that CO_2 expansions may be divided into three distinct regions: At $S_0/R < 58$ only CO_2 and O_2 recombination is important, while at $S_0/R > 68$ only CO recombination and the ionization reactions are significant. In the narrow transition region $58 < S_0/R < 68$ all of the reactions must be considered. This behavior is accompanied by a larger rate of increase of the frozen specific enthalpy h_f with S_0/R for $S_0/R > 64$ because of the high dissociation energy of CO, of which more and more remains dissociated as S_0/R is increased. The correlation with reservoir entropy of the deviation of pressure and temperature from their equilibrium values which was observed for air[3,4] also applies here, so that a particular nonequilibrium expansion could be solved by using an equilibrium solution together with the results of the correlation.

Table 2 Effect of uncertainties in reaction rates

Reaction number		Uncertainty considered in k_f	Effect on flow variables, %			Effect on species concentration, % of highest concentration				
			p	T	ρ, u	C	O	CO_2	CO	O_2
1	low	×1.6	0.7	0.8	0.01	0	0.30	0.24	0.24	0.02
1	h_0	×1/1.6	2.5	4.4	0.8	0	0.02	4.8	4.8	1.5
2–4	↓	+75%	0.01	0	0	0	0	0	0	0
2–4		−75%	0	0	0	0	0	0	0	0
5–7		×2	0.1	0.06	0.03	0	0.04	0.05	0.05	0
5–7		×1/2	0.06	0.03	0.01	0	0.02	0.03	0.03	0
1	high	×1.6	0.12	0.04	0.02	0.07	0.04	0	0	0
1	h_0	×1/1.6	0.06	0.02	0.01	0.04	0.05	0	0	0
2–4		+75%	7.0	8.5	0.38	2.0	2.0	0	2.0	0
2–4	↓	−75%	19	22	1.2	7.0	7.0	0	7.0	0
5–7		×2	0.29	0.5	0.08	0.3	0.20	0	0.3	0.03
5–7		×1/2	0.29	0.35	0.03	0.1	0.13	0	0.2	0

Throughout the range of S_0/R considered, the variation of composition (and, therefore, the variation of compressibility factor) with A/A^* is small for $A/A^* > 100$ with the exception of C, O_2 and CO_2 in the transition region $58 < S_0/R < 68$. This is indirectly evident in Fig. 3 which (for $A/A^* = 256$ and 700) shows the nozzle efficiency dropping off to about 60% as the equivalent flight velocity is increased to about 5 km sec^{-1}, and remaining approximately constant thereafter.

The effect of uncertainties in the reaction rates is shown in Table 2. The uncertainties considered are obtained from the scatter of various authors' results or represent their stated errors. It can be seen that the only case in which there is a significant effect is that of reactions 2–4 at high enthalpy.

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