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MOLECULAR DIFFUSION STUDIES IN GASES AT HIGH TEMPERATURE

RESULTS AND INTERPRETATION

OF CO_2 , O_2 , CH_4 , O_2 , H_2 , O_2 , CO_2 AND H_2 SYSTEMS

by
R. W. Johnson and A. A. Westenberg

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**Molecular Diffusion Studies
in Gases at High Temperature**
Results and Interpretation
of the $\text{CO}_2\text{-O}_2$, $\text{CH}_4\text{-O}_2$, $\text{H}_2\text{-O}_2$, CO-O_2 , and $\text{H}_2\text{O-O}_2$ Systems

by
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ABSTRACT

Experimental measurements of the binary diffusion coefficients for the $\text{CO}_2\text{-O}_2$, $\text{CH}_4\text{-O}_2$, $\text{H}_2\text{-O}_2$, CO-O_2 , and $\text{H}_2\text{O-O}_2$ systems over the nominal temperature range 300-1000°K are reported. The measurements were made by the point source technique. The data have been analyzed in terms of intermolecular potential energies and the rigorous kinetic theory by using the Lennard-Jones (12-6), modified-Buckingham (Exp-6), point center of repulsion (inverse power), and the exponential repulsion potential energy functions. It is shown that all four of these functions are capable of fitting the diffusion data with about the same precision (within experimental error). However, the potential energy values themselves which are calculated from these four different fitted models are shown to be widely at variance--especially in the range of interaction corresponding to the lower temperatures. Thus, these results provide an example of the high degree of ambiguity (previously noted by several others) involved in deducing intermolecular potential energies from transport data. The use of such fitted potentials to extrapolate transport data to higher temperatures, on the other hand, is probably a more reliable procedure, and diffusion coefficients for the above five gas pairs (in their unexcited, undissociated states) have been estimated to 3000°K from the potentials based on the 300-1000°K measurements.

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MOLECULAR DIFFUSION STUDIES IN GASES AT HIGH TEMPERATURE
RESULTS AND INTERPRETATION OF THE $\text{CO}_2\text{-O}_2$, $\text{CH}_4\text{-O}_2$,
 $\text{H}_2\text{-O}_2$, CO-O_2 , AND $\text{H}_2\text{O-O}_2$ SYSTEMS

I. INTRODUCTION

In a recent paper (Ref. 1)¹ the authors have presented a new method of measuring molecular diffusion coefficients of gases that is well suited for measurements at high temperatures (300-1200°K). Basically, this technique uses concentration profiles determined downstream of a point source of trace gas in a uniform (heated) laminar jet of carrier gas to evaluate the binary diffusion coefficients. In two subsequent publications (Refs. 2 and 3), results of using this technique on the He- N_2 , $\text{CO}_2\text{-N}_2$, and He-A systems were reported, and the measurements interpreted by means of the kinetic theory of gases to obtain intermolecular forces.

The present paper presents similar measurements and analysis for the gas pairs $\text{H}_2\text{-O}_2$, $\text{H}_2\text{O-O}_2$, CO-O_2 , $\text{CO}_2\text{-O}_2$, and $\text{CH}_4\text{-O}_2$ over the nominal temperature interval 300-1000°K and at atmospheric pressure. The particular choice of gas pairs was motivated by the need for reliable data on the stable species found in the lean methane-oxygen combustion system presently under analysis at this Laboratory, and should find additional application to other hydrocarbon combustion systems as well as the usual thermophysical applications. As in Refs. 1 and 2, the data have been analyzed with the rigorous kinetic theory of gases to obtain intermolecular forces between the unlike molecules. Four kinds of intermolecular potentials have been used--the point center of

¹References may be found on pages 23 and 24.

repulsion, the Lennard-Jones (12-6), the modified-Buckingham (Exp-6) (Ref. 4), and the exponential repulsion potential for which the collision integrals have recently been computed by L. Monchick of this Laboratory (Ref. 5). The comparison of these different results provides an interesting and instructive example of the perils and possibilities of this kind of use of transport data.

II. EXPERIMENTAL METHODS AND RESULTS

In general, the experimental methods and equipment used for these measurements were identical to those described in Ref. 1, so that the details need not be repeated here. However, certain modifications required by the peculiarities of some of the gas pairs are discussed below.

In all measurements the trace gas was the light component and the carrier gas the heavy component; this arrangement is particularly suited to this technique² and entirely compatible with the gas pairs being studied. The oxygen (hydrogen free) and carbon dioxide (extra dry) were supplied as compressed gases by the Southern Oxygen Company, while the hydrogen (prepurified), methane (commercial), and carbon monoxide (high purity) were supplied by the Mathieson Company. All gases were used directly from the high-pressure container. In general, small amounts of impurities are unimportant in the measurements; however, the sensitivity of the thermal conductivity gas analysis instrument to light gas impurities required that hydrogen-free gases be used.

Improvements in the thermal conductivity gas analysis instrument used for these measurements have been reported elsewhere (Ref. 6).

² Experience has shown that somewhat better precision is attained when the light gas is used as the tracer. This is probably connected with its lower jet momentum and penetration distance in entering the carrier stream.

Carbon Dioxide-Oxygen

Diffusion coefficients for the O_2 (trace)- CO_2 system were obtained in exactly the same way as the N_2 (trace)- CO_2 measurements reported in Refs. 1 and 2 so that no further comment on the experimental technique is required. The measurements were obtained over the temperature interval 297-1080°K and are reproduced in Fig. 1.

It is worth noting that both sets of diffusion measurements for $D_{CO_2-N_2}$ and $D_{CO_2-O_2}$ are larger than the D_{CO_2-Air} values given by Klibanov et al. (Ref. 7) and previously compared in Ref. 1. This is an interesting comparison inasmuch as these are the only other diffusion data covering the same temperature range.

An additional comparison between these measurements and values reported in the literature is given in Table I. No significant concentration effects would be

Table I
Comparison of Measured Diffusion Coefficients with Previously Reported Values, p - 1 Atmosphere

Gas Pair	T (°K)	D_{12} ($cm^2 sec^{-1}$) (other work)	D_{12} ($cm^2 sec^{-1}$) (this work)	Reference
H_2-O_2	273.2	0.697	0.688	16
H_2O-O_2	308.1	0.282	0.301	17
	329.0	0.318	0.338 ⁺	17
	352.4	0.352	0.381 ⁺	17
$CO-O_2$	273.2	0.185	0.191 ⁺	16
CO_2-O_2	273.2	0.139	0.137 ⁺	16
	293.2	0.16	0.153	18

+ Extrapolated Values

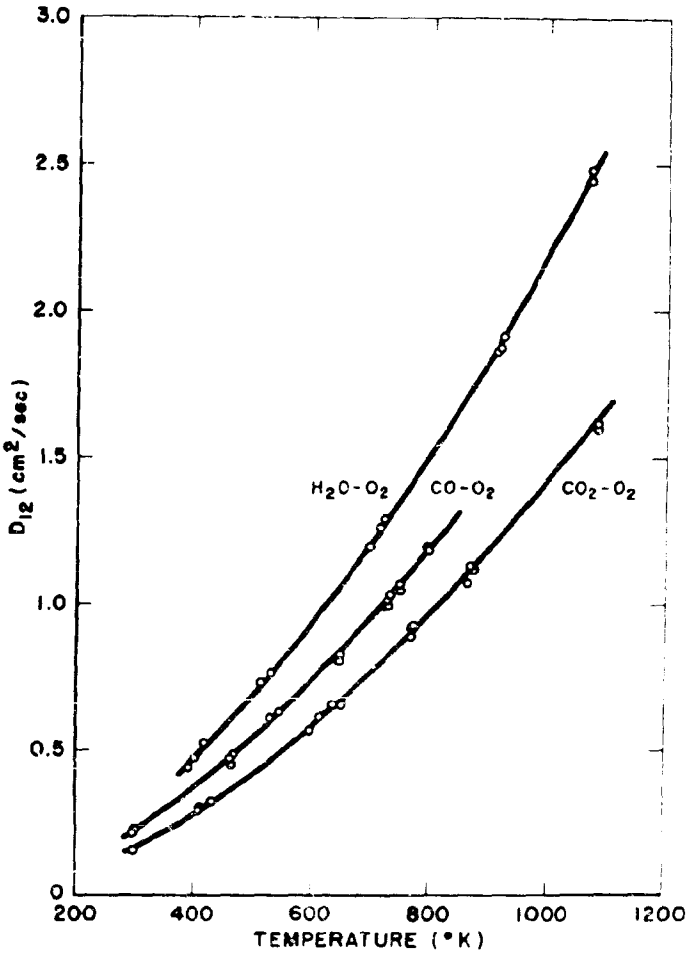


Fig. 1 DIFFUSION MEASUREMENTS AS A FUNCTION OF TEMPERATURE FOR THE CO_2-O_2 , $\text{CO}-\text{O}_2$, AND $\text{H}_2\text{O}-\text{O}_2$ SYSTEMS

expected for the $\text{CO}_2\text{-O}_2$ system since the molecular weights are not widely different. (For a discussion of these concentration effects see Refs. 1 and 2.)

Methane-Oxygen

Diffusion measurements for the $\text{CH}_4(\text{trace})\text{-O}_2$ system were made in the usual manner and are presented graphically in Fig. 2. The temperature interval covered was 297-980°K, and no measurements at higher temperatures were possible because spontaneous ignition of the methane in the hot oxygen occurred at about 1020°K. The possibility was raised that prior to ignition there might be some slow reaction occurring in the mixing zone which would render the thermal conductivity gas analysis--and hence the diffusion data--invalid. In order to check this, a Pt-Pt(10 per cent Rh) thermocouple was placed downstream of the injection tube and at various high temperatures the methane flow was alternately turned on and off and the changes in thermocouple reading noted. At no time prior to ignition was a temperature change greater than 2°C observed. From this brief experiment, it was concluded that slow reaction (if any) was of no significance prior to visible ignition.

Since there have been no other diffusion data for $\text{CH}_4\text{-O}_2$ reported, no comparison is possible.

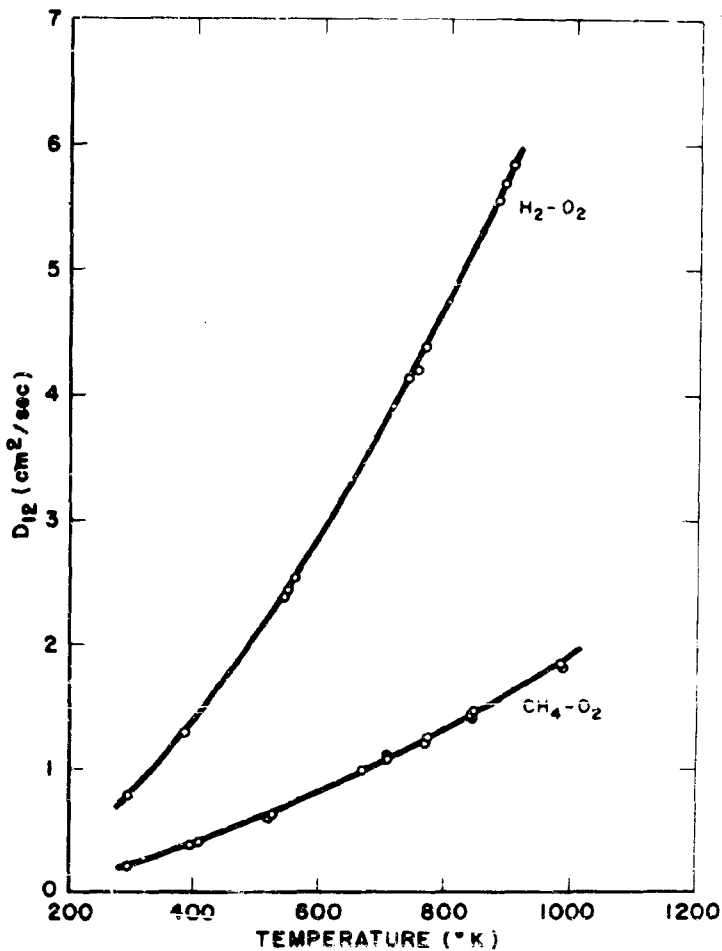


Fig. 2 DIFFUSION MEASUREMENTS AS A FUNCTION OF TEMPERATURE FOR THE $\text{H}_2\text{-O}_2$ and $\text{CH}_4\text{-O}_2$ SYSTEMS

Hydrogen-Oxygen

Data for the $H_2(\text{trace})-O_2$ system are presented in graphical form in Fig. 2. The temperature interval for these measurements was 295-900°K--the upper limit being established (as in the previous case) by the spontaneous ignition of the hydrogen trace in the hot ambient oxygen at about 920°K. The smoothness of the diffusion data approaching this ignition limit tends to indicate that there was no slow reaction in the mixing gas, as did the thermocouple measurements made in the (presumably slower) CH_4-O_2 case discussed previously. No additional proof in the H_2-O_2 case was considered necessary.

A comparison between these measurements and a value reported in the literature is made in Table I--the agreement is within the experimental error. No attempt was made to measure the effect of composition on $D_{H_2-O_2}$ by interchanging the trace and carrier gases because of the difficulty in handling large amounts of hydrogen. A theoretical calculation (Ref. 4) of $D_{H_2(\text{trace})-O_2} / D_{H_2-O_2(\text{trace})}$ yields a value of 1.03 which can be expected to be quite reliable (Refs. 2 and 3).

Carbon Monoxide-Oxygen

Without some chemical change, it is very difficult to analyze quantitatively for the presence of trace amounts of CO in O_2 using thermal conductivity gas analysis. Therefore, in order to get around this difficulty, the sample was first passed over heated platinum gauze to

oxidize the CO to CO₂. This combustion furnace was tested at different temperatures³ while the product composition was monitored with the thermal-conductivity analyzer--in this manner a safe operating temperature was determined at which complete conversion was attained. Because only trace amounts of CO were present, the depletion of the oxygen was negligible and the usual methods of data reduction applied.

Measurements of diffusion coefficients for the CO(trace)-O₂ system were obtained without difficulty up to a temperature of about 800°K. At this point, reproducibility of the measurements became very poor. Detailed sampling and analysis (the usual thermal-conductivity gas analysis with and without conversion of CO to CO₂) revealed that disproportionation of the CO ($2\text{CO} \rightarrow \text{CO}_2 + \text{C}$) in the stainless steel injection tube (Ref. 8) was occurring in varying amounts at various temperatures above about 700°K. This disproportionation eventually deposited enough carbon to completely plug the injection tube. The measured diffusion coefficients showed that reliable data could be obtained only over the temperature interval 295-800°K, and these are presented in Fig. 1. As before, Table I gives a comparison of our measured values (extrapolated) with values already in the literature.

At temperature above about 900°K a visible reaction was apparent in the diffusion (mixing) zone, and thermocouple temperature measurements in this region with and without CO trace gas flow showed definitely that a slow gas phase reaction was occurring without a sharp ignition point as in the CH₄-O₂ and H₂-O₂ systems. It seems worth

³The temperature of the platinum was not measured directly but rather the voltage to the furnace heating elements.

pointing out that detailed measurements of local temperature and composition in a case such as this, along with appropriate diffusion coefficients, might be an excellent method of studying gas phase reaction kinetics. The rapid dilution of the trace gas (in this case CO) should lend itself to treating the reaction as pseudo first order. It will be recognized that such a system has similarities to a Polanyi diffusion flame, except that spherical symmetry does not exist because of the finite carrier gas flow. Partial theoretical solutions to problems of this type are available. (Ref. 9).

Water-Oxygen

The anticipated difficulty of accurately metering a liquid tracer in this experiment was conveniently avoided by preparing the water from gaseous H_2 and O_2 in the trace gas injection tube and using carrier-gas temperatures only above $100^\circ C$ to insure against condensation. Combustion of the trace gas mixture containing excess oxygen⁴ was conveniently accomplished by electrically heating a portion of the injection tube upstream of the injection point. A 5-mil-diameter platinum wire was inserted into the tube to serve as a catalyst. Completion of reaction and proper stoichiometry (only the H_2 was accurately metered) was established by analyzing a sample of the gases withdrawn from a point immediately downstream of the injection tube. This sample was passed through a liquid nitrogen trap before

⁴The slight excess of oxygen was unimportant since the carrier gas was also oxygen.

going to the thermal conductivity gas analysis instrument capable of detecting about 10 ppm of H_2 in O_2 ; no output was an indication that no residual H_2 was being emitted from the injection tube. Adsorption of the water on the walls of the gas analysis flow system only required that sufficient time be allowed for equilibrium to be reached between readings. No condensation in the thermal conductivity cell (operated at $273^\circ K$) was encountered since the cell pressure was only about one cm Hg and the partial pressure of the water trace was less than 2 per cent of this value.

Diffusion measurements of the $H_2O(\text{trace})-O_2$ system were obtained over the interval $390-1070^\circ K$ and are presented in Fig. 1. An extrapolation of our measurements to a somewhat lower temperature permits a comparison with the data of Schwertz and Brow--see Table I. The agreement in this case is less satisfactory than in previous comparisons, and no explanation is offered to explain the 7 per cent difference.

III. INTERPRETATION OF THE RESULTS

For gas molecules that have nearly spherically symmetric force fields, the rigorous kinetic theory of gases permits measured transport properties to be related to intermolecular forces (Ref. 4). In particular, the measurement of molecular diffusion coefficients as a function of temperature is one of the best known methods of determining intermolecular forces between unlike molecules since, to a very good first approximation, unlike interactions alone determine this transport property. In such an analysis, the procedure is to select a particular analytic function which approximates the actual (unknown) potential energy and to determine a set of parameters for this function that best reproduces the experimental data. This fitting procedure has already been detailed in Ref. 2. In the present work, four of the most realistic potential functions have been used to fit the data and then compared with each other. The results afford an interesting example of this type of procedure.

The four potential functions used are the Lennard-Jones (12-6)

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \quad (1)$$

the modified-Buckingham (Exp-6)

$$\phi(r) = \frac{\epsilon}{1-6/\alpha} \left[\frac{6}{\alpha} e^{\alpha(1-r/r_M)} - \left(\frac{r_M}{r}\right)^6 \right], \quad (2)$$

the point center of repulsion

$$\beta(r) = d/r^{\delta} \quad (3)$$

and the exponential repulsion

$$\beta(r) = A \exp(-r/\rho) \quad (4)$$

In these expressions, r is the intermolecular separation distance, and the other quantities (ϵ , σ , α , r_m , d , δ , A , ρ) are constant parameters. For the potential functions given by Eqs. (1), (2), and (3), the appropriate collision integrals have already been published (Refs. 4, 10, and 11). Collision integrals for the exponential repulsion potential [Eq. (4)] have been recently computed by L. Monchick (Ref. 5) of this Laboratory and were available to us. Potentials (1) and (2) are realistic functions for low temperature interactions since they include the London dispersion energy (attractive) term ($\beta\alpha r^{-6}$) which has a reasonably firm theoretical basis. Potentials (3) and (4) find particular application to the analysis of high-temperature phenomena where the attractive forces are less important in the molecular collisions. Molecular diffusion coefficients tend to be associated with more penetrating collisions than other transport properties at the same temperature (Ref. 12). It should be noted that the above potentials may be used in the case where only one member of the diffusion pair is a polar gas (for example, $\text{H}_2\text{O}-\text{O}_2$), since the interaction may still be regarded as effectively spherically symmetric.

The general kinetic theory expressions used in analyzing the diffusion data have been summarized in Ref. 2. The theory to the second approximation was used in all cases,

although this was actually necessary only in the cases where the molecular weights of the two gases in the pair were quite different (H_2-O_2 , H_2O-O_2 , CH_4-O_2).

To determine the potential parameters that best fitted the experimental measurements, a least squares method was employed. The quantity

$$S = \left(\frac{1}{N} \sum_{n=1}^N \left\{ \frac{D_{\text{expt}} - [D_{12}]_2}{D_{\text{expt}}} \right\}^2 \right)^{1/2}$$

was minimized with respect to the parameters involved in the theoretical $[D_{12}]_2$. Because the point center of repulsion [potential (3)] involves a simple mathematical description of the transport properties, the fitting procedure is straightforward; fitting the other potentials to the data, however, is not so simple. In these cases, the procedure outlined in Ref. 2 was generally followed, that is, ϵ , ϵ and α , or A was chosen for the Lennard-Jones, modified-Buckingham, or exponential repulsion potentials, respectively, and a value of σ , r_m , or ρ determined satisfying the least squares requirement. This procedure was repeated for different choices of σ , σ and α , or A until a minimum value of S was found. To facilitate this rather tedious operation, the appropriate dimensionless collision integrals were fit to polynomial functions⁵ in T and the entire procedure was programmed on an IBM 650 digital computer. As noted in Ref. 2, high-temperature transport data are not especially sensitive to the choice of compatible potential parameters, so that the standard deviation S of the measurements varies slowly (generally

⁵These polynomial expressions are available from the authors.

within experimental error) at its minimum with respect to these parameters (see Table II). For this reason it was felt that the three parameters for the modified-Buckingham (Exp-6) potential could not be unambiguously specified with the available data--rather, several choices of the parameter α were investigated and are reported below without discrimination. Actually, none of the reported potential parameters should be considered as being unique in view of the insensitivity of S .

A summary of the potentials fit to the diffusion measurements reported earlier in this paper is given in Table III. Also included is the range of r over which the determined potential can be expected to be valid (see Ref. 2 for a discussion of this rigid sphere range of validity). It will be apparent from a survey of the standard deviations provided in this table that all of these intermolecular potentials are about equally successful in fitting the diffusion data within the estimated experimental error. An equivalent compatibility does not exist, however, between the actual potential energies given by the fitted parameters of Table III. Figures 3 and 4 give examples of typical interactions which illustrate this important fact. Figure 3 is a plot of the $\text{CO}_2\text{-O}_2$ potential energy of interaction where the range of validity extends into the "well" created by a combination of attractive and repulsive forces, whereas Fig. 4 is the potential energy of interaction for the $\text{H}_2\text{O-O}_2$ system where the range of validity does not extend into the well. It is obvious that, although the repulsive potentials (3) and (4) are quite adaptable to the analysis of high temperature transport data, the corresponding potential energies of interaction so predicted do not include the attractive forces

Table II
Variation in Standard Deviation of Experimental
CO₂-O₂ Data from Values Fitted by Lennard-Jones
(12-6) Potential

Chosen ϵ/k (°K)	σ^2 from least squares (Å ²)	Standard Deviation, S (per cent)
160	12.259	2.75
180	11.883	2.17
200	11.538	1.81
220	11.220	1.75
240	10.924	1.99
260	10.649	2.41

TABLE III
Numerical Values of Potential Parameters for Various Unlike Molecular Interactions
With Associated Range of Validity and Precision of Fit to the Experimentally
Measured Diffusion Data

Gas Pair	Range of Validity		Modified-Hastingsham (Eq. 4)				Lennard-Jones (12-6)				Point Center of Repulsion			Exponential Repulsion			
	Min λ	Max λ	ϵ/h	r_m	a	Std. Dev. (per cent)	ϵ/h	σ	Std. Dev. (per cent)	d	σ	Std. Dev. (per cent)	A/k	ρ	β	Std. Dev. (per cent)	
	\AA	\AA	\AA	\AA	\AA		\AA	\AA		$\times 10^{10}$	\AA		$\times 10^{-5}$	\AA			
CO ₂ -O ₂	3.09	3.76	165	4.071	12	1.83	213	3.365	1.74	3.75	6.54	2.60	6.5	0.5263	2.94		
			202	3.848	14	1.78											
H ₂ -O ₂	2.50	2.94	117	3.421	12	0.58	152	2.825	0.63	1.62	7.13	1.01	9.0	0.3948	1.22		
			143	3.234	14	0.59											
			183	3.033	17	0.64											
CH ₄ -O ₂	3.08	3.80	145	4.061	12	2.37	162	3.367	2.25	4.56	6.83	3.04	8.0	0.4915	3.30		
			170	3.853	14	2.30											
			220	3.612	17	2.25											
CO-O ₂	3.01	3.38	40	4.525	12	2.30	91	3.480	1.73	75.6	9.52	1.85	106	0.3392	1.97		
			76	4.040	14	1.77											
			110	3.733	17	1.73											
H ₂ O-O ₂	2.78	3.10	55	4.154	12	2.5	49	3.335	1.40	358	11.41	1.46	900	0.2610	1.50		
			100	3.567	17	1.4											

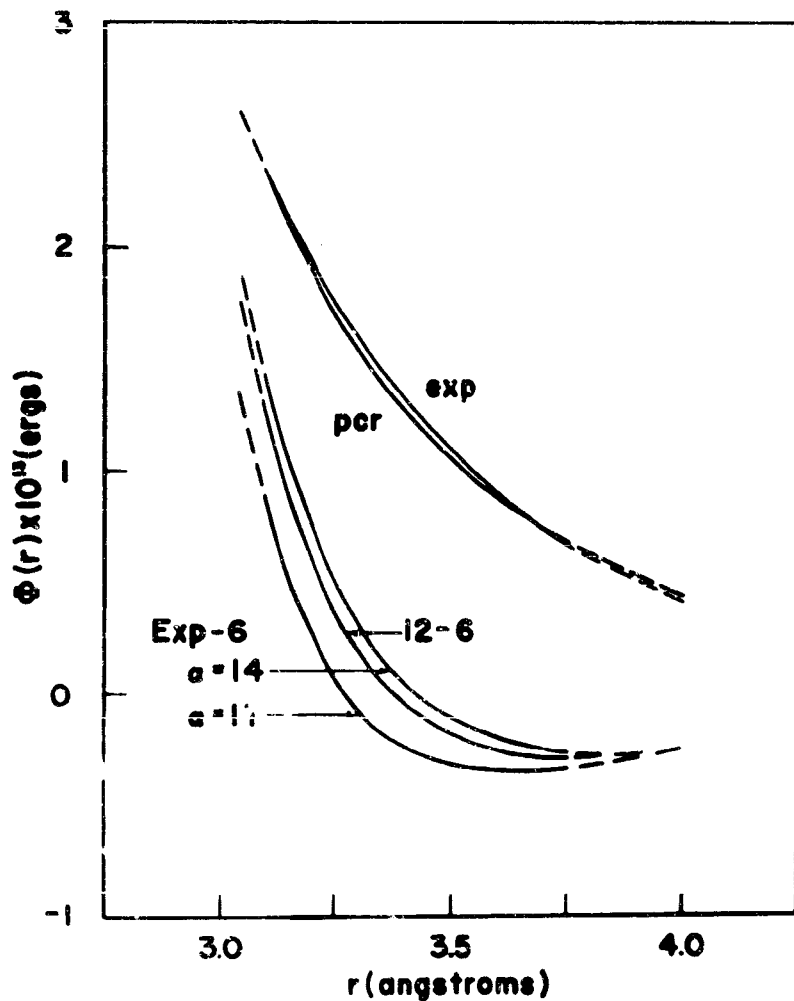


Fig. 3 POTENTIAL ENERGY OF INTERACTION FOR $\text{CO}_2\text{-O}_2$ USING POTENTIAL PARAMETERS LISTED IN TABLE III

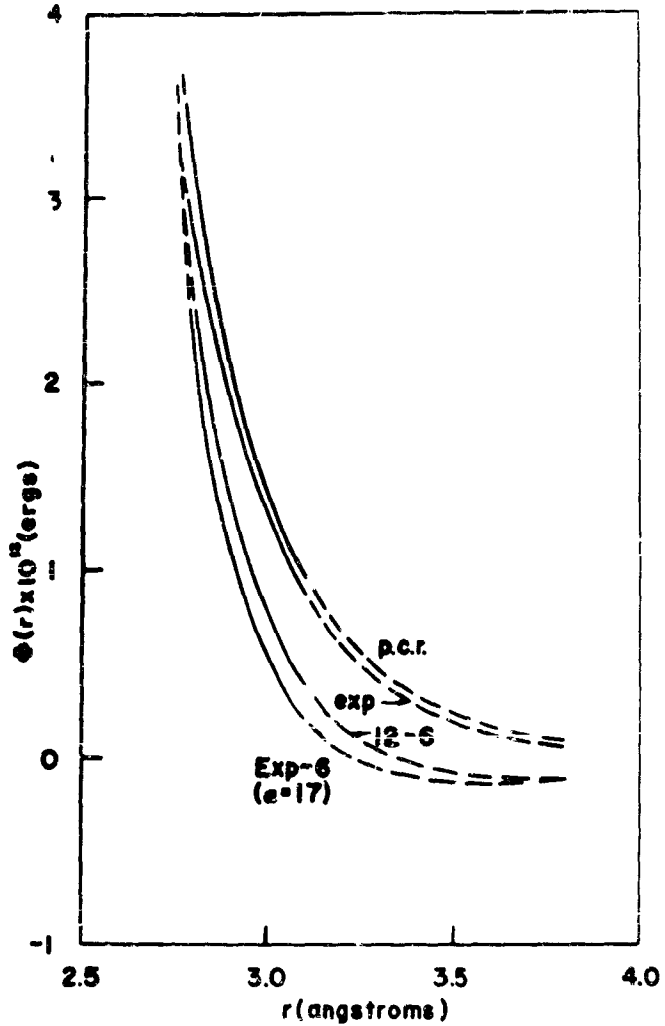


Fig. 4 POTENTIAL ENERGY OF INTERACTION FOR H_2O-O_2 USING POTENTIAL PARAMETERS LISTED IN TABLE III

of the interaction and hence differ significantly from the potential energies predicted by use of the Lennard-Jones (12-6) or modified-Buckingham (Exp-6) models. The differences are especially marked when the range of validity is close to the "well". Better agreement between all four potentials exists when the range of validity lies farther up on the (mainly) repulsive part of the curve--note the improved agreement in Fig. 4 as compared to Fig. 3. For more penetrating collisions (that is, higher temperature) the particular choice of the potential appears to be less critical. It should be emphasized that potentials determined in this way should not be extrapolated much beyond their ranges of validity--especially in the region of the "well". Even within the range of validity, it is impossible to state (without other evidence) which of the potentials is closest to the "true" potential, although it seems likely that potentials such as (1) and (2) which contain an attractive term would be more nearly correct. Conversely, the errors introduced by extrapolation of a transport property to a higher temperature may not be excessive in spite of the disagreement between the various potentials, as is shown in the following section. This point has been made before (Ref. 13), but it is well to stress it again.

IV. PREDICTION OF HIGH-TEMPERATURE DIFFUSION COEFFICIENTS

In our previous work (Refs. 2 and 3) on the He-N₂ and He-A systems, it was fortunate that detailed information on the intermolecular potential at closer distances of approach (corresponding to higher temperature interactions) had been provided by the molecular beam scattering experiments of Amdur and his co-workers (Refs. 14 and 15). These potentials provided an excellent foundation for predicting high-temperature diffusion coefficients ($1000^\circ < T < 10,000^\circ\text{K}$) of the unexcited species. The agreement between our measured values and the scattering predictions in the common temperature interval was quite good.

Unfortunately, no such scattering experiments have been done for the several gas pairs reported here. Table IV gives values to 3000°K for the diffusion coefficients obtained by extrapolation using the rigorous kinetic theory and the various fitted intermolecular potential parameters given in Table III. Although the various intermolecular potentials for a particular interaction are, in general, quite different in themselves, the diffusion coefficients extrapolated from them are not necessarily so, as can be seen by examining Table IV. Which of these extrapolated diffusion coefficients is more nearly correct is impossible to state.

Table IV
Comparison of Predicted Diffusion Coefficients Using the
Various Potential Functions Given in Table III
(Trace of Light Gas, $p = 1$ Atmosphere)

System	Potential Function	Temperature, °K						
		300	500	1000	1500	2000	2500	3000
CO ₂ -O ₂	12-6	0.161	0.419	1.43	2.84	4.59	6.66	9.01
	Exp-6 ($\alpha = 17$)	0.162	0.418	1.42	2.81	4.55	6.58	8.89
	p.c.r.	0.164	0.412	1.44	3.00	5.04	7.54	10.48
	exp	0.184	0.410	1.44	3.04	5.19	7.90	11.15
CH ₄ -O ₂	12-6	0.226	0.581	1.95	3.86	6.23	9.03	12.22
	Exp-6 ($\alpha = 17$)	0.230	0.583	2.00	3.95	6.38	9.23	12.45
	p.c.r.	0.229	0.574	1.99	4.11	6.88	10.26	14.23
	exp	0.230	0.570	1.99	4.18	7.11	10.77	15.18
H ₂ -O ₂	12-6	0.821	2.09	3.93	13.7	22.2	32.1	43.4
	Exp-6 ($\alpha = 12$)	0.818	2.07	6.99	14.1	23.1	34.0	46.6
	p.c.r.	0.828	2.06	7.06	14.5	24.3	36.1	50.0
	exp	0.830	2.05	7.10	14.9	25.2	38.1	53.6
CO-O ₂	12-6	0.224	0.542	1.73	3.40	5.48	7.93	10.72
	Exp-6 ($\alpha = 17$)	0.224	0.542	1.74	3.39	5.45	7.88	10.52
	p.c.r.	0.224	0.538	1.76	3.52	5.76	8.44	11.53
	exp	0.225	0.537	1.77	3.57	5.89	8.70	11.99
H ₂ O-O ₂	12-6	0.285	0.692	2.21	4.32	6.96	10.09	13.65
	Exp-6 ($\alpha = 17$)	0.286	0.691	2.20	4.31	6.93	10.00	13.45
	p.c.r.	0.294	0.691	2.21	4.35	7.05	10.24	13.90
	exp	0.294	0.690	2.21	4.37	7.11	10.38	14.16

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