

Pressure Dependence and Third Body Effects on the Rate Constants for $\text{H}+\text{O}_2$, $\text{H}+\text{NO}$, and $\text{H}+\text{CO}$

J. J. Ahumada, J. V. Michael, and D. T. Osborne

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Pressure Dependence and Third Body Effects on the Rate Constants for $\text{H} + \text{O}_2$, $\text{H} + \text{NO}$, and $\text{H} + \text{CO}$

J. J. AHUMADA, J. V. MICHAEL, AND D. T. OSBORNE

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

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This paper presents measurements of the third order rate constants for the reactions



The measurements were made by concentration analysis of hydrogen atoms by means of Lyman α photometry. All experiments were performed at room temperature. Particular emphasis was placed on the effect of changing the third body and, therefore, experiments were performed with M being H_2 , He, Ne, Ar, and Kr for all three reactions.

INTRODUCTION

$\text{H} + \text{O}_2 + \text{M}$ has been studied rather extensively with a variety of techniques. These include second explosion limit studies, shock tube studies, flow reactor studies, pulse radiolysis studies, and resonance fluorescence studies. Thrush¹ and Kaufman² have listed the more recent values.

In general, the second explosion limit studies give termolecular rate constants which range from 1.2 to 2.3×10^{-32} $\text{cc}^2 \text{ molecule}^{-1} \cdot \text{sec}^{-1}$ for $\text{M} = \text{H}_2$ in the temperature range, 700 – 900°K .^{3,4} Also relative third body effects have been studied with this technique, and reasonable agreement is obtained from laboratory to laboratory.^{5–7} The most striking result of this work is that the termolecular rate constant with $\text{M} = \text{H}_2$ is 4 to 5 times larger than that with $\text{M} = \text{Ar}$ in this temperature range.

This reaction has also been studied with $\text{M} = \text{Ar}$ by shock tube methods.^{8–10} In the latest work,^{9,10} values ranging from 0.6 to 0.8×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ have been obtained in the 1260 – 1910°K range. Gutman and co-workers obtained a value at 1100°K of 0.9×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$.¹¹

The values of the termolecular rate constant at room temperature have been obtained by discharge-flow, pulse radiolysis–Lyman α photometric, and flash photolysis–Lyman α fluorescence techniques. Clyne and Thrush's values, in a discharge flow system with Ar as the heat bath molecule, were 2.2×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ at 293°K , 4.0×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ at 244°K , and 3.5×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ at 225°K .¹² Values for the efficiencies of H_2O and He as third bodies relative to Ar were found to be 24 ± 10 and 1.0 ± 0.2 , respectively. More recently, Moortgat and Allen¹³ have obtained values of 1.9×10^{-32} , 1.5×10^{-32} , and 1.4×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ for M equal to H_2 , Ar, and He, respectively. These data were also obtained in a discharge flow system at room temperature with electron spin resonance detection. Westenberg and de Haas, also with electron spin resonance

detection, report identical room temperature values for M equal to Ar and He of 1.9×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$.¹⁴ Values reported at room temperature for M equal to H_2 and Ar have been reported by Dorfman and co-workers.^{15,16} This was the first study over a large pressure range (100 – 1500 torr total pressure). These workers employed a pulse radiolysis Lyman α absorption technique and obtained values of 4.7×10^{-32} and 1.6×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ for H_2 and Ar third bodies, respectively. Finally, Kurylo¹⁷ has also studied the reaction in He and Ar over a wide pressure range with the Lyman α fluorescence technique and finds identical values of 1.6×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ for both third bodies.

Clyne and Thrush have studied the reaction, $\text{H} + \text{NO} + \text{M}$, in a discharge flow system and have reported a value of 1.33×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ at 294°K when $\text{M} = \text{H}_2$ ¹⁸ and a later value in the same system of 4.12×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$.¹⁹ In the later study the relative efficiencies of third bodies were found to be $\text{H}_2:\text{He}:\text{Ne}:\text{Ar} = 1.7:0.8:0.8:1.0$. Simonaitis also studied the reaction at room temperature and found a value of 3.1×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ for $\text{M} = \text{H}_2$.²⁰ Hartley and Thrush measured the rate constant at 293°K to be 3.1×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ for $\text{M} = \text{Ar}$ and 5.6×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ when $\text{M} = \text{H}_2$.²¹ These workers also studied many more third bodies than the earlier work. Recent results have also been reported by Dorfman and co-workers on this reaction.¹⁶ A value of 3.8×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ has been obtained at room temperature with $\text{M} = \text{H}_2$. Atkinson and Cventanovic²² have measured this rate constant at room temperature to be 5.9×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ for $\text{M} = \text{H}_2$ with a phase sensitive detection method which utilizes the HNO emission as an atom detection technique. Finally, Moortgat and Allen¹³ report values of 3.8 , 1.6 , and 1.9×10^{-32} $\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ for H_2 , He, and Ar third bodies, respectively.

The reaction, $\text{H} + \text{CO} + \text{M}$, has not been studied in as much detail as the $\text{H} + \text{O}_2 + \text{M}$ or $\text{H} + \text{NO} + \text{M}$

reactions. Dorfman and co-workers have recently reported values of 1.1×10^{-34} and 0.72×10^{-34} $\text{cc}^2 \text{molecule}^{-2} \cdot \text{sec}^{-1}$ for H_2 and Ar third bodies, respectively.¹⁶ Also, Bennett and Blackmore have reported an upper limit value of 3.3×10^{-34} $\text{cc}^2 \text{molecules}^{-2} \cdot \text{sec}^{-1}$ with an electron spin resonance technique.²³ These data were obtained at room temperature.

EXPERIMENTAL

The apparatus which was used in the present study has already been fully described^{24,25} and, therefore, only a brief description will be given here. Hydrogen atoms generated by the mercury photosensitization of molecular hydrogen were observed by means of Lyman α absorption spectrophotometry. The gaseous sample which contained mercury at room temperature, was subjected to transient irradiation from a low pressure mercury resonance lamp. The duration of exposure was varied from ~ 20 to 200 msec and depended on the time needed to establish a steady state atom concentration. The lamp was then extinguished, and the decay of atoms was monitored oscilloscopically in the dark period by Lyman α photometry. If reactant is added to the system in sufficient excess so that little is consumed, the decay constants are first order in $[\text{H}]$ and follow the equation

$$\ln[\text{H}] = -k_{1st}t + c, \quad (\text{I})$$

where

$$k_{1st} = k_w + k_{app}[\text{R}]_0. \quad (\text{II})$$

k_w in Eq. (II) is an apparent wall termination constant and was measured routinely in each set of experiments with no reactant present. Reactant was then added in varying amounts and values of the apparent bimolecular rate constant, k_{app} , were obtained as slopes of linear plots of k_{1st} against $[\text{R}]_0$ (usually consisting of five to six points). In the present study the apparent bimolecular rate constant exhibited total pressure dependence, so it was necessary to hold pressure constant for one determination of k_{app} and then systematically vary pressure in order to assess the pressure dependence.

In this study the reactants were O_2 , NO , and CO . The third body gases were H_2 , He , Ne , Ar , and Kr . When experiments with rare gases were made, molecular hydrogen had to be introduced, but partial pressures never exceeded 8 torr so that hydrogen was generally negligible in comparison to rare gas pressures.

Research grade CO and O_2 were obtained from the J. T. Baker Chemical Company and Linde Corp., respectively. Research grade H_2 , Ne , and Kr were obtained from Air Products and Chemicals, Inc. Ar was purchased from Air Products and Chemicals, Inc. in ultrahigh purity grade. He from Airco, Inc. was high purity grade and was used only after passage through liquid nitrogen traps. Finally, NO was

TABLE I. Apparent bimolecular rate constants for the reaction $\text{H} + \text{O}_2 + \text{M}$.

P_T (torr)	k_{app} ($\text{cc molecule}^{-1} \cdot \text{sec}^{-1}$) $\times 10^{14}$
M = H_2	
9.84	1.5 ± 0.1
9.87	1.8 ± 0.2
9.98	1.4 ± 0.1
15.13	2.0 ± 0.1
24	2.5 ± 0.2
52	3.6 ± 0.4
52	2.9 ± 0.1
103	5.3 ± 0.7
105	4.7 ± 0.5
202	8.7 ± 0.5
205	9 ± 1
205	9.6 ± 0.5
206	9.0 ± 0.7
206	8.0 ± 0.5
208	8.5 ± 0.9
300	12 ± 2
303	13 ± 1
401	16 ± 3
406	14 ± 2
403	16 ± 2
594	22 ± 2
597	27 ± 2
598	25 ± 4
600	24 ± 4
603	19 ± 2
M = Ar	
54	1.2 ± 0.1
62	1.2 ± 0.2
103	1.6 ± 0.1
203	3.8 ± 0.6
301	5.3 ± 0.8
403	8.9 ± 1.5
599	11 ± 4
M = Ne	
202	1.2 ± 0.1
300	1.6 ± 0.1
401	1.6 ± 0.1
595	3.6 ± 0.5
M = Kr	
105	2.8 ± 0.6
204	7.0 ± 0.7
400	13 ± 1
600	23 ± 5
M = He	
58	0.9 ± 0.1
107	2.6 ± 0.3
206	4.2 ± 0.8
308	7.2 ± 0.9
404	9.9 ± 0.5
598	15 ± 2

TABLE II. Apparent bimolecular rate constants for the reaction
H+NO+M.

P_T (torr)	k_{app} (cc molecule ⁻¹ •sec ⁻¹) $\times 10^{13}$
M = H ₂	
57	1.3 \pm 0.3
106	2.6 \pm 0.2
207	3.8 \pm 0.4
208	4.3 \pm 0.3
305	5.6 \pm 0.3
407	8.3 \pm 0.3
504	10.7 \pm 0.8
602	12 \pm 0.5
M = Ar	
57	0.65 \pm 0.04
107	1.2 \pm 0.1
203	2.6 \pm 0.1
300	3.9 \pm 0.4
400	4.9 \pm 0.1
599	7.8 \pm 0.8
M = Ne	
107	0.8 \pm 0.1
208	1.6 \pm 0.2
309	2.1 \pm 0.3
405	2.7 \pm 0.1
601	4.1 \pm 0.3
M = Kr	
99	1.6 \pm 0.1
206	3.3 \pm 0.1
405	6.7 \pm 0.1
605	11 \pm 1
M = He	
58	0.8 \pm 0.1
102	1.3 \pm 0.1
208	2.9 \pm 0.1
306	4.0 \pm 0.4
406	5.8 \pm 0.8
604	8.6 \pm 0.7

obtained from Matheson Gas Products as technical grade. It was purified by bulb to bulb distillation from -183 to -196°C , and the middle third was used. All research grade and ultra high purity grade chemicals were used as received.

The possible problem of small amounts of reactive impurities arises when large pressures of rare gas are used. If the impurity is reactive with hydrogen atoms, the decay constant with no added reactant would become smaller and smaller with repetitive exposure to resonance radiation as the impurity is used by atomic reactions. In earlier experiments this phenomenon was noticed with ultra high purity grade H₂ and has necessitated the change to research grade.

Since routine values of k_w are obtained in each determination of k_{app} , any anomalies due to reactive impurities can be assessed immediately.

RESULTS

The apparent bimolecular rate constants for the reactions are listed in Tables I-III as a function of total pressure (10-600 torr) and third body. Within experimental error these rate constants are linearly proportional to total pressure for all three reactions, as seen in Figs. 1-3 where k_{app} against total pressure is plotted. Thus, these reactions are termolecular, and the slope of the lines in Figs. 1-3 gives the value of the third order rate constant after conversion of pressure to concentration. The termolecular rate constants are listed in Table IV for all three reactions as a function of third body. These values were obtained by least squares analysis where the lines were con-

TABLE III. Apparent bimolecular rate constants for the reaction
H+CO+M.

P_T (torr)	k_{app} (cc molecule ⁻¹ •sec ⁻¹) $\times 10^{16}$
M = H ₂	
57	1.8 \pm 0.2
113	3.7 \pm 0.2
209	5.3 \pm 0.2
412	10 \pm 0.6
586	15 \pm 1
M = Ar	
52	1.2 \pm 0.2
101	2.4 \pm 0.4
203	5.2 \pm 0.2
404	7.2 \pm 0.5
591	11 \pm 1
M = He	
106	2.8 \pm 0.1
200	4.2 \pm 0.6
304	6.0 \pm 0.4
400	8.7 \pm 0.6
601	10 \pm 1
M = Ne	
102	2.4 \pm 0.3
202	3.7 \pm 0.3
301	4.9 \pm 0.7
402	5.5 \pm 1.0
600	9.3 \pm 0.8
M = Kr	
99	2.2 \pm 0.2
201	4.5 \pm 0.6
300	6.0 \pm 0.6
399	9.2 \pm 0.7
601	14 \pm 1

strained to pass through the origin. The errors shown are standard deviations. Also listed are the relative third body effects with $k_{\text{ter}}(\text{Ar})$ taken to be unity in each case.

In an attempt to assess the importance of secondary reactions, a series of experiments were performed with variable initial hydrogen atom concentrations. The initial atom concentration was varied with screens of varying transmittances placed in the path of the mercury resonance radiation. The results of these studies are shown in Table V for the $\text{H} + \text{O}_2 + \text{H}_2$ reaction. For reasons mentioned in the following section, this reaction should have the highest probability for secondary reaction complications than any other in the present study.

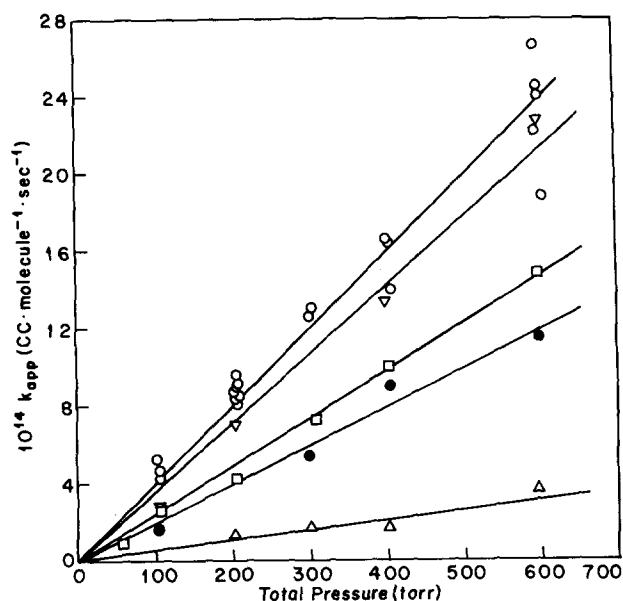
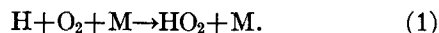


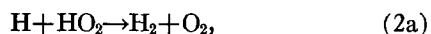
FIG. 1. k_{app} as a function of total pressure for the reaction, $\text{H} + \text{O}_2 + \text{M}$. M is: H_2 , \circ ; He, \square ; Ne, \triangle ; Ar, \bullet ; Kr, ∇ .

DISCUSSION

The oxygen reaction is always third order so that the over-all reaction can be considered to be



Bishop and Dorfman measured k_1 at 298°K to be 4.7 and $1.6 \times 10^{-32} \text{ cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ for $\text{M} = \text{H}_2$ and Ar, respectively, in the pressure range of 100 to 1500 torr.¹⁵ These values were based on the assumption that no secondary reactions of the type



were present. This was inferred by these workers be-

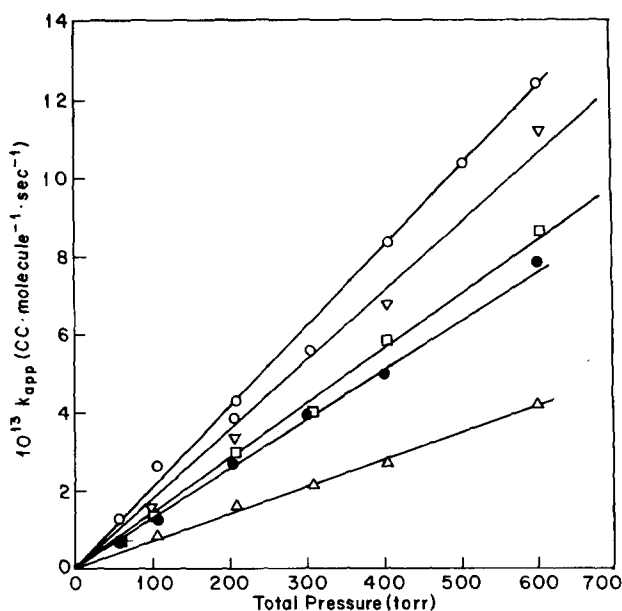


FIG. 2. k_{app} as a function of total pressure for the reaction, $\text{H} + \text{NO} + \text{M}$. M is: H_2 , \circ ; He, \square ; Ne, \triangle ; Ar, \bullet ; Kr, ∇ .

cause $[\text{O}_2] \gg [\text{H}]$ ($[\text{O}_2] \approx 10^{16} \text{ molecule cc}^{-1}$, $[\text{H}] \approx 10^{11} \text{ atom cc}^{-1}$).

Clyne and Thrush studied this reaction with $\text{M} = \text{Ar}$ in a discharge flow system and found k_1 at 293°K to be $2.2 \times 10^{-32} \text{ cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ in the pressure range 1–4 torr.¹² These workers considered the above secondary reactions to be important since their molecular oxygen concentration ($\sim 10^{15} \text{ molecules cc}^{-1}$) was not much greater than the hydrogen atom concentration ($\sim 10^{14} \text{ atom cc}^{-1}$). Several test experiments were performed by Clyne and Thrush for $\text{M} = \text{H}_2$ and they found that the effect of Reaction (2b), which is known to occur,¹⁴ was modified by the regeneration of H atoms from the process

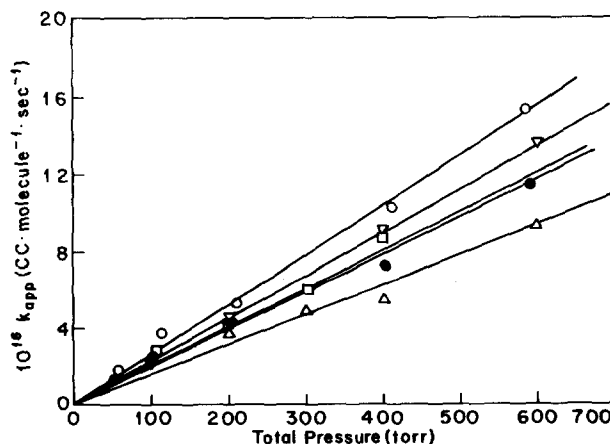
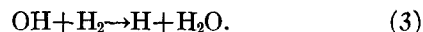


FIG. 3. k_{app} as a function of total pressure for the reaction, $\text{H} + \text{CO} + \text{M}$. M is H_2 , \circ ; He, \square ; Ne, \triangle ; Ar, \bullet ; Kr, ∇ .

TABLE IV. Apparent termolecular rate constants for the reactions $\text{H} + \text{O}_2 + \text{M}$, $\text{H} + \text{NO} + \text{M}$, $\text{H} + \text{CO} + \text{M}$ as a function of M, and third body effects relative to $\text{Ar}\{k_{\text{ter}}(\text{M})/k_{\text{ter}}(\text{Ar})\}$.

M	k_{ter} ($\text{cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$) $\times 10^{32}$	Relative M effect
H + O₂ + M		
H ₂	1.2 ± 0.1	2.0
Kr	1.1 ± 0.1	1.8
He	0.75 ± 0.03	1.2
Ar	0.60 ± 0.04	1.0
Ne	0.15 ± 0.03	0.2
H + NO + M		
H ₂	6.3 ± 0.3	1.6
Kr	5.4 ± 0.3	1.4
He	4.3 ± 0.1	1.1
Ar	3.9 ± 0.1	1.0
Ne	2.1 ± 0.1	0.5
H + CO + M^a		
H ₂	0.80 ± 0.04	1.3
Kr	0.69 ± 0.03	1.1
Ar	0.62 ± 0.07	1.0
He	0.60 ± 0.07	1.0
Ne	0.48 ± 0.05	0.8

^a $k_{\text{ter}} \times 10^{34}$.

These workers suggested that Reaction (3) had about the same probability as (2a) and (2c) with $\text{M} = \text{H}_2$. If argon was the third body, Reaction (3) was apparently unimportant, and this has been confirmed in more recent work.¹⁴

In this work $k_{\text{ter}}(\text{M} = \text{H}_2) = 1.2 \times 10^{-32} \text{ cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ and $k_{\text{ter}}(\text{M} = \text{Ar}) = 0.60 \times 10^{-32} \text{ cc}^2 \text{ molecule}^{-2} \cdot \text{sec}^{-1}$ at 298°K (see Table IV). Typical $[\text{O}_2]$ was 10^{14} – $10^{15} \text{ molecule cc}^{-1}$ and $[\text{H}]$ was $< 5 \times 10^{12} \text{ atom cc}^{-1}$ so that secondary reactions might also be unimportant in this work. The rate constant observed in H_2 is lower by about a factor of 4 from Bishop and Dorfman¹⁵ and a factor of 2 from Moortgat and Allen.¹³ In the Ar case $[\text{Ar}]/[\text{H}_2]$ was typically 25:1 to 600:1 so that Reaction (3) should be negligible here, also. The value obtained with Ar in this work is lower by about a factor of 2 from the most recent reports.^{13–17}

In order to further assess the importance of secondary reactions an estimate of the rate constant for reaction scheme (2) is needed. Clyne and Thrush estimated $k_2 \geq 5 \times 10^{-13} \text{ cc molecule}^{-1} \cdot \text{sec}^{-1}$. If a steric factor of 10^{-2} for an atom-nonlinear polyatomic reaction is assigned, a reasonable value for k_2 might then be $\sim 10^{-12} \text{ cc molecule}^{-1} \cdot \text{sec}^{-1}$. Even if the over-all rate of reaction scheme (2) is considered to be $\sim 10^{-12}$

$\text{cc molecule}^{-1} \cdot \text{sec}^{-1}$, typical $[\text{H}]$ is sufficiently low that the contribution to the decay of H atoms from Reaction (2) would be no more than $2\text{--}3 \text{ sec}^{-1}$. Typical values for k_{1st} over the complete set of experiments were $30\text{--}60 \text{ sec}^{-1}$ so that secondary reactions should be unimportant.

In order to further test this hypothesis experimentally, experiments were performed with neutral density filters in the path of the mercury resonance radiation such that $[\text{H}]$ was decreased by about a factor of 10. The initial $[\text{H}]$ would then be $\sim 5 \times 10^{11} \text{ atom cc}^{-1}$ and even a very large rate constant of $\sim 10^{-11} \text{ cc molecule}^{-1} \cdot \text{sec}^{-1}$ for k_2 (nearly the collision rate) would still result in a negligible contribution to the H-atom decay from Reaction (2). If secondary reactions are important, a change in stoichiometry would have been reflected as a change in k_{app} by the abovementioned neutral density filter experiments. Inspection of Table V shows that no change within experimental error in k_{app} was observed. Therefore, either k_2 is less than $\sim 10^{12} \text{ cc molecule}^{-1} \cdot \text{sec}^{-1}$ and Reactions (2) are unimportant, or k_2 is greater than $\sim 10^{-11} \text{ cc molecule}^{-1} \cdot \text{sec}^{-1}$ and Reactions (2) are occurring so rapidly that they are important in all of the work reported here. The former conclusion is most reasonable in view of the fact that the upper limit of k_2 is nearly equal to the collision rate and is therefore not reasonable from a theoretical point of view. The measured k_{ter} values can then be considered as values for k_1 .

Bishop and Dorfman suggested in their H_2 third body experiments that at low hydrogen pressures the rate of Reactions (2) may no longer be negligible in comparison with Reaction (1). In their plot of k_{app} vs H_2 pressure, it was noted that the data below 300 torr showed a positive deviation from linearity. In the present work a positive deviation was also noted at H_2 pressures below 100 torr (Table I), and an increase in the importance of the secondary reactions may be the explanation.

It appears that there is no satisfactory explanation for the difference in rate constants between the present work and that of Dorfman and co-workers^{15,16} since

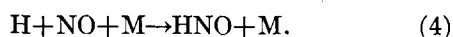
TABLE V. Values of apparent bimolecular rate constants for $\text{H} + \text{O}_2 + \text{H}_2$ ($\text{cc molecule}^{-1} \cdot \text{sec}^{-1}$) as a function of relative absorbed intensity, I_a , of Hg 2537 Å light. $P_{\text{H}_2} = 300 \text{ torr}$.

Relative I_a	$k_{\text{app}} \times 10^{14}$	$k_{\text{app}} \times 10^{14}$	$k_{\text{app}} \times 10^{14}$	$k_{\text{app}} \times 10^{14}$
1.00	16 ± 3	12 ± 2	12 ± 2	13 ± 2
0.725	11 ± 1	15 ± 2
0.456	15 ± 2	10 ± 1
0.214	12 ± 2	...	12 ± 2	...
0.095	15 ± 2
$[\text{O}_2] \times 10^{-14}$ (molecule/cc)	2.90	3.03	3.01	2.82

the conditions are such that both techniques should have isolated k_1 for H_2 and Ar third bodies. Also there is no clear explanation as to the discrepancy between the present result in Ar and that of Kurylo.¹⁷ The present work and these three cited studies¹⁵⁻¹⁷ are the first to study this reaction over a large pressure range.

Since the rate of Reaction (1) is dependent on $[\text{M}]$ and the effects of different third bodies on such reactions is of continuing theoretical interest, further experiments were performed with He, Ne, and Kr. The rate constants and relative M effects are tabulated in Table IV. If these values are compared with the reported values from other investigations, it can be seen that the largest discrepancy is in the relative efficiency of H_2 to Ar. In this work the ratio is found to be 2.0 ± 0.4 . The value of 4-5 for the ratio was determined from explosion limit studies at higher temperatures, and it is conceivable that the efficiencies may increase with temperature. At room temperature the comparisons of relative efficiency can be made with the data of Moortgat and Allen¹³ and Dorfman and co-workers^{15,16} who find ratios of 1.3 ± 0.3 and 2.9 ± 0.8 , respectively. However, the rather large uncertainties in these values and the present value probably reflect no strong conflict in results.

The reaction of a hydrogen atom with nitric oxide is termolecular throughout the pressure range studied, as was the case for the oxygen reaction. The over-all reaction can then be represented by



Hartley and Thrush²¹ found this reaction to be followed by the rapid reaction



These workers reported a value for k_4 ($\text{M} = \text{Ar}$) of 3.1×10^{-32} cc² molecule⁻²·sec⁻¹ and k_4 ($\text{M} = \text{H}_2$) of 5.6×10^{-32} cc² molecule⁻²·sec⁻¹, and both were based on a stoichiometry factor of two because of the occurrence of Reaction (5). In an earlier study Simonaitis,²⁰ who assumed the same stoichiometry factor, found k_4 ($\text{M} = \text{H}_2$), to be 3.1×10^{-32} cc² molecule⁻²·sec⁻¹ with the isothermal calorimeter technique. Dorfman and co-workers¹⁶ have obtained a value of 3.8×10^{-32} cc² molecule⁻²·sec⁻¹ while Atkinson and Cvetanović²² note a value of 5.9×10^{-32} cc² molecule⁻²·sec⁻¹ with $\text{M} = \text{H}_2$. Moortgat and Allen¹³ report values of 3.8 and 1.9×10^{-32} cc² molecule⁻²·sec⁻¹ for H_2 and Ar, respectively. The values obtained in this research were k_{ter} ($\text{M} = \text{Ar}$) = 3.9×10^{-32} cc² molecule⁻²·sec⁻¹ and k_{ter} ($\text{M} = \text{H}_2$) = 6.3×10^{-32} cc² molecule⁻²·sec⁻¹.

In the flow system work (1-4 torr) where $[\text{NO}]$ was not in large excess over $[\text{H}]$, the rate constant for Reaction (5) was listed as $\sim 10^{-14}$ cc molecule⁻¹·sec⁻¹.²¹ Since these workers were measuring an apparent bimolecular rate constant of 4 to 16×10^{-15} cc molecule⁻¹·sec⁻¹, Reaction (5) was in direct competi-

tion with Reaction (4). On this basis, a stoichiometry factor of two was then included in their calculations for k_4 .

The values for the apparent bimolecular rate constant in this work were in the range 10^{-13} - 10^{-12} cc molecule⁻¹·sec⁻¹. Since these observed values are 10-100 times larger than that of Reaction (5), Reaction (5) should be negligible here, and the k_{ter} values should be true values for k_4 . On this basis, the agreement between this work and the above mentioned values of Hartley and Thrush and Atkinson and Cvetanović for k_4 is excellent. Also the comparison with the values of Dorfman and co-workers,¹⁶ Simonaitis,²⁰ and Moortgat and Allen¹³ probably reflects no strong discrepancy when experimental errors are considered.

Hartley and Thrush found k_4 ($\text{M} = \text{H}_2$)/ k_4 ($\text{M} = \text{Ar}$) to be 1.9 while the corresponding ratio found here is 1.6. Moortgat and Allen note the same ratio to be 2.0. Earlier work of Clyne and Thrush reported

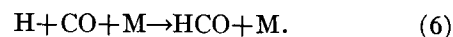
$$k_4 (\text{M} = \text{Ne})/k_4 (\text{M} = \text{Ar}) = 0.8$$

and

$$k_4 (\text{M} = \text{He})/k_4 (\text{M} = \text{Ar}) = 0.8$$

which can be compared with the corresponding values from this research of 0.5 and 1.1, respectively.

The carbon monoxide reaction is termolecular throughout the range of pressure used in the present study. The over-all reaction is, then,



Dorfman and co-workers¹⁵ have measured the rate constant for this reaction to be 1.1×10^{-34} and 0.72×10^{-34} cc² molecule⁻²·sec⁻¹ for H_2 and Ar third bodies, respectively. The apparent termolecular rate constants obtained in the present work are 0.80 and 0.62×10^{-34} cc² molecule⁻²·sec⁻¹, respectively. The agreement between the present results and those of Dorfman and co-workers is gratifying.

In this case the secondary process



may be negligible as in the cases of oxygen and nitric oxide for the same reasons. Even though Reaction (6) is quite slow, the apparent bimolecular rate constants were adjusted to be in the range of $\sim 10^{-13}$ cc molecule⁻¹·sec⁻¹ by increasing the carbon monoxide concentration. Even though Reaction (6) is slow the rate of formation of HCO is about similar to the rate of formation of HNO or HO_2 . A final decision on the importance of Reaction (7) on the over-all stoichiometry must rest on presumed values for the rate constant for the reaction. Since the rates of formation of HCO are always comparable and are adjusted by variation of the product, $[\text{CO}][\text{M}]$, the effects of secondary reactions, if they are important, should be invariant and independent of either carbon monoxide or third body concentrations. Thus, the relative third

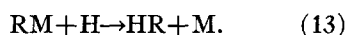
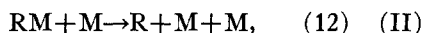
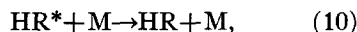
body effects observed on this reaction should refer to Reaction (6) above.

Mechanism

Various points of view regarding the mechanisms of termolecular recombination reactions or their reverse, bimolecular dissociation reactions, have been expressed in the literature. These are discussed in detail by Bunker.²⁶ Many workers, predominantly in room temperature studies, have endorsed the atom or molecule-third body complex mechanism^{26,27} even though a simple energy transfer mechanism has not been ruled out in some instances. In this discussion both mechanisms will be considered even though it is recognized that both mechanisms represent extreme assumptions about the behavior of the image points in the phase space of the three interacting particles.

Bunker and Davidson have derived theoretical expressions which can be used to assess the importance of the complex mechanism.²⁷ Since the basic criterion for the theory is that bound states occur in Lennard-Jones complexes, it is unlikely that this mechanism could be important for light third bodies (H_2 and He) or for recombinations which have appreciable activation energy. The mechanism for recombination in these cases is probably energy transfer. On the other hand, calculations for the iodine recombination show that for polyatomic third bodies, the complex mechanism predominates over the energy transfer mechanism.²⁸ For heavy monatomic and diatomic third bodies both mechanisms contribute and, in these cases, the reaction probably takes place through trajectories that approximate both the complex and energy transfer mechanisms, i.e., the mechanism is mixed. In these intermediate cases it is necessary to adopt a formalism which assesses the importance of all possible trajectories, and such a phase space theory has been developed and used by Keck and co-workers.^{29,30}

The present cases can then be discussed in terms of the two mechanisms discussed above. They are energy transfer (I) and complex (II);



The mechanism which would involve HM complexes is ruled out because there are no bound vibrational states in these Lennard-Jones complexes. In Mechanisms (I) and (II), R refers to O_2 , NO, or CO and M is H_2 , He, Ne, Ar, or Kr.

Several features of these three reactions are similar. The masses of reactants are nearly the same. Also

the Lennard-Jones parameters for CO, NO, and O_2 ³¹ are similar so that collision frequencies and concentrations of complexes are nearly the same for all three reactions with a given third body. The feature which is not similar is the energetics of the reactions. The $H+CO+M$ reaction is clearly different from the other two.

$H+CO+M$

Much is known about the potential surface for HCO.³² The absorption spectrum has been studied, and a predissociation in the $^2A''$ first excited state has been noted 35.4 kcal/mole ($12\,400\text{ cm}^{-1}$ above the ground $^2A'$ state).³³ Both the ground and first excited states ($^2A'$ and $^2A''$) correlate with $H(^2S)+CO(^3\Pi)$. The observed predissociation exists because of the presence of a repulsive, $^2A'$ state, which correlates with the lower lying $H(^2S)+CO(^1\Sigma^+)$ ground state of the separated species. The recombination of H and CO could occur by a potential crossing of the $^2A'$ repulsive state and the ground $^2A'$ state of HCO through an avoided crossing. Whether the reaction has an activation energy or not depends on the heat of dissociation of HCO. This has been a subject of considerable controversy for a long time. A high value, 28 kcal/mole, is favored by some workers, but there is considerable evidence for a lower value of 17 ± 3 kcal/mole. The work up to 1958 has been reviewed.³⁴ Two more recent studies suggest values of 26.3 and 17 ± 4 kcal/mole, respectively.^{35,36} If the level crossing of the repulsive $^2A'$ state into the $^2A'$ ground state and the $^2A''$ first excited state occurs at approximately the same energy (35.4 kcal/mole), then an activation energy for the recombination should exist. The activation energy should be between 18 or 7 kcal/mole depending on which extreme value for the dissociation energy is chosen. The activation energy will be somewhat lower than either of these values if the level crossings are not at the same energy since the $^2A'$ repulsive to $^2A'$ attractive crossing occurs at an energy lower than the $^2A'$ repulsive to $^2A''$ attractive crossing to which the predissociation is attributed.

Inspection of Table IV indicates that the $H+CO+M$ reaction is about two orders of magnitude slower than either the $H+O_2+M$ or $H+NO+M$ reaction. This effect is attributed to the probable presence of an avoided crossing and, therefore, to an appreciable activation energy. It is quite doubtful that this activation energy could be even 7 kcal/mole, however. The exact value will have to await studies of the temperature dependence for this reaction.

If an appreciable activation energy exists it is unlikely that the termolecular reaction could involve the complex mechanism (II). Even though Lennard-Jones complexes are present in the system, these complexes are lower lying than are the separated reactants, and therefore, they would tend to increase the activation

energy to products and would act as an inhibiting rather than a catalyzing agent to products. It is then probable that systems which can surmount this rather appreciable barrier must be approximating the energy transfer mechanism and have relative energy in excess of the energy barrier.

If the energy transfer mechanism is then adopted to explain the $\text{H} + \text{CO} + \text{M}$ reaction then the termolecular rate constant can be written as²⁸:

$$k_r = PgZ_{\text{H,R}}\tau_{\text{HR}^*}Z_{\text{HR}^*,\text{M}} \exp(-E_a/RT), \quad (\text{III})$$

where $Z_{\text{H,R}}$ and $Z_{\text{HR}^*,\text{M}}$ are the collision rate constants for H and R species and HR^* and M species, respectively. τ_{HR^*} is the average lifetime of HR^* (HCO^* in this case), and E_a is the activation energy for the reaction. P is a factor which represents an average probability for deactivation of HR^* and g is an electronic degeneracy ratio which is the number of attractive states which correlate with separated species divided by the total number of states. In the $\text{H} + \text{CO}$ reaction the entire third body dependence is contained in the product, $PZ_{\text{HR}^*,\text{M}}$. Values for $Z_{\text{HR}^*,\text{M}}$ were calculated from the Lennard-Jones diameters and reduced masses for $\text{HR}^* = \text{HCO}^*$ and $\text{M} = \text{H}_2$, He, Ne, Ar, and Kr interactions. Corrections were made for long range attractions through the tabulated collisions integrals for the Lennard-Jones potential.³¹ The force constant for HCO^* was taken as that of CO itself, but σ_{HCO} was assumed to be $1/2(\sigma_{\text{CO}} + \sigma_{\text{H}})$. A value of σ_{H} of 1.67 Å can be derived from data on the diffusion coefficient for H atoms in H_2 .³⁷

At 300°K the values calculated are: $Z_{\text{HCO}^*,\text{H}_2} = 5.8 \times 10^{-10}$; $Z_{\text{HCO}^*,\text{He}} = 3.4 \times 10^{-10}$; $Z_{\text{HCO}^*,\text{Ne}} = 2.0 \times 10^{-10}$; $Z_{\text{HCO}^*,\text{Ar}} = 2.6 \times 10^{-10}$; and $Z_{\text{HCO}^*,\text{Kr}} = 2.6 \times 10^{-10}$ in units of $\text{cc molecule}^{-1}\text{sec}^{-1}$. These values predict without any assumptions being made about the P factor that the termolecular rate constant with Ne as the third body should be the smallest. This is observed as indicated in Table IV.

In the absence of the exact value for the activation energy in Eq. (III) no attempts have been made to calculate the other factors which are independent of the nature of third body, namely, τ_{HCO^*} and $Z_{\text{H,R}}$. Relative values for P can, however, be calculated by dividing the experimental termolecular rate constant (Table IV) by $Z_{\text{HCO}^*,\text{M}}$. These are: 1.0, 1.3, 1.7, 1.7, and 1.9 for H_2 , He, Ne, Ar, and Kr, respectively. P_{rel} in H_2 was taken to be unity. As expected the probability for collisional deactivation increases with increasing mass.

$\text{H} + \text{NO} + \text{M}$

Of the three reactions studied here, the potential surface for the interaction of H and NO is probably best known.³² HNO has been studied in absorption³⁸ and emission³⁹ and a clear predissociation has been noted in the first excited electronic state, $^1A''$, 48.6

kcal/mole ($17\,000\text{ cm}^{-1}$) above the ground $^1A'$ state. As in HCO , both of these states correlate with higher energy configurations of separated species whereas the ground state configuration is $\text{H}(^2S) + \text{NO}(^2\Pi)$. The ground state of separated species can correlate with $^1A'$, $^1A''$, $^3A'$, and $^3A''$, all of which are repulsive except perhaps $^3A''$. It is this $^3A''$ state which is believed to be responsible for the predissociation in the $^1A''$ state¹⁹; however, theoretical studies do not agree with this conclusion.⁴⁰ Even though an avoided crossing may exist between the $^1A'$ repulsive and $^1A'$ ground states, the observation of a negative activation energy for recombination tends to rule out an appreciable barrier.^{18,19} Thus, recombination can occur with no electronic energy barrier at least into the $^1A'$ attractive state. This case is then similar to the iodine atom recombination case, and the complex mechanism (II) may partially contribute for heavy monatomic third bodies. The extent to which it does contribute rests critically on the magnitude of τ_{HNO^*} in Eq. (III). For light third bodies, however, the complex mechanism should not contribute since no bound complexes should exist. The mechanism should in these cases be energy transfer and Eq. (III) should hold.

As in the case of $\text{H} + \text{CO}$, the quantities $Z_{\text{HNO}^*,\text{M}}$ can be calculated under the same assumptions. Since Lennard-Jones force constants, collision diameters, and masses are all nearly the same in this case as in the $\text{H} + \text{CO}$ case,³¹ the quantities $Z_{\text{HNO}^*,\text{M}}$ are essentially the same. Relative P factors can be calculated as before, only it ought to be recognized that if the termolecular rate constant is the sum of that due to energy transfer and the complex mechanism, the collisional efficiency sense of this factor will only have meaning for light mass third bodies (H_2 and He). The values for P_{rel} (P_{rel} in $\text{H}_2 = 1.0$) are 1.0, 1.2, 1.0, 1.4, and 1.9 for H_2 , He, Ne, Ar, and Kr, respectively. In this case the relative factors also tend to increase as a function of mass, but the relationship of these factors to one another is different in this case than in the $\text{H} + \text{CO}$ case where a regular increase in the factor from low to high mass was noted. In this case the factor seems to be constant at low mass and then increases as third body mass increases. A somewhat similar behavior exists for the $\text{I} + \text{I} + \text{M}$ reaction where the relative factors are 1.0, 1.3, 1.1, 1.7, and 2.6 for H_2 , He, Ne, Ar, and Kr.⁴¹ Since it is believed that the complex and energy transfer mechanism are both contributing to the iodine atom recombination, and these factors exhibit some similarities, it suggests that the recombination mechanism for $\text{H} + \text{NO} + \text{M}$ may also be mixed. If assumptions about τ_{HNO^*} , g , and force constants are made then the fraction of the reaction which occurs by each mechanism can be calculated. Such assumptions are arbitrary and are therefore only approximate. A better approach would be to assess the importance of all types of interactions

through the previously mentioned phase space formulation.^{29,30}

H+O₂+M

The potential energy surface for HO₂ is the least known of any of the cases considered here. The ground state is a ²A'' state whereas the first excited state is ²A' state.²¹ No emission or absorption has been detected between these states so the exact energy relationship between the states is unknown. The separated species can correlate with a ²A'' state among others, and, therefore, recombination can take place, possibly through an avoided crossing. The observation of a negative activation energy for recombination may rule out this possibility.¹² The bond dissociation energy for H-O₂ has been estimated to be 47.1 kcal/mole, a value which is similar to that of H-NO. Thus, the similarities in potential energy surface and energetics between H+O₂+M and H+NO+M are apparent.

If the previous procedure is adopted in order to assess the importance of the energy transfer mechanism, the relative factors (P_{rel} in H₂=1.0) are 1.0, 1.0, 0.4, 1.1, and 2.0. Again the values for $Z_{HO_2^*,M}$ are nearly identical to those for $Z_{HCO^*,M}$ since force constants, collision diameters, and masses are all about the same.³¹ These values compare favorably with those obtained for H+NO+M except for the low value for Ne. As in the case of the H+NO+M recombination, the relationship of these relative factors to one another and their similarity to the iodine atom recombination, tends to suggest for higher mass third bodies a partial contribution to the recombination by the complex mechanism. Again the assessment of these interactions should be made with the phase space theory mentioned previously.^{29,30}

SUMMARY

The reactions, H+CO+M, H+NO+M, and H+O₂+M, have been studied at room temperature, where M=H₂, He, Ne, Ar, and Kr, respectively. The absolute agreement of the termolecular rate constants with other workers is generally good except for H+O₂+M where the present values are lower. However, the relative effects of third body gases on all three reactions are generally in agreement with most workers who have studied the reactions at room temperature.

These recombinations have been discussed in terms of energy transfer and complex mechanisms. Third body effects due to the energy transfer mechanism have been evaluated, and it is predicted on this basis alone that the reaction with Ne as third body should be the slowest reaction in all cases. This is observed. Relative collisional deactivation efficiencies for the H+CO+M reaction appear to be regular, i.e., the factor increases with increasing third body mass. This suggests that the energy transfer mechanism is dominant in this case. Arguments are given for the H+NO+M

and H+O₂+M reactions (where there is no electronic barrier) that both energy transfer and complex mechanisms may be operative for heavy monatomic third body gases.

If these conclusions are correct, additional studies of these reactions with polyatomic third body gases at room temperature would be quite interesting. The H+NO+M and H+O₂+M reactions should exhibit similar behavior to that of the iodine atom recombination where the complex mechanism apparently becomes dominant for polyatomic M. On the other hand, the H+CO+M reaction should be less dependent on the nature of the third body than either of the other two reactions and should be interpretable on the basis of an energy transfer mechanism with relative collision efficiencies which approach a constant and non-varying value with increasing third body complexity.

ACKNOWLEDGMENT

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⁴¹ These relative factors ($P_{\text{H}_2}=1.0$) may be obtained by division of the calculated energy transfer rate constant into the experimental values for the $\text{I}+\text{I}+\text{M}$ reactions. All necessary estimates and data are tabulated in Ref. 28.

Thermodynamics of Curved Boundary Layers

J. J. VIECELI AND H. REISS*

Department of Chemistry, University of California, Los Angeles, California 90024

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A general thermodynamic theory of curved boundary layers in one-component, one-phase fluids is presented; final results are displayed as the boundary analogs of the Gibbs adsorption equation and the Gibbs-Tolman-Koenig-Buff equation. The derivation does not rely on the conventional cone or wedge shaped container of interfacial thermodynamics and therefore avoids the difficulty associated with these containers when dealing with a microscopic boundary surface as in scaled particle theory. The method of derivation and results, although of particular importance to scaled particle theory, are of general interest because of the fundamental distinction between boundary and interfacial effects.

I. INTRODUCTION

In a recent article on scaled particle theory,¹ Reiss and Tully-Smith made use of the thermodynamic formalism presented by Ono and Kondo in a review article² devoted to the thermodynamics and statistical thermodynamics of interfaces. Except for the details of presentation, that formalism summarizes the efforts of many workers in the field and has gained a wide measure of acceptance. In their article, Reiss and Tully-Smith simply referred to the derivations in Ref. 2 and did not reproduce them. Since that time, the authors, one of whom (Reiss) coauthored the original paper, have noticed an inconsistency in applying interfacial thermodynamics to scaled particle theory and boundary layers in general.

The difficulty is best observed through the Gibbs adsorption equation for a planar interface in a one-component system at constant temperature,³

$$d\gamma_i = -\Gamma_i d\mu. \quad (1)$$

In this equation, γ_i is the interfacial tension (associated with a given surface), Γ_i is the superficial density of matter associated with the same dividing surface, and μ is the chemical potential. Now it is well known that the interfacial tension for a planar interface is in fact independent of the choice of dividing surface, while the superficial density is not. Equation (1) therefore appears to lead to an inconsistency, since it

predicts that a change in μ induces different changes in γ_i for different dividing surfaces (Γ_i depends on dividing surface). Actually, since Eq. (1) is applied to an *interface* (the existence of an interface necessitates a two-phase system), no change in chemical potential can in fact occur at constant temperature. The variation leading to the inconsistency therefore does not exist. On the other hand, in a one-phase, one-component system in which we deal with a planar boundary surface rather than an interface, it is possible to vary μ at constant temperature. Under these circumstances, it can be shown that⁴

$$d\gamma_i = -\Gamma_i d\mu + \text{additional terms}, \quad (2)$$

so that with the variation $d\mu$, now possible, the additional terms act to specify $d\gamma_i$ in a manner consistent with maintaining γ_i independent of dividing surface. This difference in interpretation of Eqs. (1) and (2) led the authors to formulate a general thermodynamic theory of boundary surfaces, and this is the subject of the present paper.

The above discussion implies that the results obtained in Ref. 1 concerning scaled particle theory must also be modified. Actually, the entire philosophy of that paper and most of the conclusions (even many of the quantitative ones) retain their validities. There are some relations, however, which must be changed, although again the changes are not significant quantitatively. We will deal with this problem in a separate forth-