

## SHOCK FRONT STRUCTURE - A CHEMICAL KINETICS VIEW

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## INTRODUCTION

In the analysis of shock front structures in real gases, intermolecular processes which fall within the province of chemical kineticists play a dominant role. The determination of shock front profiles in density, temperature and in the concentrations of chemical species, provide kineticists with powerful techniques for exploring mechanisms for reactions which cannot be studied otherwise. This has been recognized for over a decade. Advances made in the state of the art through 1963 can be measured by the content of an 850-page treatise on shock tubes by H. Qertel<sup>(1)</sup>, which covers theory, practice and applications in a detailed and thorough manner. More recent assessments may be obtained from the 94 abstracts of papers which were submitted for presentation at the 6th International Shock Tube Symposium,<sup>(2)</sup> and the 37 reports given at the AGARD Colloquium on "Recent Advances in Aerothermochemistry."<sup>(3)</sup>

In this summary attention is called to several developments which have advanced the "state of the art" during the past year. A brief overall assessment shows that there is continued emphasis on the improvement of experimental techniques. These center around cleanliness of operation (good vacuum technique, insistence on low leak rates, etc.), the use of polished inner walls to reduce boundary layer perturbations, improved control of species concentrations, increased precision in shock speed measurements, refinement in sensitivity and reduction of response times for diagnostic devices used in recording the profiles of shock fronts, etc. In addition there is greater sophistication in the design of experiments. The improvements may be categorized into three groups: (1) use is being made of newly available devices, such as lasers; (2) it is now general practice to record in many channels concurrently, such as the mass spectra of several species, the concurrent recording of emission and absorption spectra at different wavelengths as a function of time; (3) combining shock tube techniques with other techniques for the preparation of samples to be studied; for example, preliminary flash photolysis or imposition of a glow discharge through the sample prior to its being exposed to the shock wave. Along with increased sophistication in the performance of experiments, extended computer programs are used routinely, both for equilibrium compositions and for obtaining kinetic profiles; also, to facilitate data reduction.

These trends will continue because they have already proved their worth, but they occur at the expense of increased complexity in equipment, leading inevitably to the need for collaboration among several persons in operating a facility. What remains for the lone experimenter? It appears to me that for some time to come the single-pulse shock tube technique will remain one of a few individualistic activities. The investigator will have to be ingenious in designing kinetic experiments in which knowledge of the concentrations of species after a specified reaction time permits an identification of a mechanism. Single-pulse shock tubes allow the exploration of complex systems in a qualitative manner, and provide the basis for selecting reactions which are critical steps in a complex reaction scheme for detailed study by other techniques.

## TECHNIQUES AND DIAGNOSTIC DEVICES

A representative selection of interesting developments in technique is presented in Table 1. The use of narrow electron beams for exciting molecular spectra in a flowing medium merits an additional comment. The characteristic spectra excited permit identification of the species present, and an estimation of their densities (if proper calibrations are made). Vibrational and rotational temperatures can be obtained from band contours. In the hands of a careful experimentalist, this technique may give translational speeds as well (Doppler widths of spectral lines). For example, in a supersonic jet of nitrogen expanding from room temperature in an axi-symmetric nozzle, (8) the rotational temperature was observed to follow the isentropic curve initially, but at the lower temperatures the rotational population "froze" to a fixed distribution leading to a substantial degree of non-equilibrium.

Perhaps one of the most sensitive devices for measuring gradients at a shock front with high resolution is the laser-schlieren method described by Kieffer and Lutz. (11) Gradients as low as  $10^{-5}$  gm/liter mm can be detected in argon, and characteristic times (lab scale) as short as  $0.2\mu$  sec. have been measured. Vibrational relaxation times for hydrogen and deuterium have thus been quantitatively determined for the first time. This technique has been effectively used to scan the heat release profile during the high temperature oxidation of acetylene. (12)

The best illustration of concurrent multichannel recording to provide a large amount of information for a single shock, and thus to correlate a variety of parameters, is the use of a rapid-scan mass spectrometer. A time-of-flight spectrometer coupled to a shock tube via a minute leak has been described by Kistiakowsky, (13) Dove, (14) Diesen (15) and Modica. (16) The successful application of a quadrupole mass filter for the analysis of products extracted from a back-reflected shock has been recently reported by Gutman. (17) As described this relatively low cost instrument could be set to record only one mass at a time; however, current developments in Gutman's laboratory indicate that it may be possible to set four mass filters for concurrent recording. The fidelity of sampling of back-reflected shocked gases through 0.002 inch apertures remains to be demonstrated. To avoid confusion of the desired sample with end-wall cooled gases and boundary layer perturbations, Marsters (18) extracts the sample from a rapidly quenched incident shock and by a sequence of large aperture nozzles converts the jet to a molecular beam for analysis by a time-of-flight spectrometer.

There is an intriguing possibility of using a small mass spectrometer to detect the onset of ionization (in particular, the onset of production of a particular species) and correlating this profile with spectroscopic data (chemiluminescence, or the appearance of a characteristic absorption). In this connection one should mention the successful application of a Nier-type mass spectrometer by Sturtevant (19) who demonstrated that the first ions to appear in shock-heated argon, at a threshold approximately four volts below the ionization potential of argon, were  $H^+$  and  $O^+$ , presumably from a very low level water impurity.

The technique of preparing equilibrium samples at elevated temperatures (as with reflected shocks) and quenching them so rapidly that one may study kinetic processes which occur during the cooling path has not attracted many devotees, although expansion through a small aperture in the end wall of a shock tube for sampling purposes is being used by mass spectrometrists. To avoid boundary layer problems and to achieve very rapid cooling, Wilson (20) inserted a pair of divergent airfoils in a shock tube, so that the incident shock passed through a double Prandtl-Meyer

expansion. This setup was used effectively for measuring the recombination rate of oxygen atoms at elevated temperatures, and is currently being developed in our laboratory for investigating condensation processes in metal vapors produced under supersaturated conditions by shock-heating metal carbonyls. The expansion generated by the interaction of the contact surface with the reflected shock was used for a kinetics study of the association of CN radicals prepared by shock-heating  $C_2N_2/Ar$  mixtures to about  $2000^\circ$ ,<sup>(21)</sup> the CN concentration was followed spectrophotometrically. It was found that the rate of CN disappearance was first order in CN and first order in  $C_2N_2$  (or  $C_mN_m$  polymers), and that the average polymer number under these conditions,  $m \approx 10$ . Finally, a rapid-quench sampling probe for non-equilibrium air flows has been described by Stoddard and Watt<sup>(22)</sup> in which a small sample scooped from the free stream region in a shock tunnel is rapidly cooled by contact with the walls of an explosively sealed probe.

An example of interesting results obtained from use of combined techniques is the glow tube described by Hartunian, *et al*<sup>(23)</sup> in which a steady-state concentration of reactive species is prepared in a glow-discharge flow system, and fully characterized (at room temperature). The plasma is then subjected to a shock, initiated by rupture of a diaphragm upstream from the rf source. Typically, the shock strength is less than that which causes further dissociation; the shock compresses, heats and accelerates those species which are already present in the glow tube. Thus, a means is provided for studying the temperature dependence of the gas phase recombination processes and of chemiluminescent reactions. This combination provides a considerable extension of atom fluxes for study of kinetic processes. In contrast to heating with shock waves, Petrella *et al*<sup>(24)</sup> describe a combination flash photolysis-flash pyrolysis system in which heating is accomplished by the comparatively slower process of allowing the gaseous sample to contact a flash-heated solid grid.

References to several current analyses on the non-ideal behavior of shock tube operation are listed in Table II, while Table III is a summary of papers in which the measurement of ionization cross-sections and of optical oscillator strengths are discussed.

#### MEASUREMENT AND CONTROL OF VIBRATIONAL STATE POPULATIONS

During the past two years much effort has been devoted to the study of the excitation of vibrational modes due to intra- and inter-molecular energy transfer processes. For many decades it has been accepted by kineticists that the measured reaction rate constants depend on the facility for energy transfer between the various parts of reacting molecules when in the transition state. The mere difficulty of properly estimating the density and symmetry character of the highly excited states even in simple systems, led to an attitude of futility, as expressed by the observation that there seems to be little relation between the states of interest to chemical kineticists and the transition probabilities measured for low-lying vibrational states. However, several examples are now known for which the measured rate constants may be calculated from measured vibrational relaxation times. The basis for the current activity is in part due to the recognition of the presence of strong coupling between vibrational modes and dissociation, and in part to the current explosive development in laser technology.

It has been known for several years that vibrational relaxation times for small molecules containing hydrogen atoms are much shorter than those predicted on the basis of the Slawsky-Schwartz-Herzfeld theory, and the observed relaxation times did not fit the correlation diagram proposed by Millikan and White. For example, the

vibrational relaxation times for HCl, DCI and HI measured by the spectrophone method<sup>(43)</sup> (at room temperature) are consistent with the high temperature data (infrared emission from shocked gases at 2000°)<sup>(44)</sup> in that the relaxation times were several orders of magnitude shorter than those predicted by the SSH theory. They are in better agreement with Cottrell's vibration-rotation theory<sup>(45)</sup>. That rotational motion plays a role in exciting vibrational states was demonstrated by Millikan<sup>(46)</sup> who measured the relative rates of collisional deactivation of vibrationally excited CO by ortho and para hydrogen. Another example of the inadequacy of the SSH theory are the vibrational relaxation times for H<sub>2</sub>-Ar, H<sub>2</sub>-H<sub>2</sub>, D<sub>2</sub>-Ar, D<sub>2</sub>-D<sub>2</sub> reported by Kiefer and Lutz<sup>(11)</sup>. These data are better accounted for by Parker's semi-classical theory<sup>(47)</sup> with an angle-dependent potential used for calculating both rotational and vibrational relaxation times. Even though there is agreement for collision numbers with argon and krypton as collision partners, there remains an order of magnitude disagreement for self collisions of H<sub>2</sub> and D<sub>2</sub>. A good summary of relaxation processes involving rotational-vibrational interactions and resonance collisions was given by R. C. Millikan;<sup>(48)</sup> a simple two-parameter model was developed by C. B. Moore.<sup>(49)</sup>

The relaxation of NO X<sup>2</sup>Π (v = 1) in D<sub>2</sub>S, H<sub>2</sub>O, H<sub>2</sub>S, D<sub>2</sub>O and CH<sub>4</sub> was investigated by microwave-flash pulse-flash spectroscopy.<sup>(50)</sup> Deactivation by all the hydrides was very fast compared with the rate of self deactivation. The rate coefficient showed a systematic variation with the minimum energy which had to be converted to translation. The authors propose that the uniformly fast relaxation by the triatomic hydrides may arise from the formation of an intermediate complex between NO and the H<sub>2</sub>S or H<sub>2</sub>O. However, this does not account for the effect of isotopic substitution. For comparison, helium is ≈0.1 as effective as NO, which in turn is ≈0.01 as effective as H<sub>2</sub>S.

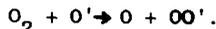
The vibrational relaxation of oxygen in the presence of small amounts of methane (0.5% to 1.6%) was measured at room temperature by ultrasonic techniques.<sup>(51)</sup> The relaxation frequency did not vary linearly with the methane concentration. It appears that translation-vibration excitation occurs only for methane, but that oxygen molecules become excited only by vibration-vibration transfer from the methane. A similar mechanism for energy transfer was reported by Millikan in the quenching of carbon monoxide fluorescence by methane.<sup>(48)</sup> In contrast, for nitrogen-hydrogen mixtures (≈2% H<sub>2</sub>) White<sup>(52)</sup> found that the vibrational relaxation time fitted their systematical correlation diagram.

The density profile at the shock front due to vibration relaxation in oxygen was explored with the laser-schlieren technique, in pure oxygen and in oxygen-ozone mixtures.<sup>(53,54)</sup> Kiefer and Lutz report:

$$p\tau_{(O_2-O_2)} = (2.92 \pm 0.20) \times 10^{-10} \exp \left[ \frac{(126.0 \pm 0.9)}{T} \right]^{1/3}, \text{ atm. sec.}$$

$$p\tau_{(O_2-O)} = (4.35 \pm 0.19) \times 10^{-8} - (7.75 \pm 0.81) \times 10^{-12} T, \text{ atm. sec.}$$

The latter is the deduced value for oxygen molecules dilute in an atmosphere of atoms. These clearly differing temperature dependencies indicate a strong chemical effect, possibly similar to those previously suggested for the CO<sub>2</sub>-H<sub>2</sub>O system and CO-CI<sub>2</sub> systems, but more likely due to atom exchange: <sup>(55)</sup>



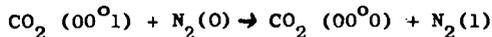
Measurement of the vibrational relaxation times in nitrogen presents an interesting case history. Sodium-spectrum line-reversal measurements for N<sub>2</sub> in

normal shocks gave vibrational relaxation times which checked well with interferometer-shock tube investigations. (Extrapolation to temperatures below 1500°K gives values which are orders of magnitude higher than sound dispersion and impact tube results.) However, when the line reversal technique was used to scan the vibrational non-equilibrium produced in supersonic expansions of undissociated nitrogen from reservoir temperatures 2800-4600°K (15° axi-symmetric nozzle, coupled to the end of a shock tube), the probability for de-excitation appeared to be  $\approx 50$  times greater.<sup>(56)</sup> This short relaxation time has now been confirmed by following the CO vibrational relaxation (introduced as a tracer in the expanding nitrogen stream), and by the electron beam technique in a low density non-steady expansion. For a while it was believed that the rapid relaxation was due to impurities present in the reservoir gas, but this was proven untenable.<sup>(57)</sup> A plausible explanation has now been proposed by Treanor and coworkers.<sup>(58)</sup> They point out that inadequate consideration has been given to effects of anharmonicity on vibrational relaxation for vibration-vibration exchange dominated regimes. When the translation temperature is quite low and the vibrational energy content is high (as in a rapidly expanding nozzle flow) vibration-vibration exchange introduces a slight but definite non-Boltzmannian vibrational population distribution. In such a case the population of the lowest vibrational level may be considerably lower than what it would be if the system were to relax through a sequence of Boltzmann distributions, thus indicating an apparent rapid relaxation time. Current experiments at CAL on the vibration relaxation in expanding nozzle flows for CO parallel the above observations reported for nitrogen. It is interesting to note that for the ascending path, i.e., the vibrational excitation of nitrogen, as followed by monitoring the  $v''=9$  level (U.V. absorption at 1176Å), the recorded times<sup>(59)</sup> are consistent with the Shuler-Rubin-Montroll theory that the populations of vibrational levels relax via a continuous sequence of Boltzmann distributions (3000°-5500°K). For temperatures in excess of 5500°K, the local value for the characteristic relaxation time ( $\tau_v$ ) becomes increasingly dependent on the degree of vibrational excitation.

A large amount of attention is currently being devoted to studies of the vibrational relaxation processes that occur in carbon dioxide. One must consider not only intermolecular energy exchange (V-T) and (V-V) with various colliders for CO<sub>2</sub> molecules in its different vibrational states, but also vibrational energy redistribution in CO<sub>2</sub> molecules due to collisions with ambient gases. To date ultrasonic dispersion studies have uncovered only three gases which show two dispersion frequencies: SO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and C<sub>2</sub>H<sub>6</sub>. Many shock tube investigations have shown that the vibration-translation relaxation in CO<sub>2</sub> follows a single relaxation time. On the basis of careful measurements of the variation of density behind incident shock waves in carbon dioxide, up to temperatures 2500°K, Simpson, et al<sup>(60)</sup> report that only a single relaxation time is discernable even though the density behind the shock front does not change strictly exponentially with distance; the departure is due to changes in the translational temperature which must accompany the relaxation process. A similar conclusion was reached by Weaner, et al<sup>(61)</sup> who made simultaneous measurements of the flow density with a Mach-Zehnder interferometer at the shock front and of the infrared emission at 4.3 $\mu$ . While the emission intensity monitored the population of the  $\nu_3$  level, the density provided a measure of the energy flow into all the vibrational modes. The single relaxation time was thus interpreted as evidence that equilibrium among all the vibrational modes was attained within the rise time of their detector (1.5 $\mu$ sec). However, the situation gets more complicated when one considers (V-V) energy transfer.

Moore and coworkers<sup>(62)</sup> measured decay curves of laser-excited vibrational fluorescence from the (00<sup>1</sup>) level of CO<sub>2</sub> (asym. stretch), as dependent on the admixed gases. He

deduced (V-V) transfer rates at room temperature which ranged from 15.5 atm- $\mu$ sec for He as a collision partner, to 3.76 (self), to 0.34 ( $H_2$ ) to 0.055 ( $H_2O$ ). Ultrasonic data give relaxation times for the (01'0) level (V-T). Corresponding values, for self collision,  $CO_2$   $6.8 \pm .3$  atm- $\mu$ sec; with He (0.39),  $H_2$  (0.015) and  $H_2O$  (0.0030). They also deduced the energy transfer probability for the reaction.



to be  $(2.0 \pm .4) \times 10^{-3}$ . The significant catalytic role of water for  $CO_2$  laser operation is now evident. At elevated temperatures over the range 800 to 3000°K shock tube measurements<sup>(63)</sup> with very short response time detectors show comparable differences between the several relaxation processes. Taylor and Bitterman<sup>(64)</sup> have prepared an exhaustive survey of vibrational relaxation data for processes important in the  $CO_2$ - $N_2$  laser system. A brief review on (V-V) transfer efficiencies as deduced from ultrasonic measurements has been published by Lambert.<sup>(65)</sup>

#### UNSOLVED PROBLEMS IN THE DISSOCIATION OF SMALL MOLECULES

One of the basic problems in chemical kinetics is the detailed analysis of the processes which occur when in diatomic molecules are dissociated thermally but homogeneously. Although a qualitative description has been given decades ago, it was not possible to perform the experiments nor to test details of the theory until the advent of shock tube techniques. One of the essential features required is the possibility to separate in time the vibrational excitation processes from the dissociation steps. It is now evident that conventional kinetic descriptions are not adequate. For example: The dissociation rate of very pure hydrogen at low concentrations in argon (0.01%-1.0%) has been measured by Watt and Myerson<sup>(66)</sup> using atomic absorption spectrophotometry (Lyman  $\alpha$  line). An Arrhenius plot for the bimolecular rate constant gives an activation energy of 94.5 kcal over the temperature range 2200°K. These rates are approximately a factor of five lower than rates reported by previous investigators, presumably because their samples were contaminated with slight amounts of oxygen which accelerated the dissociation rate through the reaction  $H + O_2 \rightarrow OH + O$ , followed by  $O + H_2 \rightarrow OH + H$ . For contrast Hurler reported about a year ago<sup>(67)</sup> his studies of dissociation rates in hydrogen-argon mixtures (20% to 60%  $H_2$ ) covering the temperature range 2500° to 7000°K, based on the Na-spectrum line-reversal technique for temperature measurement. He then deduced degrees of dissociation as a function of time (or distance behind the shock front), and was able to assign relative efficiencies to Ar,  $H_2$ , and H atoms as colliders. When his results were converted to recombination rate constants it appears that  $H_2$  is several times more efficient than argon as a chaperon for the  $2H \rightarrow H_2$  recombination but both show an approximate  $T^{-1}$  dependence. However, the efficiency of H atoms as chaperons appears to be equal to that of  $H_2$  for temperatures above 5500°K but as the temperature is lowered the efficiency rises sharply and at 3000° is about 30 times greater than that for  $H_2$ . Furthermore, there are indications that for temperatures below 2500°K the efficiency drops again and the room temperature H atoms may be only three times as effective as  $H_2$ .

The following observations are typical of most of the homoatomic diatom dissociation processes.<sup>(68)</sup> In all cases the self atom is much more efficient for the dissociation-association steps as a chaperon than is the molecule or an inert gas. That is not surprising since there are strong indications that the vibrational excitation efficiency of the self atom as a collider is greater than of any other molecular species.<sup>(54,55)</sup> However, it is difficult to explain the observed temperature dependence of the atom-chaperon rate constants; they do not fit into the scheme proposed by Keck under the "variational theory of reaction

rates."<sup>(69)</sup> I believe it is essential for the experimentalists to provide boundary conditions for the theories which will be developed; in this instance, data on deuterium are needed to check the effect of mass (possible tunnelling).

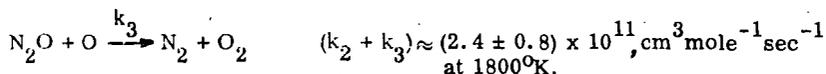
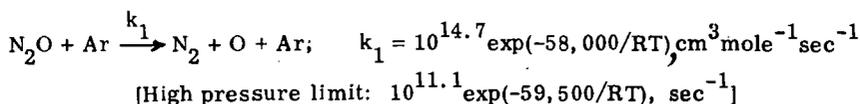
Recent publications describing dissociation rate studies of various diatoms are listed in Table IV. Inspection of such data shows that for the homatomic diatoms, simple Arrhenius plots gives lines with a slope for effective activation energies which are 7 to 10 kcal lower than the spectroscopic values. This is believed to be due to a statistical factor, i.e., the depletion of the upper vibrational states due to the slowness of the recombination reaction (3 body) such that their populations fall below the Boltzmann value calculated for the ambient translational temperature. This explanation is clearly not adequate to account for the much larger departures between the effective activation energies deduced from Arrhenius plots and the spectroscopic  $D_0$ 's for the hydrides HF, HCl, and DCℓ. The dissociation rate of HF in shock waves has been studied in two laboratories. When the data published by Jacobs *et al*<sup>(76)</sup> were replotted and fitted by least squares, the bimolecular rate constant was well represented by  $k_d = 10^{14.14} \exp(-108,600/RT)$ ,  $\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$ . Independently Spinnler<sup>(77)</sup> found  $k_d = 10^{14.16} \exp(-113,700/RT)$ . The close agreement is striking, since Jacobs followed the rate of reaction by recording the IR emission intensity behind incident shocks while Spinnler looked at absorption behind reflected shocks. A larger discrepancy has been reported for HCl and DCℓ by Jacobs and coworkers<sup>(78)</sup> and confirmed by Fishburne.<sup>(79)</sup> The observed apparent activation energy is 70 kcal for both gases while the spectroscopic values are 102 for HCl and 103 for DCℓ. It does not make sense to try to force these data to a rate expression with a  $T^{-1}$  or  $T^{-2}$  pre-exponential factor, when the resulting coefficient has a magnitude of over  $10^{21}$  in units of  $\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$ .

In summary, considerable progress has been made in formulating an appropriate statistical mechanics for a dissociation reaction in a thermal bath, in which cognizance is taken of the departure from Boltzmann distribution in the upper vibrational levels.<sup>(80)</sup> Virtually no progress has been made in calculating transition probabilities for molecular encounters which produce dissociation. No explorations have been undertaken of the sensitivity of such probabilities to the shape of the interaction potentials but it is established experimentally that diatoms are specially sensitive to the self atoms as colliders.

#### THE HOMOGENEOUS PYROLYSIS OF POLYATOMIC MOLECULES

While the theoretical underpinnings of current collision theories for diatom dissociations are of dubious dependability, there are even more questions regarding the interpretation of rate data for triatomic fragmentations. The minimum activation energy anticipated for the first step is the thermochemical value minus some correction for the depletion effect due to depopulation of the upper vibrational levels. Shock tube data for one case ( $\text{N}_2\text{O}$ ) gave an  $E_A$  value which was greater than the corresponding  $\Delta E_T^0$ , in full agreement with results obtained by conventional kinetics; there are several systems in which  $E_A$  was slightly less than  $\Delta E_T^0$ , as expected, but there are a disturbing number of studies which led to  $E_A < \Delta E_T^0$  by 25-50 kcal/mole.

The molecule which has been subjected to the most intensive investigation has been nitrous oxide. The homogeneous unimolecular decomposition (high dilution in argon) was studied in both the low and high pressure regimes. Shock temperatures were  $1300^\circ$  to  $2500^\circ\text{K}$ , and pressures between 0.8 and 300 atm (concentration range  $5 \times 10^{-6}$ - $2 \times 10^{-3}$  moles per liter).<sup>(81)</sup> This pyrolysis was also studied in an adiabatic compression device,<sup>(82)</sup> and the overall results may be summarized in the following equations:



The pyrolysis of the  $\text{N}_2\text{O}$  was also studied with a shock tube leaking into a quadruple mass filter. (17)

At the AGARD Colloquium, Troe and Wagner<sup>(83)</sup> proposed a general treatment for the dissociation of small molecules, as a semi-quantum mechanical extension of unimolecular reaction rate theory. They considered both tri- and tetra-atomics and divided the former into two groups, those which follow spin-allowed dissociations and those which require a net change in spin. The latter include  $\text{N}_2\text{O}$ ,  $\text{CS}_2$ , and  $\text{CO}_2$ . This analysis was amplified by Olschewski, Troe and Wagner.<sup>(84)</sup> The first step in the decomposition of 0.001%  $\text{CS}_2$  in argon was observed, completely isolated from the consecutive reaction  $\text{S} + \text{CS}_2 \rightarrow \text{CS} + \text{S}_2$ , using a UV absorption technique. They also studied the rate of dissociation of  $\text{SO}_2$  at concentrations below 0.3% in Ar, and of very dilute mixtures of water. The spin-forbidden dissociations approach their high pressure unimolecular limits at a few hundred atmospheres, but this condition cannot be reached for molecules which dissociate to the ground state atom species, as does  $\text{H}_2\text{O}$ . It is interesting to note that when one observes the rate of disappearance of water, say from its emission intensity in the infrared, at concentrations 0.02% to 0.2%, the rate constant is given by  $k_{\text{uni}} = (\text{Ar}) 10^{14.2} \exp(-105000/\text{RT}), \text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$ . Here, as in the case of  $\text{SO}_2$ , over the temperature range 2700° to 4000°, the measured rate is twice the magnitude for the first step, because the initial dissociation of the water is followed by the very rapid reaction,  $\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2$ . Above 4500°K only the first step is recorded, since all the subsequent steps are very rapid and the first step essentially controls the overall OH production. However, if the course of the reaction is followed by recording the amount of OH produced, (OH absorption at 3063A°)<sup>(85)</sup> the energy activation is about 50 kcal/mole. This was confirmed by the Göttingen investigators. Clearly, at the lower temperatures and higher concentrations the initial dissociation step is followed by a host of radical chains which involve OH; these are so rapid that they control the overall rate of its appearance.

One of the triatomic molecules which produces a product in an electronically excited state is  $\text{CO}_2$ . Davies<sup>(86)</sup> reported that his shock tube study covered the temperature range 6000°-11000°K (1% in Ar). Dissociation was monitored by the infrared emission intensity at 2.7 and 4.3μ. His results were essentially confirmed by E. S. Fishburne and coworkers<sup>(87)</sup> (3000-5000°K; 1% to 10% in Ar or  $\text{N}_2$ ). Their results are:

$$k_{\text{Ar}} = 7.11 \times 10^{11} T^{1/2} \exp(-84500/\text{RT}); \quad k_{\text{N}_2} = 5.33 \times 10^{11} T^{1/2} \exp(-79000/\text{RT}), \text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$$

The thermochemical dissociation energy is 125.3 kcal/mole. The Göttingen investigators also studied  $\text{CO}_2$  but at low concentrations and very high pressures in Ar.

They report a preliminary rate constant,  $k_{\text{u}} \approx 2 \times 10^{11} \exp(-111,000/RT)$ ,  $\text{sec}^{-1}$ , which they found to be practically independent of the argon concentration at levels of  $5 \times 10^{-4}$  moles/cm<sup>3</sup>. Thus, in this case also, the use of reagent concentrations of 1% or higher and modest Ar pressures permits steps subsequent to the first to confuse the dissociation process. Olschewski and coworkers<sup>(88)</sup> also found the bimolecular rate constant for CS<sub>2</sub> to be:  $k_{\text{b}} = (\text{Ar}) 10^{15.56} \exp(-80,300/RT)$ ,  $\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$ .

Other tri- and tetra-atomic species have been studied but not with the care devoted to the few molecules listed above. All of these show apparent activation energies considerably lower than the corresponding. These include HCN,<sup>(89)</sup> NH<sub>3</sub>,<sup>(90)</sup> NF<sub>2</sub>,<sup>(91)</sup> C<sub>2</sub>N<sub>2</sub>,<sup>(92)</sup> and others.

The following is a brief discussion of pyrolysis investigations of more complex species. Mass spectrometer and spectrophotometric detection ( $\lambda 2536\text{\AA}$ ) of the decomposition of fluoroform on shock heating to 1600°-2200°K was reported by Modica and LaGraff.<sup>(93)</sup> As anticipated, the first step appears to be splitting of the molecules to HF and CF<sub>2</sub>, for which the limiting high pressure rate constant is  $k_{\text{u}} = 7.03 \times 10^{11} \exp(-58,400/RT)$ ,  $\text{sec}^{-1}$ . At pressures 0.29 atm they assumed that the reaction had attained the second order limit. The dissociation of C<sub>2</sub>F<sub>4</sub> into difluorocarbenes has been previously studied using Ar as the diluent; Modica and LaGraff<sup>(94)</sup> repeated this work with N<sub>2</sub>, in reflected shocks (1200°-1600°K). There is a difference in that during the course of the reaction the nitrogen was vibrationally unrelaxed. In turn, the CF<sub>2</sub> radicals generated facilitated vibrational relaxation such that in a 1% tetrafluoroethylene-nitrogen mixture the relaxation time was a factor (10-50) less than in pure nitrogen. Finally, on shocking mixtures of C<sub>2</sub>F<sub>4</sub> and NO, Modica<sup>(95)</sup> concluded from mass spectra and UV absorptions that over the temperature interval 1600°-2500°K, there were the reversible reactions:  $\text{C}_2\text{F}_4 \rightleftharpoons 2 \text{CF}_2$ ;  $\text{CF}_3 + \text{NO} \rightleftharpoons \text{CF}_2\text{NO}$ . Above 2500°K,  $2 \text{CF}_2\text{NO} \rightarrow 2 \text{CF}_2\text{O} + \text{N}_2$ . He does believe that the latter reaction occurs as a bimolecular event.

An extensive investigation of the interconversion of fluorocarbons in shock tubes has been reported by Bauer and coworkers.<sup>(96)</sup> Mixtures ranging from 0.5% to 3% in argon of perfluorinated ethylene, cyclopropane, cyclobutane, cyclohexane, propene and butadiene were investigated in a single-pulse shock tube. The reaction mixtures were maintained for about 1 millisecond at specified temperatures and rapidly quenched. Plots of product distribution as a function of reflected shock temperatures were prepared. For example, a product distribution plot for perfluoroethylene shows the initial production of cyclobutane, its rapid decline at 1000°K with a concurrent rise in the amount of propene and cyclopropane, followed by a slow rise in the production of butene-2. These products pass through a maximum between 1800 and 1900°K, and then decline. Above 2100°K, decomposition of perfluoroethylene leads to products which are not preserved in the gas phase. All the products observed may be accounted for by simple sets of fragmentation steps in which CF<sub>2</sub> is the dominant radical. The kinetic simplicity of the C/F system is in striking contrast with the still unresolved complexities of the kinetics of the C/H system; the crucial differences are (a) the relative ease of migration of hydrogen atoms and (b) the high stability of the CF<sub>2</sub> radical. Thus, C/F compounds pyrolyze by breaking C-C bonds, but there is little rearrangement in the free radicals due to F atom migration.

The pyrolysis of ethylene highly diluted in neon was investigated by Gay and coworkers.<sup>(97)</sup> The temperature range covered 1710°-2170°K in reflected shock with pressures of 225 to 1600 torr. Products of pyrolysis were analyzed by leaking into a mass spectrometer. The reported rate law shows unit order dependence on ethylene and half order dependence on neon.

$$-\frac{d[C_2H_4]}{dt} = k_{3/2} [C_2H_4] [Ne]^{1/2}; \log_{10} k_{3/2} = 0.01 - 50,500/2.303RT; \text{conc. in molecules cm}^{-3}$$

These results may be fitted equally well by a unimolecular process and by a free radical chain mechanism. However, the low activation energy is difficult to explain since it is only slightly larger than the difference between the enthalpies of acetylene plus hydrogen and of ethylene at the reaction temperatures.

Wing Tsang is continuing with his single-pulse shock tube studies of the thermal decomposition of low molecular weight alkanes and alkenes. (98,99) Many of the difficulties inherent in single-pulse shock tube techniques are minimized in this work, since he measures comparative rates, using the unimolecular decyclization of cyclohexene as an internal standard.

$$k_u (C_6H_{10} \rightarrow C_2H_4 + 1,3-C_4H_6) = 10^{15.02} \exp(-66,700/RT), \text{ sec}^{-1}.$$

His results are summarized in Table V (taken from Table II, ref. 99). The possibility of extending the comparative rate method to other types of reactions is intriguing, but it appears to be difficult to apply to other than unimolecular decompositions. It is essential that the reference reaction remain unaffected, and not participate in the reaction being studied. When free radicals abound, the possibility of maintaining parallel but independent paths for concurrent reactions is small indeed.

#### BRIEFLY ON HOMOGENEOUS ATOM EXCHANGE PROCESSES

There are very few clearly established gas phase reactions of the type  $AB + X_2 \rightarrow AX + BX$ ; those which are known do not follow the simple rate expression

$$\frac{d[AX]}{dt} = \frac{d[BX]}{dt} = k [AB] [X_2].$$

It should be noted that to force this reaction to follow a molecular mechanism (4-center transition state) it must be carried out under strictly homogeneous conditions (no hot walls), at the lowest possible temperatures, to minimize contributions from  $X_2 \xrightarrow{\text{wall}} 2X$ ;  $X + AB \rightarrow AX + B$ ;  $AB + X \rightarrow A + BX$ . The results of a shock tube study of the homogeneous four-center reaction  $H_2 + D_2$  have been reported over a year ago, as was the exchange reaction between  $CH_4$  and  $D_2$ . (100,101) Heuristic rate expressions for these systems are summarized in Table VI. These results, although unexpected, can be rationalized by assuming that exchange occurs with high probability only during the encounters between pairs of diatoms, one of which is vibrationally excited to a state approximately 0.4 of the way to dissociation. It appears that the probability for metathesis is low when molecules in low-lying vibrational states collide, even when the relative kinetic energy along the line of centers (plus vibrations) exceeds the activation energy. Support for this mechanism is provided by approximate calculations of the pre-exponential term for the exchange rate constant from vibrational relaxation data.

These simple reactions present a challenge to the theorist. The only calculation (106) which has been made of the transition probability for exchange as a function of vibrational excitation ( $H_2 + H_2$ ) does show that the probability increases rapidly with vibrational excitation. However, it does not do so rapidly enough to overcome the lower population of the vibrationally excited states as controlled by the Boltzmann term. In this calculation, the representative point for the collision event moves in a classical trajectory, but the potential surface was obtained by a semi-empirical quantum mechanical procedure. We can only reach the conclusion that

apparently classical collision theory is not adequate. This is supported by the observation that in the vibrational excitation of homoatomic diatomic molecules the self atoms have a very high efficiency for vibrational excitation and for dissociation, but these effects have not yet been deduced theoretically.

#### SHOCK TUBE STUDIES OF COMBUSTION REACTIONS

Shock tube investigation of ignition delays is continuing at a modest level. The emission of visible light was used as a criterion for ignition in estimating delays as the function of temperature and composition for propane and methylcyclohexane.<sup>(107)</sup> Inhibition of the hydrogen-oxygen reaction by small amounts of methane, ethylene, trifluoromethylbromide, and 1,2-C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub> was measured over the temperatures 970°-1300°K.<sup>(108)</sup> Ignition was detected photoelectrically from the light emitted at the 3090-3100Å band pass for OH, while the induction time was defined as that between the arrival of the reflected shock at the window and the time at which emission reached a maximum. The compounds listed inhibit ignition by reacting with the hydrogen atoms and other radicals which propagate the chain, but it is not essential that the additives first decompose. As for the initiation step of the branching chain for the H<sub>2</sub>/O<sub>2</sub> reaction, Ripley and Gardiner<sup>(109)</sup> showed, by comparing experimental ignition delays with those calculated utilizing a full set of reactions, that initiation by a path other than diatom dissociation must occur. They proposed the exchange reaction  $H_2 + O_2 \rightarrow 2 OH$  as one which would account for the data.

Gardiner and coworkers<sup>(12)</sup> have effectively used the laser-schlieren technique for measuring density gradients and correlating the time profile for chemiluminescence with that for heat release in the oxidation of acetylene. They found that the OH absorption appeared at the end of the combustion, and that the OH profile was not directly related to the induction period chemistry. Apparently the OH profiles were related to the approach to partial equilibrium, including the reaction  $OH + CO \rightleftharpoons CO_2 + H$ . The formation of C-O bonds at partial equilibrium conditions indicates that the heat of reaction is liberated without recombination steps, in contrast to the thermal sequence which is followed in the H<sub>2</sub> + O<sub>2</sub> reaction. The C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> reaction has also been investigated by Homer and Kistiakowsky<sup>(110,111)</sup> who recorded emissions by CO and CO<sub>2</sub> in the infrared, and compared them with the UV emission at the band head 433A (A<sup>2</sup>Δ - X<sup>2</sup>Π) transition for CH. They concluded on the basis of the observation that the time constants for CO and CO<sub>2</sub> were identical; that the reaction CO + OH → CO<sub>2</sub> + H does not apply to the initial stages of oxidation. They demonstrated that the time constant for CO emission was twice that for CH\*, which supports those mechanisms wherein CH\* is produced by second order processes in the chain, such as C<sub>2</sub> + OH → CO + CH\*. These results are not in disagreement with the mechanism for C<sub>2</sub>H<sub>2</sub> combustion proposed by Glass et al.<sup>(112)</sup>

A large amount of shock tube data has been assembled on the oxidation of ethylene.<sup>(113)</sup> Chemiluminescence by CH\* revealed induction periods, followed by exponential rise of the signals. Measurements of time-dependent species composition with a TOF mass spectrometer can be represented by a rather complex reaction scheme, based on branching chain oxidation steps. The most abundant chemi-ions were C<sub>3</sub>H<sub>3</sub><sup>+</sup> and H<sub>3</sub>O<sup>+</sup>. The mechanism proposed for C<sub>2</sub>H<sub>4</sub>/O<sub>2</sub> is tentative. A similar technique was followed in the study of the pyrolysis and oxidation of formaldehyde in shock waves.<sup>(114)</sup> The pyrolysis shows first order dependence on the formaldehyde and on the inert gas. There is a temperature-dependent induction period. Experiments with formaldehyde-d<sub>2</sub> show that the pyrolysis proceeds by a radical chain mechanism. The formation of the radical H<sub>3</sub>CO has been detected. The observed activation energy (28 kcal/mole) is surprisingly low but is consistent with many other low values observed for initial stages of pyrolytic reactions as measured in shock tubes. The

first stage in the oxidation consists mainly of the decomposition of  $\text{CH}_2\text{O}$  into  $\text{CO}$  and  $\text{H}_2$ , followed by a branching chain oxidation of the hydrogen as well as of the remaining formaldehyde.

The oxidation of ammonia under homogeneous conditions has been studied by Takeyama and Miyama.<sup>(115)</sup> When mixtures of  $\text{NH}_3$ ,  $\text{O}_2$  and Ar were shock-heated to temperatures  $1550^\circ\text{--}2300^\circ\text{K}$ , there was a delay in the appearance of OH, and as in the case of the  $\text{H}_2/\text{O}_2$  reaction,  $\log (\text{O}_2)\tau$  varied linearly with the reciprocal of the temperature. Following the induction period, the early stages of the reaction were monitored by recording the UV absorption by  $\text{NH}_3$  at  $2245\text{\AA}$ . They found

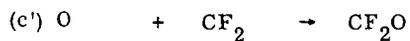
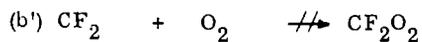
$$-d[\text{NH}_3]/dt = k_0 [\text{NH}_3]^{1.5} [\text{O}_2]^{0.5} [\text{Ar}]^{0.5}$$

The apparent activation energy is  $38.8 \pm 2.6$  kcal/mole.

The oxidation of hydrogen sulfide in shock waves<sup>(116)</sup> was observed by measuring the concentration of OH (in absorption) and of the generated  $\text{SO}_2$  at 2909A and 2812A. The studies covered the temperature range  $1350^\circ$  to  $2450^\circ\text{K}$ . Two regimes were recognized; below  $1560^\circ\text{K}$ , OH and  $\text{SO}_2$  appear concurrently after an induction period. Above  $1700^\circ\text{K}$ ,  $\text{SO}_2$  appears before OH. The authors proposed a branching chain mechanism, which at the higher temperatures includes the reaction  $\text{O} + \text{H}_2\text{S} \rightarrow \text{SO} + \text{H}_2$ . This provides an additional route for the formation of  $\text{SO}_2$  and leads to a reduction in its induction period. They also found that the addition of hydrogen did not alter the basic features of the hydrogen sulfide oxidation. Additional hydrogen did reduce the induction period for the appearance of  $\text{SO}_2$  and OH. The oxidation of  $\text{H}_2\text{S}$  is accelerated by hydrogen but the oxidation of hydrogen appears to be inhibited by  $\text{H}_2\text{S}$ .

A single-pulse shock tube study of the oxidation of perfluoroethylene was referred to above.<sup>(96)</sup> The mechanism of oxidation of fluorocarbons is characterized by comparative simplicity, in contrast to the many unresolved problems which remain in the area of hydrocarbon oxidations. The key feature is the rapid production of  $\text{CF}_2$ , which reacts with the oxygen according to the following scheme:

				$\Delta H_{300}^\circ$ (JANAF)
				kcal/mole
(a)	$\text{C}_2\text{F}_4$	$\rightleftharpoons$	$2 \text{CF}_2$	+ 76.1
(b)	$\text{CF}_2$	+ $\text{O}_2$	$\rightarrow \text{CF}_2\text{O} + \text{O}$	- 52.4
(c)	$\text{O}$	+ $\text{C}_2\text{F}_4$	$\rightarrow \text{CF}_2\text{O} + \text{CF}_2$	- 95.5
(d)	$\text{CF}_2$	+ $\text{CF}_2\text{O}$	$\rightarrow \text{CF}_3 + \text{CFO}$	+ 38.4
(e)	$\text{CF}_2$	+ $\text{CFO}$	$\rightarrow \text{CF}_3 + \text{CO}$	- 58.5
(f)		$2 \text{CF}_3$	$\rightleftharpoons \text{C}_2\text{F}_6$	- 92.8
(g)	$\text{CF}_2$	+ $\text{C}_2\text{F}_4$	$\rightleftharpoons \text{C}_3\text{F}_6$ (propene)	- 63.8
(h)	$\text{C}_3\text{F}_6$	+ $\text{O}$	$\rightarrow \text{CF}_2\text{O} + \text{C}_2\text{F}_4$	-107.8
(i)	$\text{CF}_2$	+ $\text{C}_2\text{F}_6$	$\rightarrow \text{CF}_4 + \text{C}_2\text{F}_4$	- 17.0
(j)	$\text{CF}_3$	+ $\text{CFO}$	$\rightarrow \text{CF}_4 + \text{CO}$	- 91.



~171.

This sequence accounts for the observed product distributions as functions of the temperature, for several compositions of ethylene and oxygen. The detailed confirmation of the individual steps and their reaction rate constants will have to be obtained from mass spectrometric diagnostics.

#### CONCLUSION

It is amusing to attempt to pinpoint the salient features of shock tube chemical kinetics. Among the many attractive ones, the most worthwhile in my opinion is the specificity in identification of transient species (and of states) on a time-resolved basis; the most troublesome is the lack of sufficiently precise temperature measurement; the most intriguing is the need to exploit sophisticated computer programs in order to unravel the coupling of reactions in a complex system.

#### ACKNOWLEDGMENT

This work was supported by the AFOSR under Grant No. AF49(638)-1448, to whom sincere thanks are due.

TABLE I. Instrumentation and Techniques

Description	Function	Author	Ref.
Heated shock tube; driven gas: pure Cs vapor (1 torr)	Plasma generation (16,000°K); study of magneto-fluid dynamics	H. G. Ahlstrom and P. A. Pincosy	STS #1
Heated shock tube (300° C) driven gas: Hg vapor	Plasma dynamics and spectroscopic studies	Y. W. Kim and O. Laport	STS #F10
Vaporization of aerosol in shock tube; metal wire exploded in controlled atm. prior to shock heating	0.05μ particles Al produced; spectra of vaporized ablation products	W. H. Wurster	STS #B3
Particles dispersed in test gas prior to shock heating (3-5μ teflon)-record emission and absorption spectra	Study of burn-up rates of small particles	R. Watson, <u>et al</u>	STS #F4
Alkali halide smoke in Ar - record absorption spectra	Study dissociation of MX into ions-time resolved spectra	M. Coplan, <u>et al</u>	STS #E8
Electric shock tube	Improvement in linear driver	R. G. Fowler	(4)
Spectroradiometric pyrometer; resolving time: 10μ sec	Measure temperatures of shock heated gases, and of self sustaining detonations	G. J. Penzias, <u>et al</u>	(5)
Relative emission intensities at two wavelengths in a molecular band system	Estimate temperature of shock heated gases	R. Watson	(6)
Induction flow meter (transverse Field)	Measure gas velocities in shock tubes-ionizing conditions	P. A. Croce	(7)
Electron beam probe; fluorescence stimulated by 17.5 KV electrons	Measure density in free jets and shock fronts; estimate rotational and vibrational temperatures	P. V. Marone	(8)
Laser light source	Diffusive separation of He, Ar in jets	D. E. Rothe	(9)
Single-pulse shock tube - double diaphragm design (exploding wire diaphragm opener)	For schlieren and interferometer systems - measure densities and gradients General pyrolysis studies	A. K. Oppenheim, <u>et al</u> S. Witting	(10) STS #48

TABLE II. On Non-Ideal Behavior of Shock Tubes

Topic	Coverage	Author	Ref.
Temperature variation behind attenuating shocks	2000-2700° K in O <sub>2</sub> , N <sub>2</sub> Used Na line reversal <sup>2</sup>	T. A. Holbeche and D. A. Spence	(25)
Flow non-uniformity when shock front and contact surface have reached maximum separation	All fluid properties increase in value; non-uniformity greatest when $\gamma$ is large and M is low; applies to turbulent and laminar boundary layers.	H. Mirels	(26)
Attenuation of shock due to non-equilibrium ionization and radiation	Attenuation calculated using linearized theory, with $\alpha \ll 1$ .	J. Rosciszewski	(27)
Radiative cooling and self absorption--- effect on flow field and on heat transfer behind reflected shock waves in air	Numerical calculations for radiating reflected shock heated plasmas (air)	R. M. Nerem and R. A. Golobic	(28)
Brightness temperature of shock waves in xenon and air	Effect of self-absorption of radiation emitted by shock front on estimation of brightness temperature; theoretical analysis	A. E. Voitenko, <u>et al</u>	(29)

TABLE III. Ionization Cross-Sections and Oscillator Strengths

Substances	Measurement of --	Results	Author	Ref.
Kr and Xe	Identify ions in shock heated mixtures via mass spectra	Impurity ions present; no di-atomic ions appeared	R. Creswell, <u>et al</u>	(30)
Ar, Kr and Xe (5000-9000°K)	Ionization relaxation times from micro-wave attenuation; high purity system	Quadratic dependence on density; rate controlling step is excitation to lowest group of excited states	A. J. Kelly	(31)
Ar (monitor continuum emission at 4900°A)	Effect of impurities on time required to reach half of maximum intensity.	Pronounced effects due to H containing impurities	P. B. Coates	(32)
Ar	Ionization relaxation times (micro-waves)	Impurities blamed for very short times	S. Naki, <u>et al</u>	(33)
Air	Ionization rates behind strong shocks from IR emission at 6μ (free-free bremsstrahlung).	N + O → NO <sup>+</sup> + e <sup>-</sup> is pre-dominant mechanism for shock speeds less than 9.5 mm/μsec	J. Wilson	(34)
Cr(CO) <sub>6</sub> in Ar	Ionization mechanism for Cr, from time resolved Cr(I) and Cr(II) emission spectra	Initial rate controlled by excitation to 3.1 ev lengths for Cr(I); rapid excitation to higher levels; ionization from excited states	W. L. Shackelford <u>et al</u>	(35)
Cr(CO) <sub>6</sub> in Ar--reflected shocks	gf - values for Cr(II) from emission intensities at 8000°K	21 lines in region 3118-4559Å; these values are ≈0.1 of values obtained from arc spectra	W. L. Shackelford	(36)
Ar-CO (1/1)	C <sub>2</sub> emission; matrix element for 3Π <sub>g</sub> -3Π <sub>u</sub> (Swan) bands	Calculated equi. C <sub>2</sub> concentration; Report f = -.022 ± .008	A. G. Sviridov, <u>et al</u>	(37)
Ar-CO (1/1)	C <sub>2</sub> absorption - Swan band system	Calculated equi. C <sub>2</sub> ; estimated  R <sub>e</sub>   <sup>2</sup> = 0.44 ± 0.08 a. u.	A. G. Sviridov, <u>et al</u>	(38)
C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> N <sub>2</sub> , CO	Incident shocks - Swan band emission	f <sub>Swan</sub> = -0.033 ± 0.012	A. R. Fairbairn	(39)
C <sub>2</sub> CF <sub>3</sub> , CF <sub>4</sub> , C <sub>2</sub> F <sub>4</sub>	Emission intensities for C <sub>2</sub> (A 3Π - X 3Π), and CF (A 2Σ - X 2Π)	f <sub>Swan</sub> = -0.028 ± .009 f <sub>CF</sub> = 0.0051 ± .0015	J. A. Harrington <u>et al</u>	(40a, b)
Air	Various band systems for N <sub>2</sub> , O <sub>2</sub> , NO, H <sub>2</sub> O	Oscillator strengths for intense bands; (ff) and (fb) continua	xxx	(41)
SO <sub>2</sub> -Ar	Spectroscopically resolved emission intensities	Broad band due to three excited states (C, <sup>1</sup> B <sub>2</sub> , <sup>3</sup> B <sub>1</sub> )	B. P. Levitt and D. B. Shien	(42)

TABLE IV: Dissociation Rate Studies

Molecule	Medium	Experiment or Theory	Results	Author	Ref.
O <sub>2</sub>	Ar	Analysis of ladder climbing process	$k_d \propto [1 - \exp(-h_\omega/kT)] \times \exp(-D/RT)$	N. V. Kondratiev and E. E. Nikitin	70
2O → O <sub>2</sub> + hν		Radiative recombination data; 2500° to 3800°K	Intensity $\propto (O)^2$ apparent $E_A = 28.9 \pm 2.2$	B. F. Myers and E. R. Bartle	STS #29
O	O <sub>2</sub>	Gladstone-Dale constant measured for O <sub>2</sub> and O	O <sub>2</sub> : G. D. = 1.93 cm <sup>3</sup> /gm O: G. D. = 2.04 cm <sup>3</sup> /gm	J. H. B. Anderson	STS #E4
N <sub>2</sub>	Ar	Dissociation rates; incident shocks (6000° - 9000°K)	Relative efficiencies N > N <sub>2</sub> > Ar by 15:1:½	S. Byron	71
N <sub>2</sub>	Kr	Dissociation rates; incident shocks (5000° - 9000°K) 5% - 10% - 25% - 50%	Analysis incomplete (results agree with 71)	E. Wachslar	72
F <sub>2</sub>	Ne, Ar	TOF mass spec (1650° - 2700°K)	$E_A \approx 27$ kcal/mole; general agreement with previous work	R. W. Diesen	73
F <sub>2</sub>	Kr, Xe	Light absorption; dependence on F <sub>2</sub> concentration	For Ar, $E_A = 27.3 \pm 2.5$ kcal/mole Kr essentially like Ar; Xe-F <sub>2</sub> complex indicated (under shock conditions)	D. J. Seery and D. Britton	74
Cl <sub>2</sub>	Ar	Radiative recombination rates for 1:5 Cl <sub>2</sub> -Ar mixtures; 1735° - 2582°K.	$k_r = 10^{13.94} \exp(-48,300/RT)$ cm <sup>3</sup> mole <sup>-1</sup> sec <sup>-1</sup>	R. A. Carabetta and H. B. Palmer	75
Br <sub>2</sub>	Ar	Radiative recombination rates	Details not given - cite agreement with previous investigations	T. R. Lawrence and G. Burns	STS #B5

TABLE V. Rate Parameters for the Fission of Simple Hydrocarbons  
 (from ref. 99)

Reaction Product	CH <sub>3</sub>		CH <sub>3</sub> CHCH <sub>3</sub>		CH <sub>3</sub> $\overset{\text{CH}_3}{\underset{ }{\text{C}}}$ -CH <sub>3</sub>		CH <sub>2</sub> =CH-CH <sub>2</sub>	
	log <sub>10</sub> A	E <sub>A</sub>	log <sub>10</sub> A	E <sub>A</sub>	log <sub>10</sub> A	E <sub>A</sub>	log <sub>10</sub> A	E <sub>A</sub>
CH <sub>3</sub>	15.0	82.8	16.0	80.2	16.1	78.2	15.0	70.3
CH <sub>3</sub> CHCH <sub>3</sub>			16.1	76.0	16.2	73.0	15.7	67.9
CH <sub>3</sub> $\overset{\text{CH}_3}{\underset{ }{\text{C}}}$ -CH <sub>3</sub>					16.3	68.5	15.8	65.5
CH <sub>2</sub> =CH-CH <sub>2</sub>							14.2	59.3

TABLE VI. Summary of Molecular Exchange Reactions, in Shock Tubes

$$d[AX]/dt = k[AB]^\alpha [X_2]^\beta [Ar]^\gamma$$

AB	X <sub>2</sub>	$\alpha$	$\beta$	$\gamma$	E <sub>A</sub> (kcal/mole)	A(T <sup>3/2</sup> ) [moles/liter]	Ref.
H <sub>2</sub>	D <sub>2</sub>	0.38	0.66	0.98	42.26 ± 2.1	10 <sup>9.84</sup> T <sup>1/2</sup>	100
HSH	D <sub>2</sub>	0.47	0.98	0.61	52.3 ± 2	10 <sup>10.43</sup> T <sup>1/2</sup>	103
HNH <sub>2</sub>	D <sub>2</sub>	≈ 0	≈ 1	≈ 1	39 ± 3	10 <sup>8</sup> T <sup>1/2</sup>	102
HCH <sub>3</sub>	D <sub>2</sub>	0.3	1.1	0.6	52.00 ± 2.2	10 <sup>9.04</sup> T <sup>1/2</sup>	101
N <sub>2</sub> (28)	N <sub>2</sub> (30)	0.5	0.5	1.0	116 ± 3	10 <sup>10.82</sup>	104
O <sub>2</sub> (32)	O <sub>2</sub> (36)	0.5	0.5	≈ 1.0	37 ± 4	10 <sup>9</sup>	105

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