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RECOMBINATION OF CARBON MONOXIDE AND ATOMIC OXYGEN AT HIGH TEMPERATURES*

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SUMMARY

Recombination of carbon monoxide and atomic oxygen was studied in the expansion wave of a single-pulse shock tube at temperatures from 2800° to 3600° K and pressures from 8.8 to 22.6 atmospheres. This technique was found to be a simple and valuable means of studying high-temperature recombinations. Measurements of incident shock velocity and of pressure in the reflected zone, combined with relatively simple calculations of chemical equilibria, sufficed to determine quite accurately the initial conditions before expansion.

Rate constants were derived from measurements of the intensity of carbon monoxide flame-band emission, which is proportional to the product of carbon monoxide and atomic oxygen concentrations. A three-body mechanism of recombination was assumed, and the results were consistent with this assumption. The rate constants for recombination had an average lower limit of 2×10^{13} centimeter^{6} mole^{-2} second^{-1} and an estimated upper limit of about 1×10^{14} centimeter^{6} mole^{-2} second^{-1} over the range of the experiments. These values are in the range of recombination constants derived from equilibrium constants and dissociation rates of carbon dioxide measured behind shock waves. The recombination rates found in the present work were lower than expected on the basis of previous direct measurements made at lower temperatures. It is suggested that surface and water catalysis may have combined to produce these discrepancies.

INTRODUCTION

In order to understand and to predict the performance of propulsive devices and the flow around hypersonic bodies, knowledge of the recombination rates of atoms and other

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molecular fragments at high temperatures is important. However, only a few direct measurements of these rates have been made under the conditions of interest, and it is necessary more often than not to calculate them from equilibrium constants and measured dissociation rates. The validity of this approach is no longer seriously questioned in view of recent theoretical (refs. 1 and 2) and experimental (refs. 3 and 4) work, but even so, determination of the recombination rates is important as a check on the dissociation rates.

The present work was undertaken to study the recombination of carbon monoxide (CO) and atomic oxygen (O). This reaction involves the formation of a molecule considerably more complex than the homonuclear diatomics that have been the main subject of previous high-temperature recombination studies. Furthermore, the overall process requires a change of spin. The results of previous investigators, all of whom studied the reaction at low pressures and at temperatures up to a few hundred degrees centigrade, are in considerable disagreement. For these reasons, the reaction between CO and O is a very interesting one and well worth studying under new conditions. The present experiments were carried out in a single-pulse shock tube at much higher temperatures and pressures than any employed previously.

EXPERIMENTAL

Method

Dilute mixtures of carbon dioxide (CO_2) in argon (Ar) were heated by the reflected shock wave in a single-pulse shock tube (ref. 5) and were held at high temperatures long enough to reach the equilibrium level of dissociation to CO and O. An expansion wave, generated by rupturing a second diaphragm into a large dump tank, then arrived and cooled the partly dissociated mixture, thus provoking recombination.

The primary data included incident shock velocity, pressure in the reflected zone, and intensity of the blue CO flame-band emission. Pressure and light were observed 6 millimeters from the end wall of the tube. At such a short distance, the gas is practically motionless during expansion because of the nearby reflection of the expansion wave; thus, the observed rate data did not have to be corrected for bulk gas motion.

The flame-band intensity is proportional to the product of the concentrations of CO and O in their electronic ground states (refs. 6 and 7). This relation holds if the mixture is at equilibrium (refs. 8 and 9), or if the excited species responsible for emission is in a steady state (refs. 6 and 7). Davies (ref. 10) has discussed the errors which can arise if flame-band intensity is used to follow the product $([CO][O])$ in a kinetic situation that is not steady state with respect to the emitter. However, the errors must be small in the present work; as will be seen, the data suggest that the light-producing process can indicate $([CO][O])$ in the presence of the most rapid physical and chemical changes encountered.

Apparatus

The shock tube used has been described in reference 8. Incident shock velocity was measured by means of three miniature piezoelectric pickups, which triggered the start-stop circuits of two microsecond counters. A calibrated quartz piezoelectric gage measured the pressure behind the reflected shock and during expansion. Flame-band intensity was followed at either 4000 or 4755 Å. The light was strong enough in many runs to drive the photomultiplier past its range of linear response. To correct for this, the response curve was determined with the aid of a set of neutral-density filters calibrated at the same wavelengths. Aside from differences in photomultiplier sensitivity and in the inherent strength of the emission, there was no difference in the results of experiments at the two wavelengths.

Initial Gas Mixtures

Mixtures of CO_2 and Ar were prepared as described in reference 8; high-purity gases and cold traps were used to eliminate moisture and to exclude hydrogenous material such as pump oil. The following mixtures were used: 0.03 CO_2-0.97 Ar, 0.07 CO_2-0.93 Ar, and 0.03 CO_2-0.01 O_2-0.96 Ar. The last mixture, with added O_2, was included to provide a wider range of $[CO]/[O]$ ratios in the partly dissociated gas.

Equilibrium State Before Expansion

Before recombination could be studied in the expansion wave, it was essential to confirm that the pressure, temperature, and composition of the partly dissociated gas were accurately known.

Figure 1 is a reproduction of a typical oscillogram. Because of gas dynamic effects in the tube (ref. 11), the pressure (upper trace) rose, at first gradually and then more rapidly, to a plateau considerably higher than the initial reflected-shock pressure. The initial pressure, however, agreed very closely with the value predicted (ref. 12) from incident shock velocity, assuming thermal equilibrium and no dissociation.

If the initial temperature and pressure behind the reflected shock were sufficiently

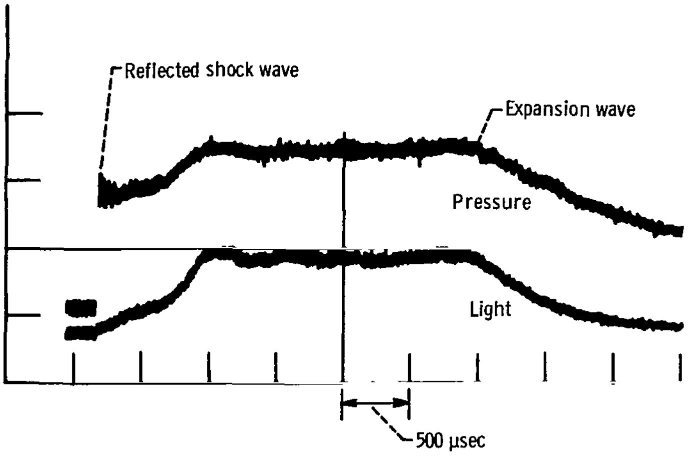


Figure 1. - Carbon monoxide flame-band emission from recombining carbon monoxide and atomic oxygen.

high, the flame-band intensity (lower trace) rose to a level plateau (about 1.7-msec duration), which was taken as a sign that chemical equilibrium had been achieved. The equilibrium temperature and composition were computed to be the result of isentropic compression with simultaneous chemical equilibrium from the initial reflected-shock pressure to the final plateau pressure. These computations made use of equilibrium compositions supplied by the machine program of Gordon and Zeleznik (ref. 13).

Figure 2 shows the calculated quantity $([CO][O])$ plotted against light intensity corrected for nonlinearity in the photomultiplier response. The relation is accurately linear, as it should be. The data points represent observations at both wavelengths; inasmuch as the optical system was not equally sensitive at both and the flame-band intensity is greater at 4000 Å, data for the shorter wavelength were multiplied by a constant to fit them on the same graph.

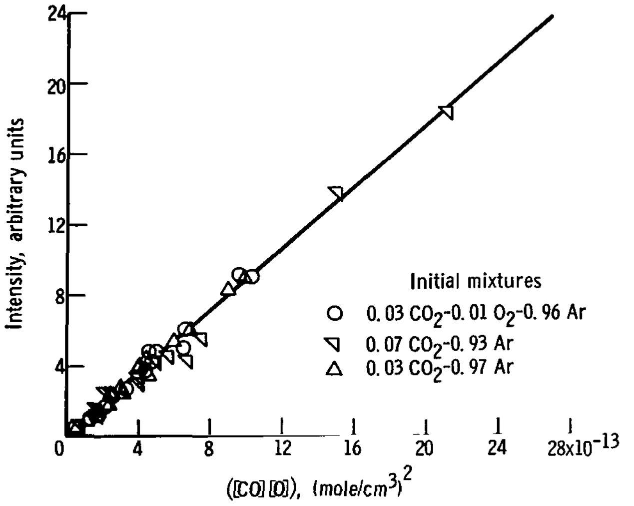


Figure 2. - Flame-band intensity in equilibrium mixture behind reflected shocks. Temperature, 2800° to 3600° K; pressure, 8 to 22 atmospheres.

It should be noted that the assumption of constant entropy employed in computing the equilibrium state cannot be rigorously correct, because chemical equilibrium obviously does not exist at every instant during compression. However, figure 1 shows that the pressure and light traces leveled off at the same time; inasmuch as the light did not lag behind, near-equilibrium evidently prevailed during the final stages and perhaps during most of the compression. The excellent cor-

TABLE I. - EXPERIMENTAL CONDITIONS AND RATE CONSTANTS

(a) Freezing-point runs

Run	Unshocked composition, mole fraction (remainder Ar)		Condition at start of expansion				Freezing point condition		Recombination rate constant, k_1, $cm^6 mole^{-2} sec^{-1}$
			Temperature, °K	Pressure, atm	Composition, mole fraction		Temperature, °K	Pressure, atm	
	CO_2	O_2			CO	O			
1	0.03	----	3542	16.67	0.0247	0.0110	3296	12.98	1.40×10^{13}
2	.03	0.01	3535	15.42	.0232	.0158	3380	12.63	.67
3	.07	----	3292	22.63	.0402	.0075	3054	16.15	1.46

(b) Normal runs

Run	Unshocked composition, mole fraction (remainder Ar)		Condition at start of expansion				Pressure-decay time constant, τ, sec	Recombination rate constant, k_1, $cm^6 mole^{-2} sec^{-1}$
			Temperature, °K	Pressure, atm	Composition, mole fraction			
	CO_2	O_2			CO	O		
4	0.03	----	3370	16.67	0.0223	0.0074	1.97×10^{-3}	1.16×10^{13}
5	.03	0.01	3237	15.15	.0179	.0075	1.94	1.66
6	.03	----	3165	17.15	.0185	.0040	1.95	1.87
7	.03	.01	3056	15.42	.0136	.0042	1.85	2.57
8	.07	----	3049	13.51	.0325	.0043	2.01	1.59
9	.03	----	3030	15.65	.0158	.0026	2.01	2.26
10	.03	.01	2913	8.75	.0120	.0033	1.89	6.55
11	.07	----	2902	15.38	.0245	.0021	1.96	1.49
12	.07	----	2784	13.17	.0199	.0013	2.00	1.83

relation shown in figure 2 indicates that the assumption of constant entropy did not introduce significant errors.

It is also worth noting that another computational scheme was tried and discarded. In this method, $([CO][O])$ was calculated as the consequence of isentropic compression of the undissociated CO_2-Ar mixture from the initial reflected-shock pressure to the plateau pressure, followed by dissociation at constant enthalpy. The results did not correlate well with light intensity data, as in figure 2 but instead were scattered, and data for the 0.07 CO_2-0.93 Ar mixture tended to lie on a separate curve.

Thus, the pressure, temperature, and composition of the equilibrium state are all known; they are listed in table I. Conditions at the start of expansion ranged from 8.75 to 22.63 atmospheres, and from 2784° to 3542° K.

RESULTS

Experimental Data

On arrival of the expansion wave, the light intensity began to fall (fig. 1). The expansion process was observed for about 1.5 milliseconds, during which time the temperature fell about 500° K and the pressure fell to about one-half its starting level.

The pressure decay was very accurately exponential except for a short period t* at the beginning of the expansion. For any time later than t*, which was usually 50 to 100 microseconds, the pressure was therefore related to initial pressure as

$$P = P_0 \exp\left[-\left(\frac{t - t^*}{\tau}\right)\right] = P_0 \exp\left(-\frac{t}{\tau}\right)\exp\left(\frac{t^*}{\tau}\right) \tag{1}$$

The time constant τ was obtained for each run by plotting the logarithm of P/P_0 against time (values listed in table I). The correction factor $\exp(t^*/\tau)$ for initial nonlinearity averaged about 1.03.

From the measured pressure history and starting equilibrium conditions, both chemically frozen and shifting-equilibrium expansions were computed (ref. 13). The resulting values of $([CO][O])$ divided by the initial value of $([CO][O])$ were plotted against time after the start of expansion. These two curves represent the boundaries between which the experimental data should lie (figs. 4 (p. 7) and 5 (p. 9).

Light intensity was measured at several times during the expansion, and its ratio to initial intensity was plotted in the same figures. If the intensity is indeed proportional to the concentrations of CO and O in the dynamic situation, the intensity ratio is equal to $([CO][O])/([CO][O])_0$. These plots revealed three distinct modes of behavior:

(1) When runs were attempted at the highest initial temperatures in table I or still higher ones, the intensity ratios often dropped below the computed equilibrium curve;

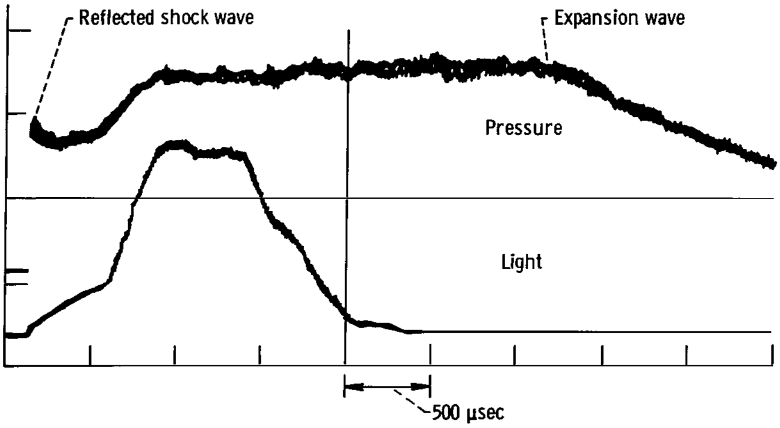


Figure 3. - Premature drop in light intensity due to arrival of cold driver gas at observation station.

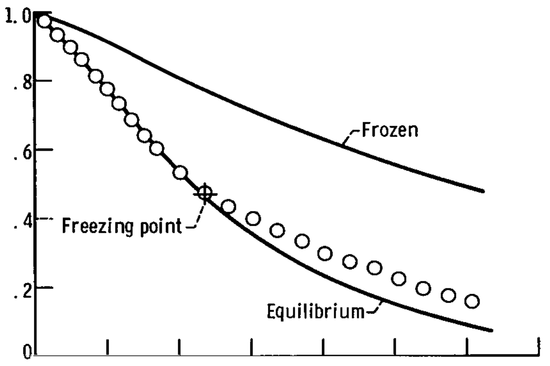
such runs were useless for kinetic purposes. This sometimes occurred during expansion, but it usually happened that the light began to decrease long before the expansion wave arrived. Figure 3 is a reproduction of the oscillogram from such a run. The plateau conditions were 14.37 atmospheres and 3473° K; inasmuch as the starting mixture contained 7 percent CO_2, much of which was dissociated at the plateau conditions, a strong incident shock was required to reach such a high temperature. Strong incident waves are inevitably accompanied by a shortened test time behind the reflected shock wave (ref. 14). Therefore, the early disappearance of light was undoubtedly due to the untimely and nonreproducible arrival of the contact zone. Inspection of figure 3 shows that a small pressure rise correlates with the abrupt drop in light intensity, and this pressure change is presumably the force that propelled the cold driver gas to the end of the tube. Such behavior explains why many of the runs yielded equilibrium intensity data for figure 2, but did not yield useful recombination data.

(2) In three cases - two at the two highest usable initial temperatures and a third at a lower temperature but at the highest pressure - the data adhered to the equilibrium curve at first and then departed from it. These runs are designated 1 to 3 in table I, and run 2 is plotted in figure 4(a). This behavior is reminiscent of the "freezing point" description of expansion in a reacting gas (ref. 15). It is reassuring that it was observed. One can scarcely attribute the close agreement between the data and the calculated curve to chance, and if the agreement is not fortuitous, the light intensity can indeed remain proportional to $([CO][O])$ under rapidly shifting conditions.

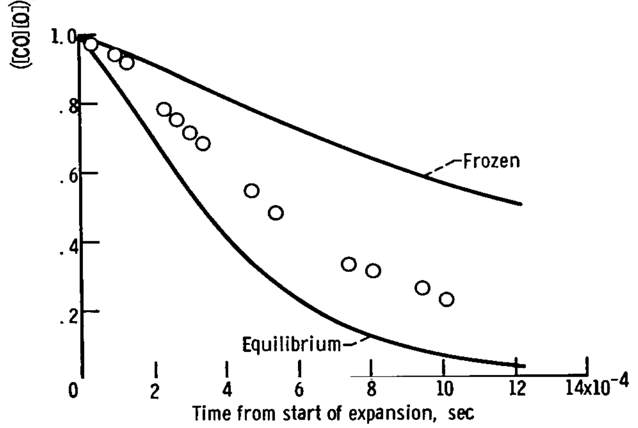
(3) The remaining nine runs, all at low-to-intermediate temperatures and pressures, behaved in a "normal" fashion. The data points fell between the computed frozen and equilibrium curves, as seen in figure 4(b).

Reduction of Data

Reaction mechanism. - The recombination reaction of CO and O was assumed to be



(a) Run showing freezing point (run 2).



(b) Normal run (run 9).

Figure 4. - Recombination of carbon monoxide and atomic oxygen during expansion.

$$CO + O + M \xrightarrow{k_1} CO_2 + M \qquad (I)$$

The question of whether the recombination is actually a three-body or a two-body reaction cannot be resolved by the present data in spite of the threefold range of pressures that was included. Previous workers, who studied the reaction at relatively low temperatures and pressures, have reported both the higher (ref. 16) and the lower (refs. 17 and 18) order. For the present work, reaction (I) is adopted as an assumption. The main advantage in so doing is that it permits direct comparison between the values of k_1 derived from this work and those calculated from the equilibrium constant and the rate constant of the reverse dissociation reaction, which is two-body over the pressure range of the present study.

To isolate the effect of reaction (I), the effect of oxygen recombination

$$O + O + M \xrightarrow{k_2} O_2 + M \qquad (II)$$

had to be taken into account. Values of k_2 were taken from the high-temperature recombination measurements of Wray (ref. 3) in which the third body was chiefly Ar, just as in the present work. Inasmuch as Wray deduced his rate constants from the expression

$$\frac{d\left[O_2\right]}{dt} = k[O]^2[Ar] \qquad (2)$$

the value of k_2 corresponding to the rate of disappearance of O in reaction (II) was just twice his reported value.

Freezing-point runs. - The three runs that exhibited a freezing point were analyzed by the method described in reference 19. The thermodynamic calculations for the equilibrium curve yielded the rate of change of the logarithm of mean molecular weight; at the freezing point, the value of this derivative is directly related to the known recombination rate constant k_2 and the unknown rate constant k_1. The reactions, of course, do not truly freeze at the freezing point, and the rate constants derived are therefore approximate. They ranged from 0.67×10^{13} to 1.46×10^{13} centimeter^6 mole^{-2} second^{-1}. Although these values must be regarded as approximate, this method of analysis does have the advantage that the rate constants it yields pertain to a well-defined temperature, namely, the temperature at the freezing point. It appears, therefore, that the rate of reaction (I) does not depend strongly on temperature.

Normal runs. - The runs that did not exhibit freezing had to be analyzed by other means. Figures such as figure 5 were helpful in determining what these means should be. The light-intensity data are plotted as before together with the equilibrium and frozen curves. In addition, there is a dashed curve, calculated on the assumption that only reaction (II), the O recombination reaction, occurred; the dissociation of O_2 was neg-

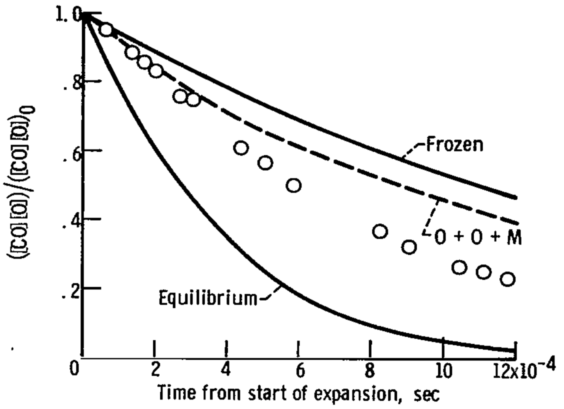


Figure 5. - Comparison of data with ([CO][O]) history calculated assuming only atomic oxygen recombination (run 12). Carbon monoxide and atomic oxygen recombination clearly contributes.

lected. Under these circumstances,

$$\frac{-d[O]}{dt} = k_2[O]^2[M]_0 \exp\left(\frac{t^*}{\gamma T}\right) \exp\left(\frac{-t}{\gamma T}\right) \qquad (3)$$

Here, $[M]_0$ is the total concentration at the start of expansion. The specific-heat ratio γ enters by way of equation (1) and the isentropic relation between pressure and density. Equation (3) can be integrated directly, and values of [O] computed for various times from the resulting expression were multiplied by the corresponding frozen CO concentrations and divided by the product of initial CO and O concentrations to produce the dashed curves. Equation (3) is valid when the mean molecular weight of the mixture is nearly constant and the density is not appreciably affected by the heat released in the chemical reaction; the equilibrium and frozen calculations showed that both conditions were well satisfied.

The dashed curves represent the fastest drop in light intensity that could possibly occur in the absence of any CO recombination, because the dissociation of O_2 was neglected. Nevertheless, in figure 5 it is seen that all the data points lie on or below the curve. It is evident, therefore, that CO-O recombination must contribute appreciably to the decay of $([CO][O])$.

In other plots like figure 5 the curves were found to lie below several points. Therefore, O_2 dissociation was not negligible in these cases. From such considerations, it became apparent that CO-O recombination was present in all cases and that the dissociation of CO_2 and of O_2 must be included in the analysis.

By definition,

$$\frac{d([CO][O])}{dt} = [O]\left(\frac{d[CO]}{dt}\right) + [CO]\left(\frac{d[O]}{dt}\right) \qquad (4)$$

Each of these concentrations varies with time because of reaction and because the total concentration [M] varies with time, even in the absence of reaction. Thus,

$$\left.\begin{aligned} \frac{d[CO]}{dt} &= \left(\frac{\partial[CO]}{dt}\right)_{[M]} + \left(\frac{\partial[CO]}{\partial[M]}\right)_t \frac{d[M]}{dt} \\ \frac{d[O]}{dt} &= \left(\frac{\partial[O]}{\partial t}\right)_{[M]} + \left(\frac{\partial[O]}{\partial[M]}\right)_t \frac{d[M]}{dt} \end{aligned}\right\} \qquad (5)$$

The first terms on the right of equation (5) are from the rate expressions for recombination reactions (I) and (II) and their reverse dissociation reactions. The second terms are derived from the relation between mole fraction and concentration in a gas mixture with nearly constant molecular weight and from the observed exponential pressure decay, as explained in connection with equation (3). When the resulting expressions are substituted into equation (4), the following equation is obtained:

$$\begin{aligned} \frac{d\ln([CO][O])}{dt} = -\left(\frac{2}{\gamma\tau}\right) &- k_1[M]_0^2\left[\exp\left(\frac{-2t}{\gamma\tau}\right)\exp\left(\frac{2t^*}{\gamma\tau}\right)\right](x_{CO} + x_O) \\ &- k_2[M]_0^2\left[\exp\left(\frac{-2t}{\gamma\tau}\right)\exp\left(\frac{2t^*}{\gamma\tau}\right)\right]x_O + k_1K_{CO_2}[M]_0\left[\exp\left(\frac{-t}{\gamma\tau}\right)\exp\left(\frac{t^*}{\gamma\tau}\right)\right]\left(\frac{x_{CO_2}}{x_{CO}} + \frac{x_{CO_2}}{x_O}\right) \\ &+ k_2K_{O_2}[M]_0\left[\exp\left(\frac{-t}{\gamma\tau}\right)\exp\left(\frac{t^*}{\gamma\tau}\right)\right]\left(\frac{x_{O_2}}{x_O}\right) \end{aligned} \qquad (6)$$

In equation (6), x is the mole fraction, and the equilibrium constants K_{CO_2} and K_{O_2} are given by

$$K_{CO_2} = \frac{k_{-1}}{k_1} = \frac{[CO][O]}{[CO_2]}$$

and

$$K_{O_2} = \frac{k_{-2}}{k_2} = \frac{[O]^2}{[O_2]} \qquad (7)$$

In other words, it has been assumed that the recombination rate constant is related to the dissociation rate constant by the equilibrium constant, in order to avoid having to specify a value for the dissociation rate constant.

Equation (6) was used in integrated form to derive values of k_1 from the experimental data obtained in the normal runs. To perform the integration, two additional assumptions were made: (1) the mole fractions were taken as constant at their initial values before expansion, and (2) the equilibrium constants were assumed to be those corresponding to the shifting equilibrium temperature history. With the aid of these assumptions, the first three terms of equation (6) could be integrated directly; however, the last two terms had to be integrated graphically because of the time variation imposed on the equilibrium constants.

Although these assumptions may seem quite arbitrary, they have desirable effects. As has been mentioned already, the reverse dissociation reactions must be incorporated into the analysis. If they are not, the rate constants deduced for various times in a given run increase continuously with time instead of remaining constant throughout the run, a result that is physically unrealistic. The question is how to assign a temperature history so that the equilibrium constants needed to produce the more realistic behavior can be specified. Choice of the shifting equilibrium temperatures, which are the highest values that could be achieved during expansion, leads to large equilibrium constants. As a result of the relative magnitudes of the various terms in the integrated form of equation (6), large equilibrium constants tend to give low values of k_1.

There is a second desirable effect of the assumptions. The mole fractions in equation (6) must be supplied because the experiment measures only the product of CO and O concentrations, and yields no independent information about the individual concentrations. The frozen mole fractions are the largest that could occur, and again, the use of these large values tends to depress k_1. Thus, these assumptions have the valuable effect of setting a lower bound on the values of k_1, and the method of analysis makes physical sense out of the data. The results are listed in table I. Eight of the nine normal runs yielded k_1 values between the surprisingly narrow limits of 1.16×10^{13} and 2.57×10^{13} centimeter^6 mole^{-2} second^{-1}.

DISCUSSION

Before the lower-limit rate constants are compared with other data, it is appropriate to inquire what the upper limit might be. The largest values of k_1 obtained by any method of analysis that could be applied resulted when dissociation was neglected and shifting equilibrium mole fractions were used to integrate graphically the appropriately modified version of equation (6). These mole fractions were the lowest that could prevail during expansion. Although the resulting values of k_1 increased with time during each run, the k_1 values near the end of the observations were approximately five times larger than the corresponding numbers listed in table I.

Infinitely large rate constants would result if the shifting equilibrium mole fractions were employed in the integration of equation (6). This trivial upper limit is due to the

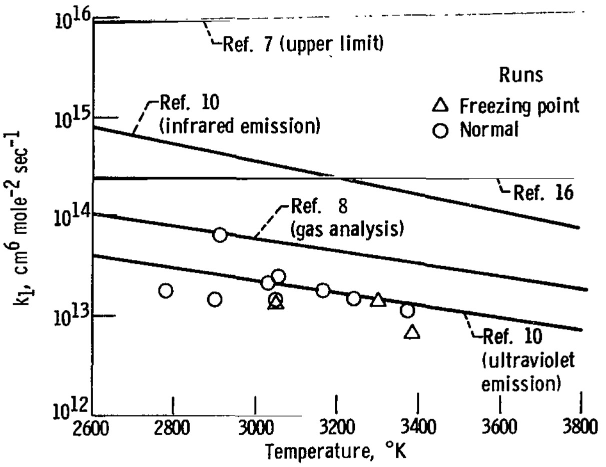


Figure 6. - Three-body recombination rate constants of carbon monoxide and atomic oxygen.

presence of the corresponding equilibrium constants in some of the terms, which causes their denominators to go to zero. However, it is clear from figure 5 (p. 9) that the mole fractions are by no means as small as the shifting equilibrium values.

In view of these considerations, it is thought that the upper limit of k_1 compatible with the data is no greater than 1×10^{14} centimeter^6 mole^{-2} second^{-1}.

The rate constants in table I are compared with other data in figure 6. Results from both the normal and the freezing-point runs are shown as data points. Also plotted are lines representing two other kinds of data. The three lines that show a strong negative temperature dependence are recombination rate constants calculated by equation (7) from three kinds of shock tube measurements of CO_2 dissociation rate; these lines represent essentially the whole k_1 range that could be obtained from dissociation data reported to date. The two nearly flat lines were obtained by long extrapolations of results from low-temperature studies of the direct CO-O recombination. Only the lower line, due to Kondrat'ev and Ptichkin (ref. 16), represents actual data deduced from CO_2 production. The other line is an upper limit based on the fact that Clyne and Thrush (ref. 7) did not detect any recombination in their flow system studies. The activation energies given in references 7 and 16 (3.7 and 2.1 kcal, respectively) were used to extrapolate to the temperature range of the present studies.

The lines calculated from dissociation rates (refs. 8 and 10) are in order-of-magnitude agreement with the lower-limit rate constants from the present work. One is even tempted to conclude that the data show a similar negative temperature dependence. This may be an illusion, however, induced by the two disparate points; in view of the approximate nature of the data reduction, the results were not thought to be precise enough to determine the effect of temperature. It seems preferable to adopt an average lower-limit rate constant of 2×10^{13} centimeter^6 mole^{-2} second^{-1} for the whole temperature range. The fact that the recombination constants deduced from dissociation rates are of similar size is gratifying, but the unresolved temperature dependence of the present data leaves open the question of whether the dissociation-recombination mechanism is simple or complex.

It is also clear that the data lie well below the recombination rates extrapolated from low temperatures. This difference would have been even more strikingly shown if the extrapolated results of low-temperature measurements that were interpreted in terms of a two-body recombination reaction (refs. 17 and 18) had been included in figure 6. These two-body rate constants, transformed to three-body constants by means of the total concentration at the pressure of the experiment, are one or two orders of magnitude higher than the Clyne and Thrush upper limit.

The present work does little to elucidate the reasons for such discrepancies. The temperature dependence cannot be determined, so it is not possible to use the high-temperature recombination rates to improve the extrapolation of low-temperature data. Furthermore, there is no new evidence on the molecularity of the reaction. It can only be said that the data are consistent with a three-body interpretation.

Nevertheless, there are qualitative arguments which suggest that the present results are more reliable than the direct measurements at low temperatures and that all the low-temperature data (with the possible exception of that from ref. 16) may well be too high. First, there is the matter of surface reaction. Its effects have been noted in explosion limit studies of the CO-O_2 system (ref. 20) and in the CO-O recombination work of references 18 and 21. Such effects are ruled out in shock tube work because the time scale is too short for the reactants to diffuse to the wall.

A second, and perhaps more important, consideration is the extraordinary sensitivity of CO oxidation to traces of water. This phenomenon can affect both shock tube experiments and experiments carried out at lower temperatures in bulbs or flow systems. Brokaw (ref. 22) analyzed induction times measured (ref. 23) behind shock waves in supposedly dry CO-O_2 mixtures in terms of the hypothetical "dry" CO oxidation mechanism (ref. 20):

$$CO + O_2 \rightarrow CO_2 + O \tag{III}$$

$$CO + O \rightleftarrows CO_2^* \tag{IV}$$

$$CO_2^* + O_2 \rightarrow CO_2 + 2O \tag{V}$$

$$CO + O + M \rightarrow CO_2 + M \tag{VI}$$

Brokaw found that physically impossible rate constants were required to explain the data. However, all the experimental facts could be explained by assuming that as little as 15 to 30 parts per million of water by volume were present. Its effects are exerted through the rapid reactions

$$O + H_2O \rightarrow 2OH \tag{VII}$$

$$OH + CO \rightarrow CO_2 + H \qquad (VIII)$$

$$H + O_2 \rightarrow OH + O \qquad (IX)$$

If such small amounts of water can exert such large effects in shock tube experiments, which have a time scale of only a few tens or hundreds of microseconds, then this ubiquitous and almost ineradicable compound may also exert a profound influence during the very much longer time scale of reactions carried out at lower temperatures in bulbs and flow systems. The course of recombination might well be influenced by reactions (VII) to (IX) despite the most strenuous efforts to eliminate water.

Thus, it is quite likely that the extremely large discrepancies in the results of various studies of the recombination reaction between CO and O can be attributed to a combination of surface and water catalysis. The present work is definitely free of only the former effect; catalysis by water may well have been present to some unknown degree, even though all practicable measures were taken to exclude it. The fact that the present recombination rates are lower than any that could have been anticipated from previous direct measurements, however, suggests that they are closer to the true values.

CONCLUSIONS

The following conclusions were reached in this work:

1. The shock tube - expansion wave method of studying high-temperature recombination is relatively simple to use and should be widely applicable.

2. The three-body recombination rate constant of carbon monoxide and oxygen has an average value of 2×10^{13} centimeter^6 mole^{-2} second^{-1} at temperatures from 2800° to 3600° K. This is a lower limit; the upper limit is less than 1×10^{14} centimeter^6 mole^{-2} second^{-1}.

3. This result is in accord with rate constants deduced from equilibrium constants and shock tube measurements of CO_2 dissociation rates.

4. It is suggested that the large discrepancies among previously measured recombination rates may arise from surface and water catalysis.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 6, 1966,
129-01-03-04-22.

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