

ELECTRICAL PERMITTIVITIES

COMPARISONS WITH OTHER DATA

WATER.—Fig. 5 compares our results at 1 bar (solid line) with those of three recent high-precision studies. Our results agree well with those of Malmberg and Maryott⁷ at all temperatures. Those of Owen *et al.*,³ and of Vidulich and Kay⁹ are up to 0.14 higher at low temperatures, and cross ours at 40°C. Owen *et al.*³ used a radio-frequency technique. We cannot explain this difference, especially as our measurements of the pressure-dependence at constant temperature agree well with those of Owen *et al.*,³ as shown in table 6 where values of $(\partial \ln \epsilon / \partial P)^*$ calculated from eqn (2) are compared with the corresponding values given by the equation of Owen *et al.*³

TABLE 6.—PRESSURE-DEPENDENCE OF THE DIELECTRIC CONSTANT OF WATER

P/bar	10°C		25°C		45°C		65°C	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
1	45.82	45.84	46.21	47.10	49.36	49.18	52.08	51.72
200	44.63	44.68	44.93	45.67	47.61	47.47	49.75	49.83
400	43.48	43.53	43.69	44.24	45.93	45.76	47.57	47.93
600	42.37	42.37	42.50	42.81	44.35	44.05	45.52	46.03
800	41.31	41.21	41.37	41.38	42.85	42.34	43.61	44.13
1000	40.28	40.05	40.27	39.95	41.43	40.63	41.82	42.23

FORMAMIDE.—The only other data at 1 bar are those of Leader⁴ at temperatures of 15–35°C. His cell was calibrated with water using an older value. On adjusting to the basis $\epsilon_{H_2O}(25^\circ\text{C}, 1 \text{ bar}) = 78.30$ his results agree with ours within 0.1%. No other results at high pressures have been reported. Values of $(\partial \ln \epsilon / \partial P)$ for formamide calculated from eqn (4) are given in table 7.

TABLE 7.—PRESSURE-DEPENDENCE OF THE DIELECTRIC CONSTANT OF FORMAMIDE AT 1 BAR

t/°C	$10^4(\partial \ln \epsilon / \partial P)^*/\text{bar}^{-1}$
10	44.59
25	44.73
45	54.24

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Heat Conductivity of the Slowly Dissociating System
 $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ from 200 to 400°C

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The thermal conductivity of the slowly dissociating system $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ has been measured from above 200 to 400°C by the hot wire technique. On comparison of the experimental data with the theories of heat transfer in reacting gases, it is found that the effect of chemical reaction upon the heat conductivity is apparent at 350°C and higher temperatures, while at 300°C and below it is negligibly small. However, the present theories of heat conductivity in reacting gas mixtures are found to be inadequate to account for the effects quantitatively.

The problem of heat transfer in dissociating and chemically reacting gas mixtures has been treated theoretically by Hirschfelder¹ and Butler and Brokaw² by assuming local chemical equilibrium. Subsequently, Secret and Hirschfelder³ considered the effect of relaxation of chemical energy on the heat conductivity. A more rigorous treatment of relaxation effects was given by Brokaw⁴ when the departure from the local chemical equilibrium is slight. It has been suggested by Rai Dastidar and Barua⁵ that, owing to the effect of chemical reaction on diffusion, the heat transport due to chemical enthalpy will be less than that obtained by using the diffusion coefficient calculated on the Chapman-Enskog theory.⁶ This effect, which should be present even when the condition of local chemical equilibrium is satisfied, has been confirmed by experiment.⁷

For the $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ system the reaction rate is fast but that for $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ is slow at ordinary temperatures and the effect of chemical reaction on heat conductivity is almost negligible. However, this rate increases with the increase of temperature.⁸ Consequently at higher temperatures transport of chemical enthalpy should play a significant role. Experiments on the system $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ have been previously confined to the range below 200°C. A study of the heat conductivity of this system at higher temperatures would enable a more critical test of the range of validity of Brokaw's theory to be made. In this paper we report the heat conductivity of $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ in the temperature range 200–400°C and at various pressures.

EXPERIMENTAL

For the heat conductivity measurements, the thick-wire-variant of the hot-wire method was used. The conductivity cell used was similar to that of Rai Dastidar and Barua.⁷ The electrical leads were insulated from the bath liquid by porcelain insulators enclosed in stainless steel tubes. The cell was immersed in a high-temperature bath prepared by melting a mixture of sodium and potassium nitrates taken in equal proportions. The insulation between the electrical leads and the body of the cell prevents any electrolytic action in the bath liquid. The temperature was controlled by an electronic controller; the control at the highest temperature was $\pm 0.2^\circ\text{C}$ and better than this at the lower temperatures.

To provide a steady state in the cell, a large cube made of stainless steel (volume 500 ml)