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THE RECOMBINATION OF OXYGEN ATOMS AT HIGH TEMPERATURES

AS MEASURED BY SHOCK TUBE DENSITOMETRY*

by

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The rate of recombination of oxygen atoms has been measured by shock tube x-ray densitometry in the range 1500 - 2700°K. Mixtures of ozone, oxygen, and argon were driven with helium in a three-inch shock tube and density records obtained for each experiment.

Within two microseconds after the arrival of the shock wave the rapid reactions

$$O_3 + M \xrightarrow{k_1} O_2 + O + M$$

$$O_3 + O \xrightarrow{k_2} 2O_2$$

have removed all but a negligible amount of the original ozone and produced excess oxygen atoms. The oxygen atom concentration at every subsequent time is then determined by the density of the gas, and the recombination rate is obtained from the gradual decrease in density behind the shock front.

The reaction

$$O + O + O_2 \xrightarrow{k_4} 2O_2$$

is the dominant recombination reaction in this system, and its rate is found to be $k_4 = 2.7 \pm 0.5 \times 10^7 \exp(7000 \pm 1000/T) \frac{\text{liter}^2}{\text{mole}^2 - \text{sec.}}$

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DISCLAIMER

INTRODUCTION

The importance of the rate of recombination of oxygen atoms is well recognized, and a number of experimenters have attempted to obtain this rate by measuring the rate of dissociation of oxygen at high temperatures through use of the shock tube.[1, 2, 3, 4, 5] The possibility of discrepancy between the recombination rate obtained from dissociation experiments via the equilibrium constant and a direct measurement of recombination has been widely discussed, and experiments which measure the recombination rate directly should be of both theoretical and practical value.

The direct measurement of recombination requires the generation of greater than equilibrium concentrations of oxygen atoms. Two shock tube methods have been devised which produce the required disequilibrium. In the method used by Wilson,[6] shock heated oxygen containing oxygen atoms is cooled by an expansion and the subsequent recombination followed by an ultraviolet absorption technique.

A second method makes use of the high temperature properties of ozone. This is the method used in this paper and is based upon the following observations.

The decomposition of ozone at high temperature has been studied by Jones and Davidson[7] and takes place according to the following mechanism:

$$O_3 + M \xrightarrow{k_1} O_2 + O + M \qquad (1)$$

$$O_3 + O \xrightarrow{k_2} 2O_2 \qquad (2)$$

where $k_1 = 5.8 \pm 0.6 \times 10^{11} \exp(-23{,}150 \pm 300/RT)$ liter/mole-sec.

$k_2 = 2.4 \pm 0.5 \times 10^{10} \exp(-5{,}600 \pm 500/RT)$ liter/mole-sec.

At temperatures above 1300°K and pressures greater than .5 atm, the ozone is removed by reactions (1) and (2) within one or two microseconds. A gas originally composed of argon, oxygen and ozone which is shocked, will then contain argon and quantities of oxygen atom and oxygen molecule determined by the balance between reactions (1) and (2). At temperatures below 3000°K the concentration of oxygen atoms will be greater than the equilibrium amount, and recombination will occur. Wray[8] has used ultraviolet absorption to measure the recombination rate of oxygen atoms generated in the above manner. Working with very low mole fractions of ozone in argon, he was able to determine the rate of:

$$O + O + Ar \xrightarrow{k_3} O_2 + Ar \qquad (3)$$

as $1.05 \times 10^9 \, T^{-1/2}$ liter^2/mole^2-sec

In the experiments described in this paper the x-ray densitometer technique of Knight and Venable[9] has been used to follow the density decrease due to the highly exothermic recombination process. The determination of density is relatively insensitive as compared to the ultraviolet absorption technique, and mixtures containing large quantities of ozone must be used. Large initial amounts of ozone imply large quantities of oxygen behind the shock wave, and the reaction which determines the overall rate in this system is

$$O + O + O_2 \xrightarrow{k_4} 2O_2 \qquad (4)$$

EXPERIMENTAL

The x-ray apparatus and the shock tube have been described by Knight and Venable[9] and Rink.[5, 10] A few changes have been made in the apparatus and will be described.

The x-ray slits were widened from 3/4 mm to 2.3 mm. The wider slits allow a better signal-to-noise ratio and do not harm the time discrimination, as the recombination rate is much slower than the dissociation rate. In these experiments negligible density changes occur during the slit passage time.

For the measurement of velocity, pressure sensitive piezoelectric gauges[11] were used to follow the progress of the shock wave. At the low temperatures of these experiments, ionization probes will not respond. The measurement of velocity is less accurate with the piezoelectric devices, and velocities could not be determined to better than 0.5%.

Table I shows the experimental conditions. The shock waves were produced by spontaneously bursting scribed brass and aluminum diaphragms with helium. All shocks were driven above the detonation velocity and no perturbations of the density records ascribable to detonation instability were seen.

Oscilloscope records of the x-ray transmission were taken in the manner described by Rink.[5] The accuracy of the density measurements was also as given by Rink.

The conversion of x-ray transmission to density requires a calibration. The x-ray transmission of mixtures of 0, 10, 30, 50, and 100 mole percent oxygen in argon was determined for a range of densities in each case. From these measurements, the absorption by argon-oxygen mixtures was found not to be an additive function of the individual component absorptions. The following semi-empirical derivation results in an expression which was used to relate the transmission data to density.

Consider a mixture of two gases--gas A, a gas of high atomic weight, and gas B, a low atomic weight gas, i.e. a first row element.

Let

T_A, T_B = the radiant energies transmitted by gas A and gas B respectively

$I_\nu d\nu$ = the intensity of the source in the frequency interval $\nu \rightarrow \nu + d\nu$

μ_ν^A, μ_ν^B = the spectral absorption coefficients at unit density for gases A and B.

T_o = the total energy of the source.

ρ_A, ρ_B = the respective densities in grams/liter.

Then

$$\frac{T_A}{T_o} = \frac{\int_o^\infty I_\nu \exp(-\mu_\nu^A \rho_A)\, d\nu}{\int_o^\infty I_\nu\, d\nu}$$

$$\frac{T_B}{T_o} = \frac{\int_o^\infty I_\nu \exp(-\mu_\nu^B \rho_B)\, d\nu}{\int_o^\infty I_\nu\, d\nu}$$

The following equation holds empirically for first row elements.

$$-\ln \frac{T_B}{T_o} = k_B \rho_B$$

This equation may be derived by expanding the T_B/T_o equation for small μ_ν^B.

$$\frac{T_B}{T_o} \approx 1 - \frac{\int_o^\infty I_\nu \mu_\nu^B \rho_B\, d\nu}{\int_o^\infty I_\nu\, d\nu}$$

Taking the logarithm of the preceding and expanding again, we have

$$-\ln \frac{T_B}{T_o} \approx \frac{\rho_B \int_o^\infty I_\nu \mu_\nu^B \, d\nu}{\int_o^\infty I_\nu \, d\nu}$$

k_B may be identified as

$$\frac{\int_o^\infty I_\nu \mu_\nu^B \, d\nu}{\int_o^\infty I_\nu \, d\nu}$$

For the total transmission of a mixture,

$$\frac{T_t}{T_o} = \frac{\int_o^\infty I_\nu \exp(-\mu_\nu^A \rho_A - \mu_\nu^B \rho_B) \, d\nu}{\int_o^\infty I_\nu \, d\nu}$$

again expanding for small μ_ν^B

$$\frac{T_t}{T_o} \approx \frac{T_A}{T_o} - \frac{\int_o^\infty I_\nu \exp(-\mu_\nu^A \rho_A) \; \mu_\nu^B \rho_B \, d\nu}{\int_o^\infty I_\nu \, d\nu}$$

Taking the logarithm, expanding, and substituting for k_B, we have

$$-\ln \frac{T_t}{T_o} \approx -\ln \frac{T_A}{T_o} + k_B \rho_B \frac{T_o}{T_A} \left[\frac{\int_o^\infty I_\nu \exp(-\mu_\nu^A \rho_A) \, \mu_\nu^B \, d\nu}{\int_o^\infty I_\nu \mu_\nu^B \, d\nu} \right]$$

Information on chromium x-radiation and the absorption coefficient for oxygen[12] indicates that the function $I_\nu \mu_\nu^B$ will be strongly "peaked" at a frequency ν_o, where $\exp(-\mu_\nu^A \rho_A)$ is not small. Thus one may approximate as follows:

$$\frac{\int_o^\infty I_\nu \exp(-\mu_\nu^A \rho_A) \, \mu_\nu^B \, d\nu}{\int_o^\infty I_\nu \mu_\nu^B \, d\nu} \approx \exp(-\mu_{\nu_o}^A \rho_A)$$

and the final relation is

$$-\ln \frac{T_t}{T_o} \approx -\ln \frac{T_A}{T_o} + k_B \rho_B \left[\frac{T_o}{T_A} \exp(-\mu_{\nu_o}^A \rho_A) \right]$$

The preceding equation fits all of the calibration data for argon-oxygen mixtures with the empirical values $\mu^{A}_{\nu_o} = 1.0$ liters/gram

$$k_B = 0.0909 \text{ liters/gram}$$

The ozone was prepared in an electrical ozonizer similar to the design of Henne and Perilstein.[13] The ozone was separated from its oxygen carrier by flowing the gas through a silica gel bed (at dry ice temperature)[14] on which the ozone is preferentially absorbed. The argon-ozone mixtures were prepared by warming the gel bed and removing the ozone with a flow of argon. The resulting ozone-argon mixture was collected in a stainless steel tank and left to stand for more than twelve hours to insure complete mixing. Mass-spectral analysis of the mixtures indicated an impurity level of less than 0.5%.

All of the ozone handling equipment was constructed of stainless steel or Teflon. Pressures were measured on a carefully calibrated sulfuric acid manometer. The ozone in the shock tube was sampled before each experiment and the concentration determined to 2% iodometrically.[15] The difference in concentration between samples taken directly from the storage tank and samples taken from the tube was less than 2%, indicating that adsorption in the tube and/or decomposition was small.

ANALYSIS AND RESULTS

A 7090 computer code was used to determine composition from the profile of density behind the shock wave. Given the initial conditions (composition, temperature, pressure and shock velocity) and any desired final composition, this code computes the density, pressure and temperature which satisfy the Hugoniot equations. Thus when the code is allowed to compute the state variables for a set of possible final compositions, (the compositions determined by setting the ozone concentration at zero) a graph of oxygen atom concentration versus density ratio may be obtained. Then for each experimental density an oxygen atom concentration may be read from this graph. The code assumes vibrational equilibrium at all points. No sign of vibrational nonequilibrium was expected or observed in these experiments.

The rate constants are then evaluated as follows. Assuming the usual termolecular process,

$$O + O + M \xrightarrow{\overline{k}} O_2 + M$$

in an expanding gas, then

$$\frac{d[O]}{dt} = \left(\frac{\partial[O]}{\partial t}\right)_\rho + \left(\frac{\partial[O]}{\partial \rho}\right)_t \frac{d\rho}{dt}$$

where $[O]$ = the oxygen atom concentration in moles/liter

ρ = the gas density in grams/liter

t = particle time

Now

$$\left(\frac{\partial[O]}{\partial \rho}\right)_t = \frac{[O]}{\rho}$$

and,

$$\left(\frac{\partial[O]}{\partial t}\right)_\rho = -2\bar{k}[M][O]^2$$

thus:

$$\frac{\rho}{\rho_o[O]^2}\frac{d[O]}{} - \frac{d\rho}{\rho_o[O]} = -d\left(\frac{\rho}{\rho_o[O]}\right) = -2\bar{k}[M]\frac{\rho}{\rho_o}\,dt$$

where, ρ_o is the initial density. Now,

$$dt_{particle} = \frac{\rho}{\rho_o}\,dt_{laboratory}$$

and

$$dt_{laboratory} = dD/U_s$$

where D is the distance behind the shock wave, and U_s is the shock velocity. Combining the above,

$$\frac{d\left(\frac{\rho}{\rho_o[O]}\right)}{dD} = \frac{2\bar{k}[M](\rho/\rho_o)^2}{U_s}$$

In the higher temperature experiments, correction for the dissociation rate results in:

$$\frac{d\left(\frac{\rho}{\rho_o[O]}\right)}{dD} = \frac{2\bar{k}[M](\rho/\rho_o)^2}{U_s}\left[1 - K\frac{[O_2]}{[O]^2}\right]$$

where K is the equilibrium constant for reaction (4). Thus a plot of $\frac{\rho}{\rho_o[O]}$ versus distance should give the overall second order rate $\bar{k}(M)$, since such plots will be approximately linear for the observed small density changes. An example is shown for one experiment in Figure 1. The rate is taken at a point in the early part of the plot since the measurements are most accurate there. Table II shows the deduced rates and conditions at the selected point for each experiment.

The overall rate is determined for each experiment in the preceding manner. It is then necessary to evaluate the contribution to this rate of each species. Accepting the argon rate obtained by Wray,[8] the argon contribution to the overall rate can be evaluated. A mechanism involving ozone as an intermediate [through reaction (2) and the reverse of reaction (1)] can contribute to the overall rate at lower temperatures. The contribution of this mechanism can be evaluated from the rates of reactions (1) and (2) and the equilibrium constant of reaction (1). This mechanism contributes approximately 5% of the overall rate in the neighborhood of 1500 - 1600°K. The oxygen atom contribution as third body cannot be determined from the data presented here. It must not dominate, as a third order (in oxygen atom) plot of the experiments deviates greatly from a straight line. If the efficiency of oxygen atoms as catalyst is taken to be three times the molecular efficiency as found by Rink,[5] a glance at Table II will show that it makes a small but not negligible contribution to the overall rate.

If the above rates are subtracted from the overall rate the remainder is the rate of reaction (4). Figures 2 and 3 show plots of log k_4 versus log T and log k_4 versus 1/T.

From Figure 2 the temperature dependence is T^{-3} to T^{-4}; however, Figure 3, the Arrhenius plot, is a better fit to the data with

$$k_4 = 2.7 \pm 0.5 \times 10^7 \exp(7000 \pm 1000/T), \frac{\text{liter}^2}{\text{mole}^2 - \text{sec}}$$

The errors are derived from the scatter of the data as shown in Figure 2. The higher temperature experiments are generally more accurate.

DISCUSSION

The most recent and detailed discussions of the dissociation of oxygen are those of Rink,[5] Byron,[2] Matthews,[2] and Camac and Vaughan.[4] The results of Rink, Matthews, and Camac and Vaughan are shown on an extended Arrhenius plot in Figure 4. The single recombination experiment of Wilson[6] is also shown with the data from Figure 2. Though there is considerable disagreement concerning the absolute value of the rate at a given temperature, the Arrhenius temperature dependence is in reasonable agreement with the temperature variations reported by the other authors. Rink[5] reported that he could not tell the temperature dependence with great accuracy, and stated that a T^{-2} function would fit his data. Camac and Vaughan[4] gave only a relative efficiency of oxygen to argon, and the temperature dependence in their case is that found for argon as catalyst.

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TABLE I

Experimental Conditions

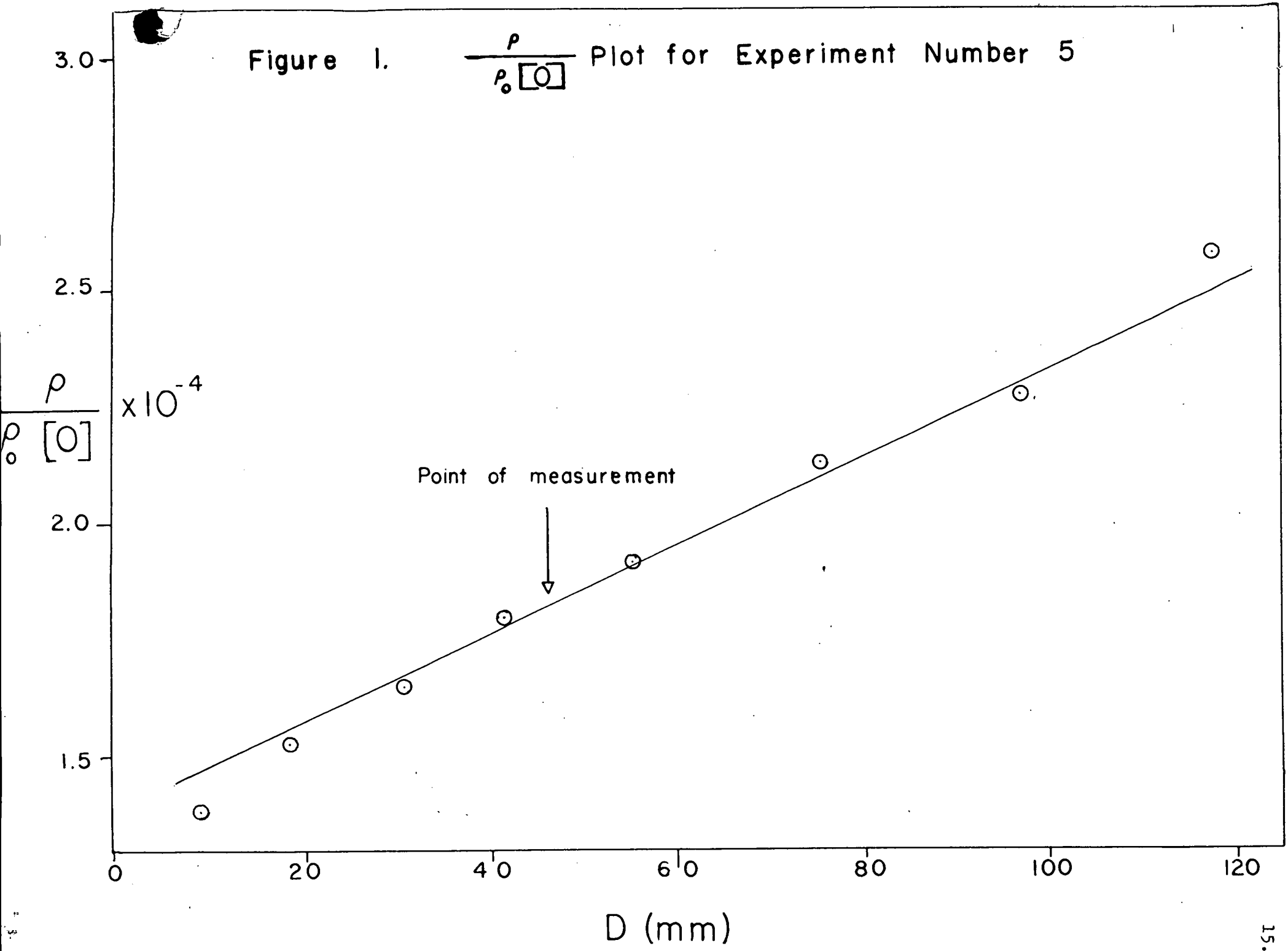
	P_o in cm Hg.	Mole fraction O_3	Mole fraction Argon	Mole fraction O_2	Shock Velocity $\frac{mm}{\mu sec}$
1	12.54	0.099	0.527	0.374	1.170
2	8.93	0.099	0.527	0.374	1.217
3	7.31	0.099	0.527	0.374	1.249
4	6.12	0.101	0.527	0.372	1.391
5	4.18	0.101	0.528	0.372	1.466
6	9.60	0.285	0.489	0.226	1.506
7	6.38	0.287	0.489	0.224	1.602
8	4.43	0.291	0.491	0.218	1.785
9	6.81	0.080	0.676	0.244	1.414
10	12.03	0.079	0.676	0.245	1.219

TABLE II

Results and Conditions at Point of Measurement

	$\bar{k}M$ $\frac{\text{liters}}{\text{mole-sec}}$	$T^{\circ}K$	Concentrations in moles/liter		
			O_2	Ar	O
1	2.6×10^{7}	1548	8.54×10^{-3}	8.61×10^{-3}	1.5×10^{-4}
2	1.0×10^{7}	1559	6.93 "	7.05 "	1.8 "
3	2.1×10^{7}	1579	6.00 "	6.14 "	1.6 "
4	7.9×10^{6}	1785	5.73 "	5.88 "	2.2 "
5	5.0×10^{6}	1879	4.20 "	4.33 "	1.9 "
6	4.7×10^{6}	2375	8.10 "	6.25 "	5.1 "
7	3.8×10^{6}	2569	5.94 "	4.59 "	4.5 "
8	2.5×10^{6}	2760	5.09 "	4.02 "	4.7 "
9	5.8×10^{6}	1909	4.49 "	8.52 "	2.2 "
10	1.8×10^{7}	1589	6.72 "	1.27×10^{-2}	2.0 "

Figure 1. $\frac{\rho}{\rho_0 [O]}$ Plot for Experiment Number 5



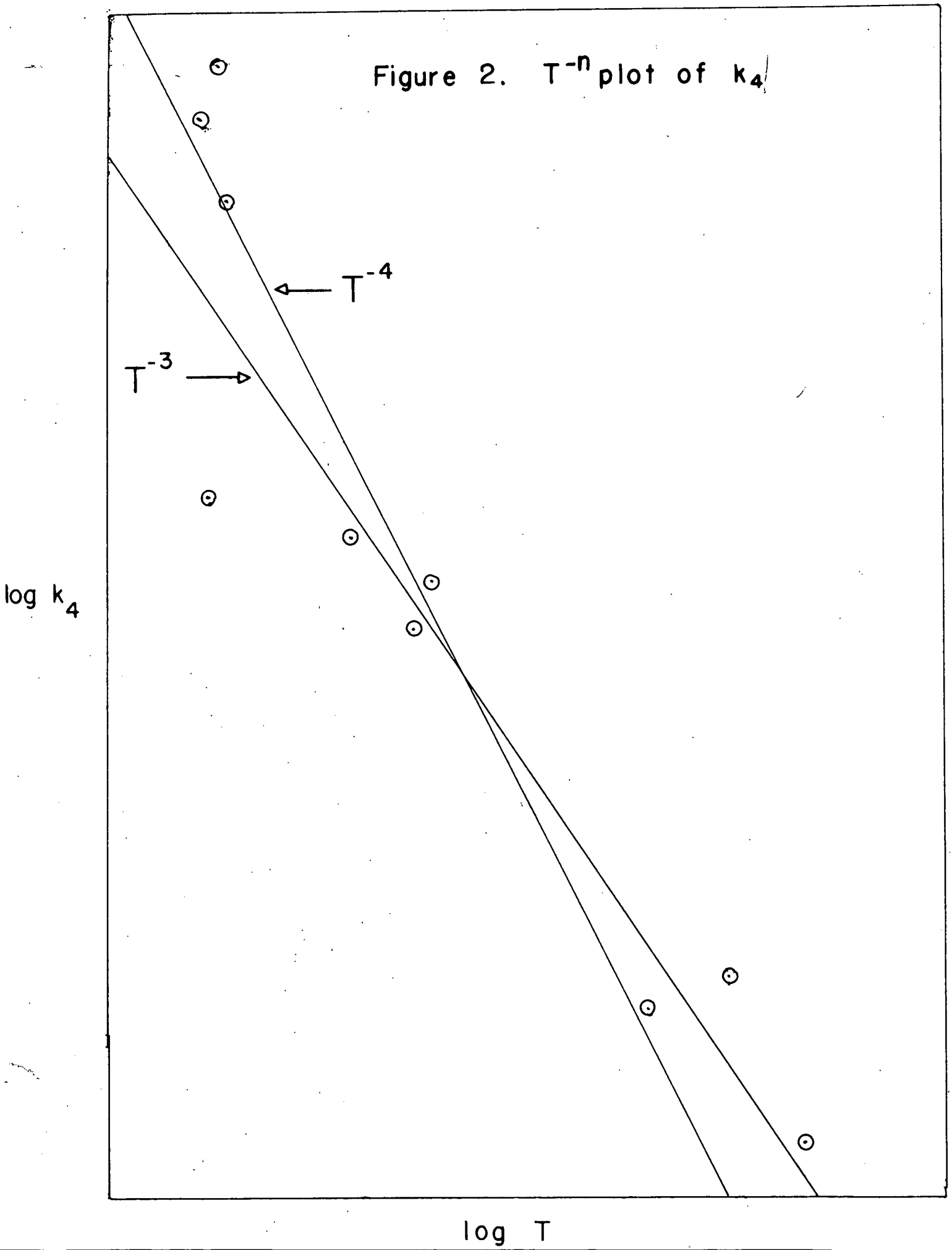


Figure 2. T^{-n} plot of k_4
T^{-4}
T^{-3}
log k_4
log T

Figure 3. Arrhenius Plot of k_4

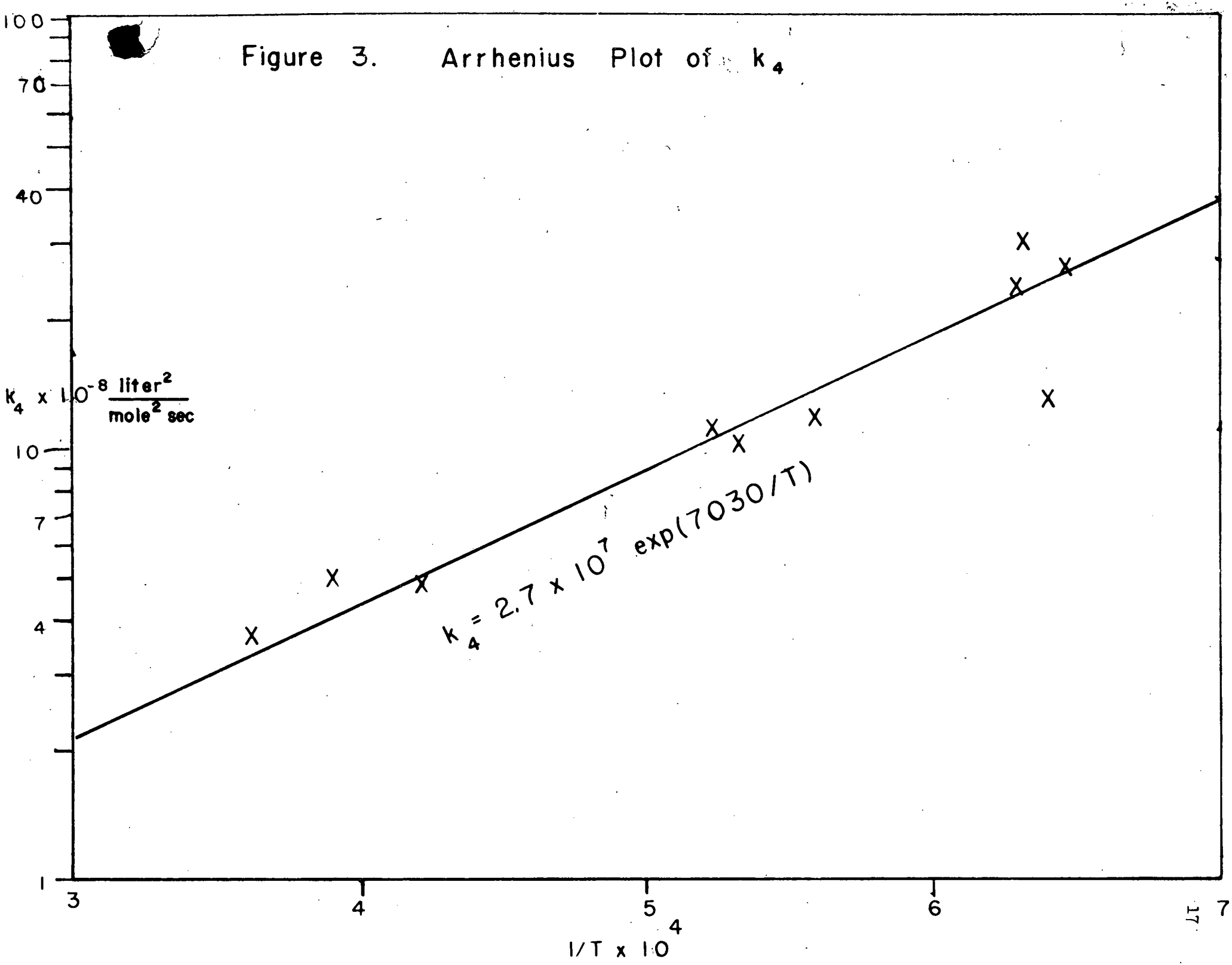
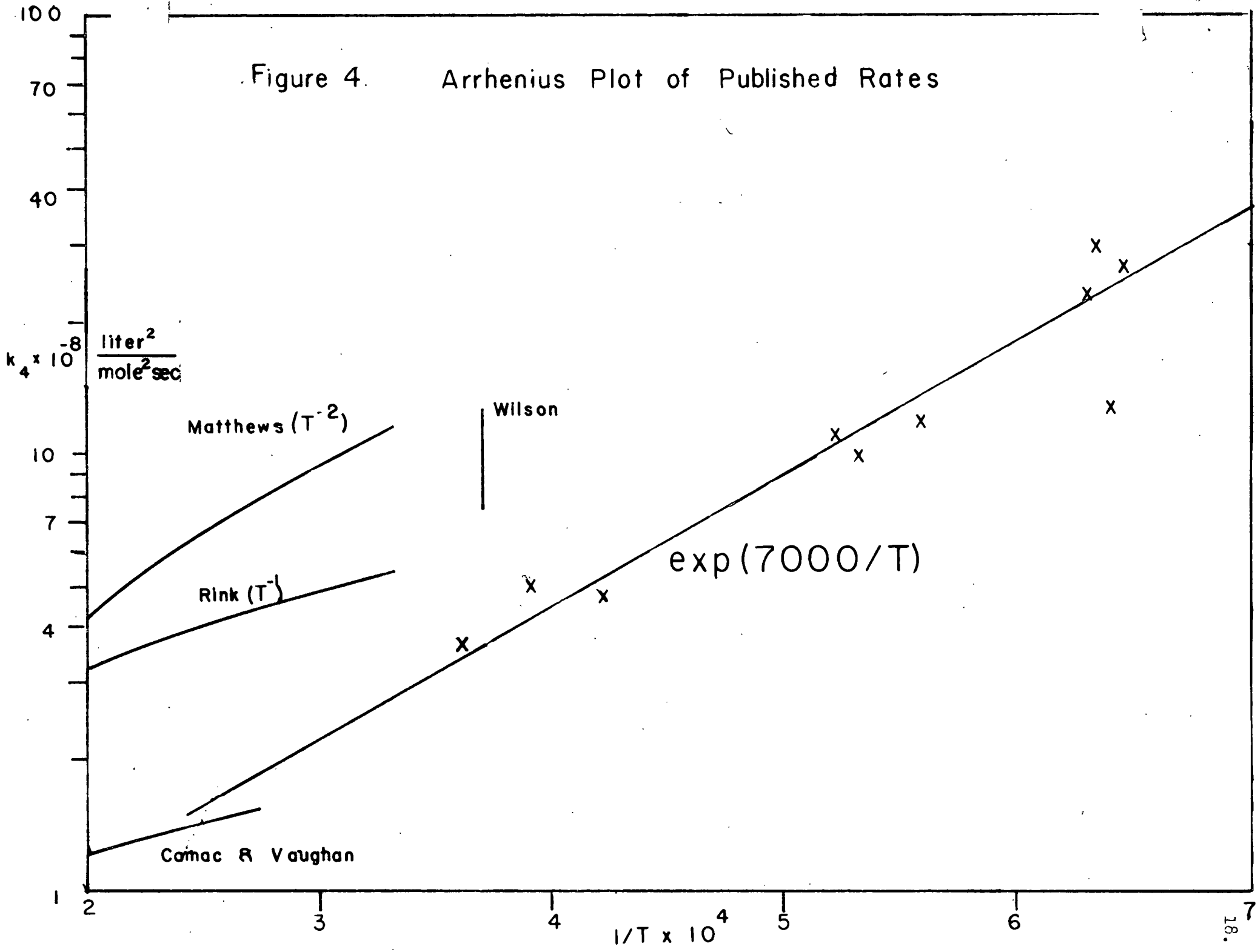


Figure 4. Arrhenius Plot of Published Rates



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