



THERMODYNAMIC DATA

T (K)	$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (J K <sup>-1</sup> mol <sup>-1</sup> )	log K <sub>p</sub> (K <sub>p</sub> in atm)	log K <sub>c</sub> (K <sub>c</sub> in mol cm <sup>-3</sup> )
298	57.11	175.57	-0.84	-5.23
300	57.11	175.55	-0.77	-5.16
500	55.54	171.71	3.17	-1.45
1000	48.82	162.55	5.94	1.03
1500	41.11	156.31	6.73	1.64
2000	33.11	151.72	7.06	1.84
2500	24.99	148.09	7.21	1.90
3000	16.80	145.11	7.29	1.90
3500	8.59	142.57	7.32	1.86
4000	0.34	140.37	7.33	1.81
4500	-7.92	138.43	7.32	1.76
5000	-16.20	136.68	7.31	1.70

SI Units:  $\log(K_p/\text{N m}^{-2}) = \log(K_p/\text{atm}) + 5.006$   
 $\log(K_c/\text{mol m}^{-3}) = \log(K_c/\text{mol cm}^{-3}) + 6.000$

RECOMMENDED RATE CONSTANT

$$k^0 = 2.5 \times 10^{17} \exp(-5550/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{M} = \text{N}_2)$$

$$= 4.2 \times 10^{-7} \exp(-5550/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (\text{M} = \text{N}_2)$$

Temperature Range: 250 - 350 K

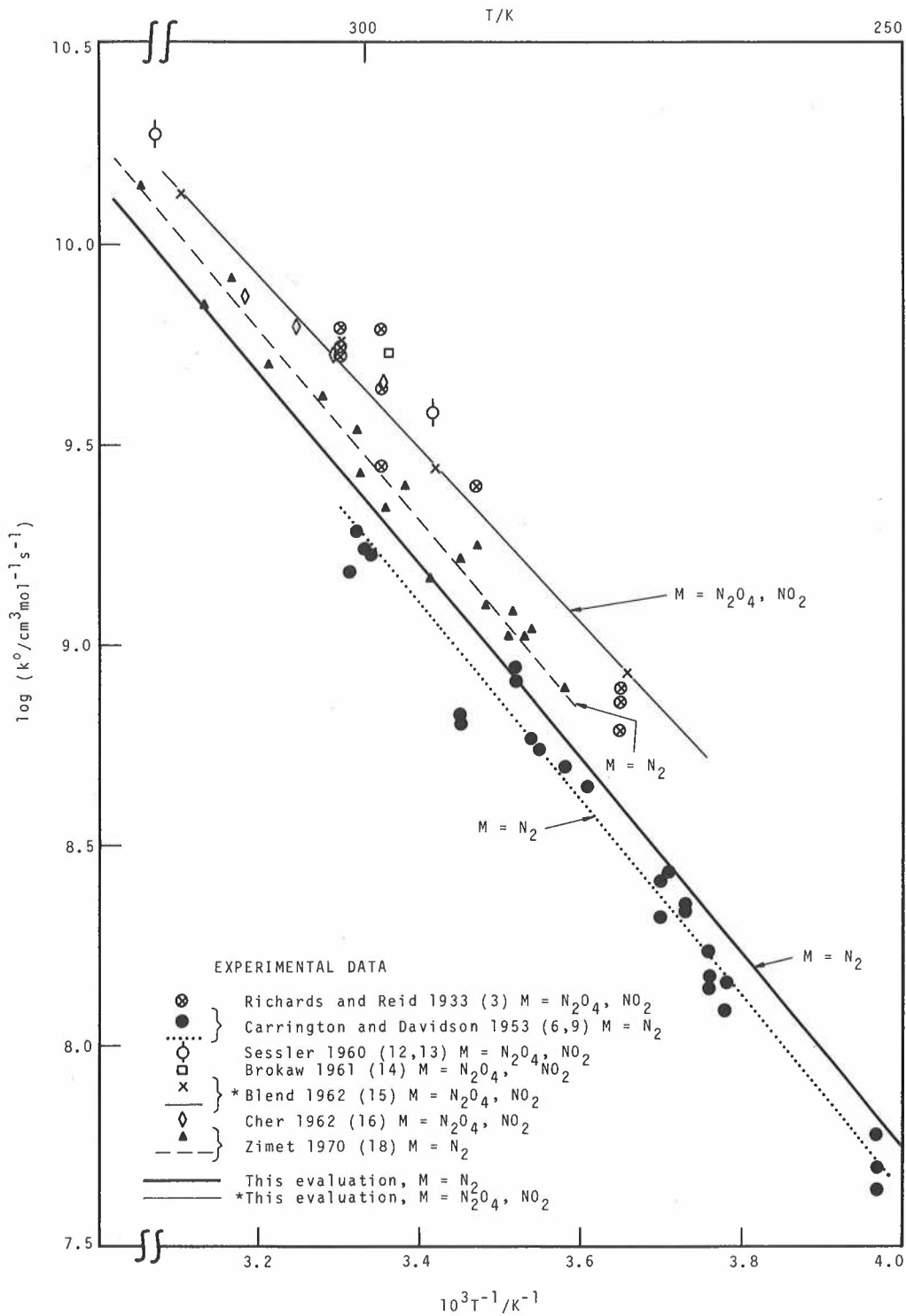
Suggested Error Limits for Calculated Rate Constant:  $\pm 30\%$  in the temperature range quoted.

Note: BLEND's expression (15) for  $\text{M} = \text{N}_2\text{O}_4/\text{NO}_2$  is also recommended. There is no recommendation for the (limiting) first order rate constant,  $k^\infty$ .

Rate Parameters:  $\log(\text{A}/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 17.40 \pm 0.40$   
 $\log(\text{A}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -6.38 \pm 0.40$   
 $E/\text{J mol}^{-1} = 46\,000 \pm 4000$   
 $E/\text{cal mol}^{-1} = 11\,000 \pm 1000$

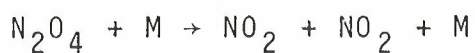


SECOND ORDER PLOT



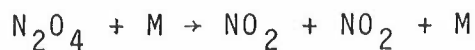


Rate Constant k	Temperature (K)	Method and Reference	Comments
<u>SECOND ORDER RATE CONSTANT <math>k_1^0</math></u>			
$> 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ M = $\text{N}_2\text{O}_4, \text{NO}_2$	298	Static system. Velocity of sound measured in $\text{N}_2\text{O}_4/\text{NO}_2$ mixtures over a range of pressures (140-760 mm Hg; 18.6-101.3 kN $\text{m}^{-2}$ ) and frequencies (20-80 kHz). KISTIAKOWSKY and RICHARDS 1930 (1)	Dispersion of sound due to dissociation of $\text{N}_2\text{O}_4$ not observed up to highest frequency used. Not plotted.
-	298	Flow system. Displacement of equilibrium in $\text{N}_2\text{O}_4/\text{NO}_2$ mixture across a perforated diaphragm. Changes in pressure and temperature measured. Initial pressure varied (300-700 mm Hg; 40-93 kN $\text{m}^{-2}$ ). Final pressure (3-50 mm Hg; 0.4-7 kN $\text{m}^{-2}$ ). BRASS and TOLMAN 1932 (2)	First attempt to use this technique. Authors quote $-\text{d}[\text{N}_2\text{O}_4]/\text{dt} = 8.2 \times 10^4 [\text{N}_2\text{O}_4] \text{ s}^{-1}$ . Uncertainties in flow pattern and measurement of temperature drop make accuracy doubtful. Not considered in this evaluation.
$\left. \begin{array}{l} 6.1 \times 10^8 \\ 7.3 \times 10^8 \\ 7.8 \times 10^8 \\ 2.5 \times 10^9 \\ 2.8 \times 10^9 \\ 4.4 \times 10^9 \\ 6.2 \times 10^9 \\ 5.2 \times 10^9 \\ 5.5 \times 10^9 \\ 6.1 \times 10^9 \end{array} \right\}$	$\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ M = $\text{N}_2\text{O}_4, \text{NO}_2$	274	Results originally quoted in terms of a pseudo-unimolecular rate constant $k_1^1$ . Values of $k_1^0$ have been calculated using $1/k_1^1 = 1/k_1^0[\text{M}] + 1/k_1^\infty$ and CHER's value for $k_1^\infty$ (16). Third body efficiencies of $\text{N}_2\text{O}_4$ and $\text{NO}_2$ are assumed to be the same (16).  $\text{N}_2\text{O}_4 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_2 + \text{M}$ 1 Authors obtained $E_1 = 58.2 \pm 3.8 \text{ kJ mol}^{-1}$ ( $13.9 \pm 0.9 \text{ kcal mol}^{-1}$ ), but because of the scatter, results are also compatible with the recommended $E_1 = 46.0 \text{ kJ mol}^{-1}$ ( $11.0 \text{ kcal mol}^{-1}$ ).
		274	
		274	
		288	
		298	
		298	
		303	
303	RICHARDS and REID 1933 (3)		
303			



Rate Constant k	Temperature (K)	Method and Reference	Comments
		RICHARDS and REID 1933 (3) (continued)	Work criticised on several grounds by TEETER (5); rebutted by RICHARDS and REID (4).
4.6 x 10 <sup>7</sup>	252	Shock tube study.	Dissociation of N <sub>2</sub> O <sub>4</sub> second order (first order in N <sub>2</sub> and N <sub>2</sub> O <sub>4</sub> ) at pressures below one atm (101 kN m <sup>-2</sup> ). Curvature in plots of pseudo unimolecular rate constant -d(ln[N <sub>2</sub> O <sub>4</sub> ])/dt vs. [M] observed at higher pressures but high pressure limiting value not reached at 7 atm (709 kN m <sup>-2</sup> ). N <sub>2</sub> and CO <sub>2</sub> have approximately same third body efficiency. Data tabulated taken from fig. 5 of (9). Authors derive k <sub>1</sub> <sup>0</sup> (M = N <sub>2</sub> ) = 2.0 x 10 <sup>17</sup> exp(-5550/T) cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> . Recommended by (17 and 19).
5.0 x 10 <sup>7</sup>	252	N <sub>2</sub> O <sub>4</sub> /NO <sub>2</sub> mixtures	
6.2 x 10 <sup>7</sup>	252	(~1%) in N <sub>2</sub> and in	
1.2 x 10 <sup>8</sup>	265	CO <sub>2</sub> subjected to weak	
1.4 x 10 <sup>8</sup>	265	incident shocks.	
1.4 x 10 <sup>8</sup>	266	Pressure range 0.5-7	
1.5 x 10 <sup>8</sup>	266	atm (50-709 kN m <sup>-2</sup> ).	
1.7 x 10 <sup>8</sup>	266	[NO <sub>2</sub> ] monitored by	
2.2 x 10 <sup>8</sup>	268	light absorption at	
2.3 x 10 <sup>8</sup>	268	404.7 and 435.5 nm.	
2.1 x 10 <sup>8</sup>	270	CARRINGTON and	
2.6 x 10 <sup>8</sup>	270	DAVIDSON 1951,1953	
2.7 x 10 <sup>8</sup>	270	(6,9)	
4.5 x 10 <sup>8</sup>	277		
5.0 x 10 <sup>8</sup>	279		
5.5 x 10 <sup>8</sup>	282		
5.8 x 10 <sup>8</sup>	283		
8.2 x 10 <sup>8</sup>	284		
8.6 x 10 <sup>8</sup>	284		
6.4 x 10 <sup>8</sup>	290		
6.6 x 10 <sup>8</sup>	290		
1.7 x 10 <sup>9</sup>	299		
1.7 x 10 <sup>9</sup>	300		
1.9 x 10 <sup>9</sup>	301		
~ 10 <sup>10</sup> cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> M = N <sub>2</sub> O <sub>4</sub> , NO <sub>2</sub>	298	Flow system. Rapid compression of N <sub>2</sub> O <sub>4</sub> /NO <sub>2</sub> mixtures by flow against impact tube placed in gas stream. Initial pressure varied (0.3-0.7 atm; 30-70 kN m <sup>-2</sup> ). Pressure change measured at impact point. BAUER and GUSTAVSON 1954 (10)	Also described in (8). Method not very accurate. Authors indicate that errors due to impurities, precision of pressure measurements and uncertainties in thermodynamic data could lead to errors of at least a factor of 2. Relaxation time τ quoted by authors; present result calculated from τ, assuming

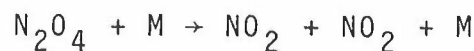




Rate Constant k	Temperature (K)	Method and Reference	Comments
$\left. \begin{array}{l} 4.5 \times 10^9 \\ 5.4 \times 10^9 \\ 6.3 \times 10^9 \\ 7.4 \times 10^9 \end{array} \right\}$	$\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ $\text{M} = \text{N}_2\text{O}_4, \text{NO}_2$	298	Static system.
		303	Measurement of sound
		308	absorption in $\text{N}_2\text{O}_4$
		314	mixtures with $\text{N}_2$ , Ar or $\text{CO}_2$ over a range of pressures (100-760 mm Hg; 13-101 kN $\text{m}^{-2}$ ) and frequencies (78-394 kHz). CHER 1962 (16)
$\left. \begin{array}{l} 7.8 \times 10^8 \\ 1.1 \times 10^9 \\ 1.1 \times 10^9 \\ 1.2 \times 10^9 \\ 1.1 \times 10^9 \\ 1.3 \times 10^9 \\ 1.8 \times 10^9 \\ 1.7 \times 10^9 \\ 1.5 \times 10^9 \\ 2.5 \times 10^9 \\ 2.2 \times 10^9 \\ 2.7 \times 10^9 \\ 3.4 \times 10^9 \\ 4.1 \times 10^9 \\ 3.9 \times 10^9 \\ 5.0 \times 10^9 \\ 8.2 \times 10^9 \\ 7.1 \times 10^9 \\ 1.4 \times 10^{10} \end{array} \right\}$	$\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ $\text{M} = \text{N}_2\text{O}_4, \text{NO}_2$	279	Shock tube study.
		283	Mixtures of $\text{N}_2\text{O}_4/\text{NO}_2$
		283	(<10%) in $\text{N}_2$ and in
		284	Ar subjected to weak,
		285	fully dispersed
		287	shocks. $[\text{NO}_2]$ monitored
		288	by light absorption at
		290	435 nm.
		293	ZIMET 1970 (18)
		296	
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320			
328			
			No explicit information given about the pressures used; fig. 1 of (18) implies pressures of $\sim 200$ mm Hg (27 kN $\text{m}^{-2}$ ). Reaction assumed to be in its second order region. Data tabulated were taken from fig. 2 of (18). Author derived $k_1^0 (\text{M} = \text{N}_2) = 2.9 \times 10^{17} \exp\{-5550/T\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Similar experiments with Ar as the diluent gave $k_1^0 (\text{M} = \text{Ar}) = 2.2 \times 10^{17} \exp\{-5550/T\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

FIRST ORDER RATE CONSTANT  $k_1^\infty$

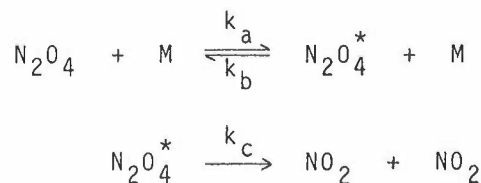
$1 \times 10^{16} \exp\{-6600/T\} \text{ s}^{-1}$	298	Shock tube study. $\text{N}_2\text{O}_4/\text{NO}_2$ (1%) in $\text{N}_2$ and in $\text{CO}_2$ subjected to weak incident shock. $[\text{NO}_2]$ monitored by light absorption at 404.7 and	Pre-exponential factor based on estimate using JOHNSTON'S method (7) multiplied by factor of 3. This factor is based on comparison of JOHNSTON'S method value for $k_1^\infty$ in case of
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Rate Constant k	Temperature (K)	Method and Reference	Comments
		435.5 nm. Pressures 0.5-7 atm (50-709 kN m <sup>-2</sup> ).	N <sub>2</sub> O <sub>5</sub> and N <sub>2</sub> O. E <sub>1</sub> <sup>∞</sup> is assumed to be the same as energy of dissociation.
		CARRINGTON and DAVIDSON 1951, 1953 (6,9)	
1.7 × 10 <sup>5</sup>	298	Static system.	Linear plots of -(dln[N <sub>2</sub> O <sub>4</sub> ]/dt) <sup>-1</sup> vs. [M] <sup>-1</sup> , where [M] is the total gas concentration, extrapolated to [M] <sup>-1</sup> = 0 to give k <sub>1</sub> <sup>∞</sup> . Long extrapolation likely to introduce substantial error.
2.4 × 10 <sup>5</sup>			
4.2 × 10 <sup>5</sup>			
5.3 × 10 <sup>5</sup>			
	303	Measurement of sound absorption in N <sub>2</sub> O <sub>4</sub> /NO <sub>2</sub> mixtures with N <sub>2</sub> , Ar or CO <sub>2</sub> over a range of pressures (100-760 mm Hg; 13-101 kN m <sup>-2</sup> ) and frequencies (78-394 kHz).	
	308		
	313.5		
		CHER 1962 (16)	

## DISCUSSION

The decomposition of N<sub>2</sub>O<sub>4</sub> occurs by the normal unimolecular mechanism



where N<sub>2</sub>O<sub>4</sub><sup>\*</sup> represents a molecule sufficiently energized to undergo decomposition according to reaction c. There is no evidence for any other mode of decomposition over the temperature range in which the reaction has been studied (250-350 K).

We may define the pseudo-unimolecular rate constant k<sub>1</sub><sup>'</sup> by

$$-d[\text{N}_2\text{O}_4]/dt = k_1'[\text{N}_2\text{O}_4]$$

We then have the relationship

$$1/k_1' = 1/k_1^\infty + 1/k_1^0[\text{M}]$$



where  $k_1^\infty = k_a k_c / k_b$  and  $k_1^0 = k_a$ .

At pressures below one atmosphere  $k_1^\infty$  is large compared with  $k_1^0 [\text{M}]$ , and the reaction kinetics approximate closely to second order; even at the highest pressures used (7 atm; 709 kN m<sup>-2</sup>) the high pressure limiting value of  $k_1^0$  (i.e.  $k_1^\infty$ ) has not been reached (9).

#### SECOND ORDER RATE CONSTANT, $k_1^0$

Most measurements of the rate of reaction 1 have been made at pressures  $\leq 1$  atm (101 kN m<sup>-2</sup>) and values of  $k_1^0$  have been derived by assuming the reaction to be second order (i.e.  $k_1^0 = k_1^0 [\text{M}]$ ). The few existing estimates of  $k_1^0$  (8,15) suggest that this approximation introduces little error into the determination of  $k_1^0$ .

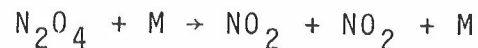
A variety of relaxation methods have been used to measure  $k_1^0$  - methods based on sound absorption and dispersion, thermal conductivity measurements, shock tube and impact tube techniques. Because the  $\text{N}_2\text{O}_4/\text{NO}_2$  system is simple, with well known thermodynamic properties, and at equilibrium at ambient temperatures there is a substantial proportion of  $\text{NO}_2$  (degree of dissociation,  $\alpha \approx 0.3$ ) which can be measured easily, this reaction has in most cases been chosen as the first to be studied by each of these techniques. Such pioneering studies are more likely to contain sources of error than well tested methods and because of this we put little weight on the results of Richards and Reid (3), Sessler (12,13), Brokaw (14) and Bauer and Gustavson (10). The authors of the last three studies themselves claim little accuracy for their results.

The remaining measurements consist of shock tube studies with  $\text{M} = \text{N}_2$  or Ar (9,18) and sound dispersion and absorption with  $\text{M} = \text{N}_2\text{O}_4/\text{NO}_2$  (15,16). The two shock tube studies give Arrhenius expressions for  $\text{M} = \text{N}_2$  which have the same  $E_1^0$  and pre-exponential factors which differ by only 30%. Giving an equivalent weight to each of these studies we recommend

$$k_1^0 = 2.5 \times 10^{17} \exp\{-5550/T\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{M} = \text{N}_2)$$

with error limits of  $\pm 30\%$  over the temperature range 250 - 350 K.





The measurements of  $k_1^0$  in  $\text{M} = \text{N}_2\text{O}_4/\text{NO}_2$  have been made by Blend (15) (sound dispersion) and Cher (16) (sound absorption). Cher's results cover a small temperature range and imply a value of  $E_1^0$  appreciably less than that of Blend and the shock tube results in nitrogen, but the absolute values of both Blend and Cher are in reasonable agreement. Blend's results cover a wider temperature range and despite a slightly different value for  $E_1^0$  are in accord with the shock tube results and the available data on relative third body efficiencies. We recommend use of Blend's expression (15)

$$k_1^0 = 1.4 \times 10^{17} \exp(-5170/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{M} = \text{N}_2\text{O}_4/\text{NO}_2)$$

with error limits of  $\pm 30\%$  over the temperature range 250-350 K.

Measurements of third body efficiencies are given in the following table. All values are at 298 K and have been expressed relative to the efficiency of  $\text{N}_2$  taken as unity.

M = $\text{N}_2$	Ar	$\text{CO}_2$	$\text{NO}_2$	$\text{N}_2\text{O}_4$	Reference
1	-	$\sim 1$	-	-	9
1	0.6	2	2	2	16
1	0.75	-	-	-	18

There is general agreement that the efficiencies are in the order  $\text{NO}_2 \approx \text{N}_2\text{O}_4 > \text{N}_2 > \text{Ar}$  but there are insufficient data to make quantitative recommendations.

#### FIRST ORDER RATE CONSTANT $k_1^\infty$

No accurate values are available. Carrington and Davidson's value (6,9) was estimated using Johnston's method (7) and a relatively arbitrary correction factor. Cher's value (16) was obtained by a long extrapolation of a plot of  $1/k_1'$  versus  $1/[\text{M}]$  to  $1/[\text{M}] = 0$ . The values differ by about a factor of 5 and at best can only be considered as giving the order of magnitude of  $k_1^\infty$ .



#### REFERENCES

1. G.B. Kistiakowsky and W.T. Richards, J. Amer. Chem. Soc., **52** 4661 (1930).
2. P.D. Brass and R.C. Tolman, J. Amer. Chem. Soc., **54** 1003 (1932).
3. W.T. Richards and J.A. Reid, J. Chem. Physics, **1** 114 (1933).
4. W.T. Richards and J.A. Reid, J. Chem. Physics, **1** 737 (1933).
5. C.E. Teeter, J. Chem. Physics, **1** 251 (1933).
6. T. Carrington and N. Davidson, J. Chem. Physics, **19** 1313 (1951).
7. H.S. Johnston, J. Chem. Physics, **20** 1103 (1952).
8. S.H. Bauer, J. Physic. Chem., **57** 424 (1953).
9. T. Carrington and N. Davidson, J. Physic. Chem., **57** 418 (1953).
10. S.H. Bauer and M.R. Gustavson, Disc. Faraday Soc., **17** 69 (1954).
11. K.P. Coffin and C. O'Neal, Jr., National Advisory Committee on Aeronautics, TN 4209 (1958).
12. G. Sessler, Acustica, **9** 119 (1959).
13. G. Sessler, Acustica, **10** 44 (1960).
14. R.S. Brokaw, J. Chem. Physics, **35** 1569 (1961).
15. H. Blend, Department of Physics, University of California at Los Angeles, Technical Report No. 19 on contract Nonr 233(48) (1962). AD 283 964.
16. M. Cher, J. Chem. Physics, **37** 2564 (1962).
17. S.W. Benson and H.E. O'Neal, National Bureau of Standards NSRDS-NBS 21 (1970).
18. E. Zimet, J. Chem. Physics, **53** 515 (1970).
19. K. Schofield, Delco Electronics, General Motors Corpn., Report TR71-57 (1971): to be published in J. Physic. Chem. Ref. Data, **1** (4) (1972).