

Estimates of Vibrational Nonequilibrium Time Scales in Hydrogen-Air Detonation Waves

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1 Introduction

Recent numerical simulations of cellular detonations in hydrogen-air mixtures [1] using detailed chemical kinetics suggest that thermally equilibrium thermochemical models may be insufficient for modeling detonation. The computed detonation cell sizes and cell regularity differ from experimental observations, indicating that the chemical kinetic model overestimates both the rate of energy release and its sensitivity to temperature behind detonation shocks. In order to better characterize and understand this behavior, Taylor et al. [1] identified the thermodynamic conditions at which the hydrogen-air mixture is reacting in a detonation wave and calculated the constant volume ignition delay time and effective activation energy at these conditions using the detailed chemical kinetic model of Burke et al. [2]. The next step is to identify possible nonequilibrium phenomena that may occur at these conditions and estimate their characteristic time scales.

When a gas undergoes a rapid change in its state, such as occurs across a strong shock wave, a finite amount of time is required in order for the gas's internal degrees of freedom to reach thermodynamic equilibrium. Vibrational degrees of freedom are the slowest to relax. The possibility that vibrational nonequilibrium could affect chemical reactions in gaseous detonations was discussed in the 1960s [3], but has been largely ignored outside of the Soviet Union and Russia since then. The goals of the present work are to (1) collect and assess vibrational relaxation time data for the reactants H_2 and O_2 as well as the diluent N_2 , (2) estimate the vibrational relaxation time of each of these species in H_2 -air mixtures, and (3) compare these vibrational relaxation times against computed ignition delay times. This should provide an indication as to which, if any, of the vibrational relaxation processes are relevant to detonations.

2 Background

Millikan and White [4] developed an equation for the vibrational relaxation time, based on experimental data as well as theoretical consideration of the Landau-Teller harmonic oscillator model [5], that has

been found to hold for many diatomic species,

$$P\tau(T) = \exp \left[A \left(T^{-1/3} - B \right) - 18.42 \right], \quad (1)$$

where P is pressure in atmospheres, τ is vibrational relaxation time in seconds, and T is temperature in Kelvin. Millikan and White [4] also developed correlations for the parameters A and B that are reasonably accurate for collisions between identical or similar species,

$$A = 0.00116\mu^{1/2}\theta_v^{4/3}, \quad B = 0.015\mu^{1/4}, \quad (2)$$

where μ is the equivalent molecular weight of colliding species i and j given by

$$\mu = \frac{M_i M_j}{M_i + M_j}, \quad (3)$$

and θ_v is the characteristic vibrational temperature. Values of θ_v for H_2 , O_2 , and N_2 are 6320 K, 2239 K, and 3395 K, respectively. The parameters A and B can be accurately predicted for many, but not all, diatomic species using the Millikan and White (MW) correlation (2). As will be shown later, the MW correlation is severely inaccurate for the relaxation of certain diatomic species containing hydrogen.

The vibrational relaxation time of a species i in a mixture of N gases is given by [6]

$$\frac{1}{P\tau_i} = \sum_{j=1}^N \frac{X_j}{P\tau_{i-j}}, \quad (4)$$

where X_j is the mole fraction of species j and τ_{i-j} is the vibrational relaxation time of species i infinitely dilute in species j .

3 Analysis of vibrational relaxation time data

Calculated and experimentally determined values of A and B are available for the vibrational relaxation of H_2 , O_2 , and N_2 in a number of bath gases. These parameters are shown in Table 1 for H_2 , Table 2 for O_2 , and Table 3 for N_2 . Graphs of calculated vibrational relaxation times for these species appear in Figures 1, 2, and 3.

Table 1: H_2 relaxation time parameters

	Process	A	B	Source
1.a	H_2 in H_2	79.99	0.019754	Ref. [6]
1.b	H_2 in H_2	136.1	0.015030	Eqn. (2)
2.a	H_2 in Ar	103.82	0.02120	Ref. [6]
2.b	H_2 in Ar	134.4	0.01494	Eqn. (2)
3.a	H_2 in O_2	134.0	0.01491	Eqn. (2)
4.a	H_2 in N_2	133.7	0.01490	Eqn. (2)

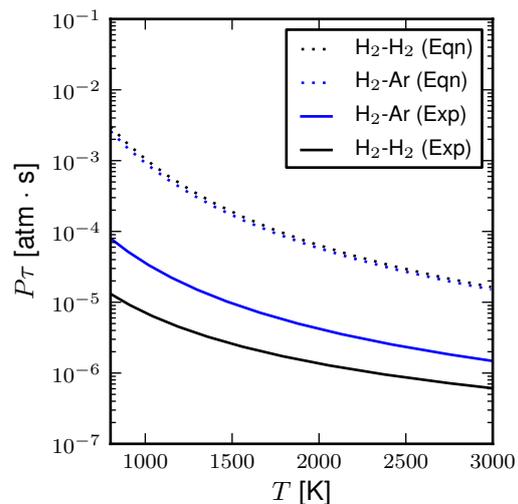
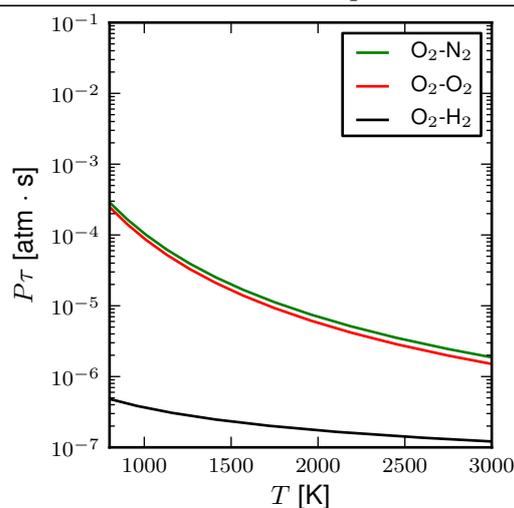


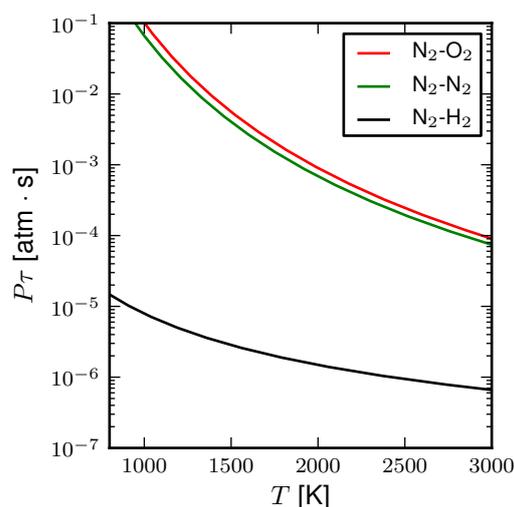
Figure 1: H_2 relaxation times in H_2 (black) and Ar (blue) from fit to experiment (solid lines) and calculated with MW correlation (dotted lines).

Table 2: O₂ relaxation time parameters

	Process	A	B	Source
5.a	O ₂ in H ₂	36.0	0.000067	Ref. [9]
5.b	O ₂ in H ₂	33.6	0.01491	Eqn. (2)
6.a	O ₂ in O ₂	133.0	0.031632	Ref. [10]
6.b	O ₂ in O ₂	135.9	0.0300	Eqn. (2)
7.a	O ₂ in N ₂	131.3	0.0295	Eqn. (2)

Figure 2: O₂ relaxation times calculated from fit to experiment (H₂, O₂) and MW correlation (N₂).Table 3: N₂ relaxation time parameters

	Process	A	B	Source
8.a	N ₂ in H ₂	80.87	0.01753	Eqn. (2)
9.a	N ₂ in O ₂	228.7	0.0295	Eqn. (2)
10.a	N ₂ in N ₂	234.9	0.03177	Ref. [11]
10.b	N ₂ in N ₂	221.5	0.02910	Eqn. (2)

Figure 3: N₂ relaxation times calculated from fit to experiment (N₂) and MW correlation (H₂, O₂).

The only available experimental data for the vibrational relaxation of H₂ is for self-relaxation and relaxation in noble gases [6]. Use of the MW correlation (2) to compute parameters A and B for the vibrational relaxation time of H₂ is very inaccurate, as can be seen by comparing the experimental and calculated times for relaxation of H₂ in H₂ and in Ar shown in Figure 1. White [7] identified H₂ as one of several diatomic species, all of which contain hydrogen, for which equation (2) fails to accurately predict the vibrational relaxation time. White attributed this to the low molecular weight of hydrogen and, in the case of H₂, to its very high characteristic vibrational temperature. For this reason, correlation (2) should not be used to calculate vibrational relaxation time parameters for H₂ and instead we must rely on the limited experimental data that is available.

Experimentally determined relaxation time parameters for O₂ and N₂ are more abundant and, in cases where experimentally determined values are not available, they can be accurately estimated from the MW correlation. Examination of cases 5.a-b and 6.a-b in Table 2 and case 10.a-b in Table (3) show

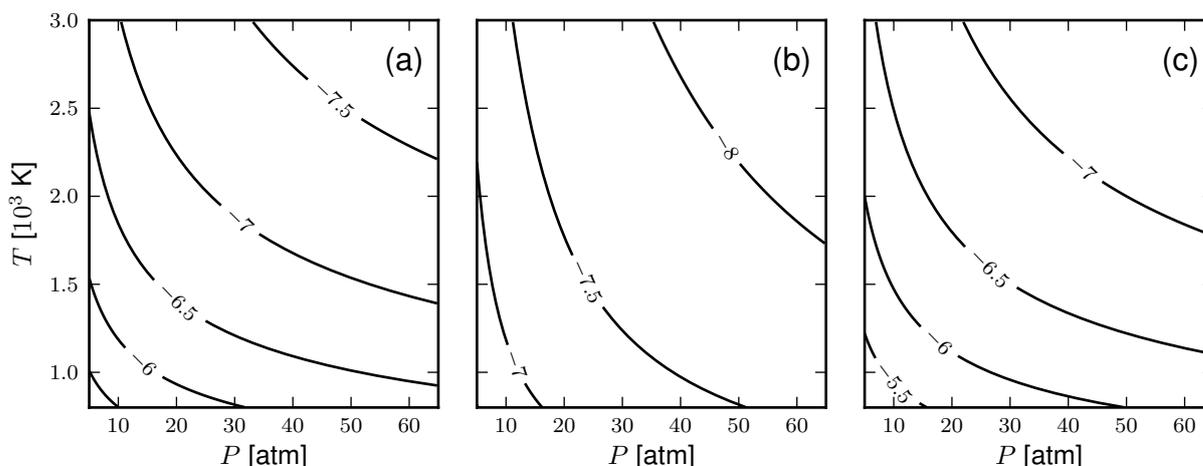


Figure 4: Contours of $\log_{10}(\tau_{\text{vib}})$ in stoichiometric H_2 -air mixture for (a) H_2 , (b) O_2 , (c) N_2 .

good agreement between experimentally determined relaxation parameters and those calculated from correlation (2). In all of the remaining cases in the O_2 and N_2 tables, experimental data are available which show good agreement with relaxation times calculated with parameters from the MW correlation.

It is important to note the large impact of H_2 on the vibrational relaxation time of O_2 and N_2 . As shown in Figure 2 and 3, H_2 is much more efficient in promoting vibrational relaxation in these species than are O_2 and N_2 . For instance, the calculated self-relaxation time of N_2 is greater than relaxation in H_2 by a factor of 400 at 2000 K, a result which is supported by experiments [8]. A similar but less dramatic effect is seen in O_2 [7], where the present results show that H_2 reduces the relaxation time by a factor of 30 at 2000 K. The effectiveness of H_2 in promoting vibrational relaxation of O_2 and N_2 is such that the relative order of vibrational relaxation among H_2 , O_2 , and N_2 may change depending on whether the mixture is rich or lean. That is, in a very rich mixture O_2 is expected to vibrationally relax much more quickly than H_2 and N_2 , which should relax at approximately the same rate. In a lean mixture, N_2 will clearly be the slowest to relax. The relative ordering of H_2 and O_2 in the lean case cannot be predicted due to the lack of data for H_2 relaxation in N_2 and O_2 .

4 Vibrational relaxation times in stoichiometric H_2 -air

In this section, vibrational relaxation times of H_2 , O_2 , and N_2 are calculated in stoichiometric H_2 -air mixtures and compared with ignition delay times computed using a detailed chemical reaction model for a thermally equilibrated gas. The effects of reaction intermediates and products are ignored, so that only the initial mixture is considered in calculating the vibrational relaxation times. The mixture rule, equation (4), is used to compute an overall vibrational relaxation time for each species based on the contributions of collisions with other species, including itself. Accurate parameters are available to calculate the relaxation times of O_2 and N_2 . The parameters used for O_2 in the present calculations are those of 5.a, 6.a, and 7.a from Table 2. The mixture rule is

$$\frac{1}{P\tau_{\text{O}_2}} = \frac{X_{\text{H}_2}}{P\tau_{\text{O}_2-\text{H}_2}} + \frac{X_{\text{O}_2}}{P\tau_{\text{O}_2-\text{O}_2}} + \frac{X_{\text{N}_2}}{P\tau_{\text{O}_2-\text{N}_2}}. \quad (5)$$

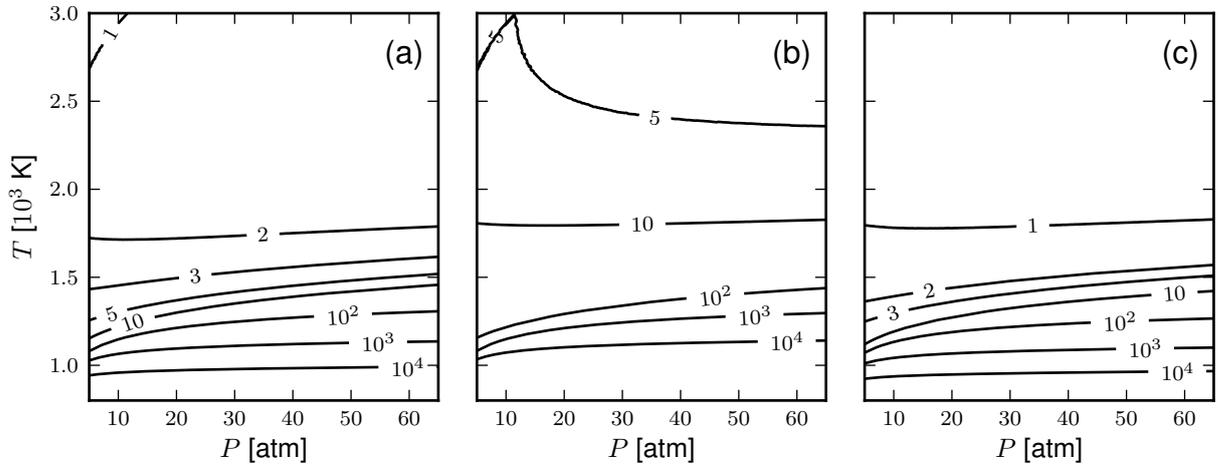


Figure 5: Contours of $\tau_{\text{ign}}/\tau_{\text{vib}}$ in stoichiometric H_2 -air mixture. τ_{vib} is computed for (a) H_2 , (b) O_2 , (c) N_2 .

The parameters used for N_2 are those of 8.a, 9.a, and 10.a in Table 3 and the mixture rule is

$$\frac{1}{P\tau_{\text{N}_2}} = \frac{X_{\text{H}_2}}{P\tau_{\text{N}_2-\text{H}_2}} + \frac{X_{\text{O}_2}}{P\tau_{\text{N}_2-\text{O}_2}} + \frac{X_{\text{N}_2}}{P\tau_{\text{N}_2-\text{N}_2}}. \quad (6)$$

As discussed previously, the mixture vibrational relaxation time of H_2 is more difficult to estimate since accurate parameters are not available for its vibrational relaxation by O_2 and N_2 . Lacking any better data, the experimentally determined relaxation time parameters for H_2 in Ar are used for H_2 relaxation in O_2 and N_2 . The only justification for this choice is that the atomic weight of Ar (40 amu) is relatively close to the molecular weight of O_2 (32 amu) and N_2 (28 amu). An alternative choice would be to use the parameters for H_2 relaxation in Ne (20 amu). The parameters used for H_2 relaxation in the present calculations are those of 1.a and 2.a in Table 1 and the mixture rule is

$$\frac{1}{P\tau_{\text{H}_2}} = \frac{X_{\text{H}_2}}{P\tau_{\text{H}_2-\text{H}_2}} + \frac{X_{\text{O}_2}}{P\tau_{\text{H}_2-\text{Ar}}} + \frac{X_{\text{N}_2}}{P\tau_{\text{H}_2-\text{Ar}}}. \quad (7)$$

A stoichiometric mixture of H_2 -air is composed of 29.6% H_2 , 14.8% O_2 , and 55.6% N_2 by mole. The base-10 logarithm of vibrational relaxation time for each species in this mixture is shown in Figure 4. Figure 5 shows the ratio of the ignition delay time to the vibrational relaxation time. The ignition delays were computed using the H_2 -air mechanism of Burke et al. [2]. For reference, the post-shock state of a Chapman-Jouguet detonation in stoichiometric H_2 -air at 1 atm and 300 K is approximately 28 atm and 1540 K, assuming the gas is at thermodynamic equilibrium. In an unsteady detonation [1], reaction occurs in the wake of moderately overdriven parts of the incident shock wave and in material which has been compressed by both the incident and transverse shocks. These post-shock states correspond to pressures and temperatures where $\tau_{\text{ign}}/\tau_{\text{vib}}$ is less than 3 in H_2 and less than 2 in N_2 .

5 Discussion

The results presented above suggest that there are vibrational relaxation processes in stoichiometric H_2 -air detonation waves that occur on the same time scale as chemical reaction. Of these processes,

H₂ and N₂ vibrational relaxation times are much slower than those of O₂ for a stoichiometric mixture. This is primarily due to the strong effect of H₂ on reducing the O₂ relaxation time. In rich mixtures, where H₂ effects on vibrational relaxation will dominate, similar results are expected. Starikovskiy and Aleksandrov [12] describe a similar conclusion regarding the relative vibrational relaxation times of H₂ and O₂. Lacking data for the vibrational relaxation of H₂ in O₂ and in N₂, we cannot make any conclusions with regard to lean mixtures, where molecular collisions with N₂ and O₂ will dominate. It would thus be very useful to have better estimates for the vibrational relaxation of H₂ in O₂ and N₂. Several of the articles cited in this work mentioned the difficulties of measuring vibrational relaxation in H₂ experimentally, so this may be better studied by computational methods.

The hypothesis motivating this study is that vibrational nonequilibrium produced by shock waves in detonations decreases the rate of chemical reaction, increasing the ignition delay time relative to reaction in a mixture at thermal equilibrium. The results of the previous section support this hypothesis. The computed vibrational relaxation times suggest that reactions involving H₂ and N₂ are more likely to be affected by vibrational nonequilibrium than reactions which only involve O₂, due to the very short vibrational relaxation time of O₂. The comparison of vibrational relaxation times and ignition delay times made in the previous section describes only gross features of these effects; namely, estimates of their time scales. The details of interactions between vibrational nonequilibrium and chemical reaction cannot be deduced from this comparison, although it is reasonable to assume that a reduced population of vibrationally excited molecules (relative to the equilibrium distribution) is likely to inhibit reactions that are particularly sensitive to their reactants' vibrational states. It should be noted that the ignition delay times were calculated using a thermally equilibrium kinetics model at conditions of simultaneously high temperature, pressure, and non-dilute reactant mixture, where direct experimental measurement of the ignition delay time is impossible. In effect, the kinetics model is being used to extrapolate outside of the conditions at which it has been calibrated and thus the calculated ignition delay times should be viewed with some skepticism.

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