

A singular perturbation approach to some problems in chemical kinetics

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A singular perturbation method is used to obtain the solution of the normal chemical kinetic differential equations in three different types of chemical reactions. The relaxation of a dilute concentration of a diatomic gas in an inert heat bath is examined. This is then modified to consider the situation in which the diatomic molecule has two states which only interact via the atomic species. Finally, the growth and decay of a dense hydrogen plasma is investigated.

In each case the time phases during the relaxation from a non-equilibrium to an equilibrium distribution are shown explicitly and there is an initial transient phase during which internal relaxation occurs. For the diatomic not involving the two states, the initial transient is followed by a period of dissociation or recombination and, in the case of the hydrogen plasma, this transient is followed by a period of ionization or recombination. During this period, the rate coefficients in both cases are easily obtained from the smallest eigenvalue of the corresponding relaxation matrices.

For the diatomic molecule involving two states, two possible cases arise when considering the behaviour of the system after the initial transient. These depend on the relationship between the ratios of the internal relaxation time to the time for dissociation in each state. The first possibility is that one of the states may dissociate or recombine and that this is then followed by the dissociation or recombination of the second state. During these two time periods, the rate coefficients for the

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overall reaction are obtained in terms of the smallest eigenvalues of the relaxation matrices of the states. The second possibility is that both states dissociate or recombine almost simultaneously. For this time period there are no well defined rate coefficients.

For each of the chemical reactions considered a model problem is formulated. Population distributions are then generated not only using the singular perturbation method but also using the variable step-length numerical integration algorithm of Gear. A comparison is made of the population distributions obtained by both methods and the advantages of each are discussed. Rate coefficients are calculated using the singular perturbation method for the diatomic molecule, not involving the two states, and the hydrogen plasma. These coefficients are compared with those previously calculated theoretically and those determined experimentally by other authors.

It is concluded that the singular perturbation method is an excellent way to examine chemical reactions in which the chemical kinetic differential equations have a form similar to those investigated in this thesis.