more tightly than sulfur, leading to smaller ϵ_2-values, hence smaller D's and more positive δ's for the phosphoryls than for the thiophosphoryls. This again is in agreement with observation, except for the two compounds $POBr_3$ and $PSBr_3$, in which the chemical shifts are completely out of line with those of compounds involving only first and second row elements, and remain unexplained.

As to the important question of double-bonding in the $P \rightarrow O$ or $P \rightarrow S$ linkages, the data unfortunately allow one to say very little. Presumably such double bonding involves a transfer of p-electrons from the oxygen or sulfur back into the $3p_x$ or $3p_y$ orbitals of phosphorus or possibly into d-orbitals. (The p-orbitals could only accept such electrons if they were partly vacant, as they might be if the group X is highly electronegative.) Such an electron transfer would tend to reduce D and increase δ. Since double bonding is believed to be more important for bonds with first-row than with second-row elements, including this effect would reinforce the prediction that the phosphoryls will have higher δ's than the thiophosphoryls. However, it appears unprofitable to attempt to estimate double-bond character by trying to separate its effect from the effects of varying the other parameters in the discussion.

Acknowledgment.—The authors wish to express their thanks to Mr. Marlan L. Shepard for his help throughout the early stages of this research.

ARMY CHEMICAL CENTER, MD.

[CONTRIBUTION NO. 1187 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

An Evaluation of the Density of Water at 5° Intervals between 45 and 85°[1]

BY BENTON B. OWEN, JAMES R. WHITE AND JAMES S. SMITH

RECEIVED FEBRUARY 15, 1956

1. Two types of precision dilatometers are described, and it is shown that by using a special platinum-tipped pipet the mercury meniscus, which determines the expansion, can be reproduced with a precision which corresponds to an uncertainty of only 0.2 p.p.m. in the density of water. 2. By means of ten such dilatometers the density of water, as determined by Chappuis, was extended over the range 45 to 85°, and values of the coefficient of expansion of water are reported. 3. It is shown that the use of three times the linear expansion for the volume expansion of "worked" tubular Pyrex vessels can lead to appreciable errors in precision dilatometry.

The values of the density of water given in the International Critical Tables[2] for the range 0 to 40° are the means of the smoothed values of Chappuis[3] and of Thiesen, Scheel and Diesselhorst.[4] These two sets of values differ irregularly, sometimes by as much as 8 parts per million. At temperatures above 40° the values calculated by an equation of Thiesen[5] are given as the best available, but they are expressed to only five decimal places and contain uncertainties in the last place. It is clear that if the I.C.T. densities of water are used to determine the coefficient of expansion of glass vessels, pronounced irregularities will be evident in the sixth decimal place below 40° and in the fifth decimal place above this temperature. These irregularities are of such a nature that they cannot be ascribed to the actual behavior of glass and are too large to be disregarded in precise measurements, such as those required for the determination of the partial molal expansibilities of electrolytes. To overcome this difficulty we have carried out what is in effect an extrapolation of the density data of Chappuis from 40 to 85° by means of ten 110-cc. Pyrex dilatometers. The choice of these particular data for extrapolation was governed by three important considerations.

(1) They are generally accepted as standard in this country and by the International Bureau of Weights and Measures.

(2) They are conveniently represented empirically by the Tilton and Taylor[6] equation

$$1 - d = \frac{(t - 3.9863)^2}{508929.2} \times \frac{(t + 288.9414)}{(t + 68.12963)} \qquad (1)$$

to within about one part per million over the whole experimental range, 0 to 42°.

(3) They lead to smooth quadratic temperature variations for the volumes of our dilatometers within the limit of reproducibility of our measurements which is comparable to that of Chappuis. The fulfillment of this last condition is, of course, subsumed in our procedure, because Chappuis expressed the volumes of his glass dilatometers as a quadratic in the temperature.

The two independent series of measurements described below differed in objective as well as in technique. Series S, performed by J. S. Smith, was carried out solely for the calibration of the series S dilatometers. Its aim was a reproducibility of two or three parts per million in the individual dilatometric measurements. When it became clear that it was necessary as well as possible to extend the precise results of Chappuis by means of such measurements, series W was undertaken by J. R. White, and every effort was made to attain a reproducibility of one part per million. The description of the experimental technique and the treatment of the data will, for brevity, be confined almost entirely to series W because of its higher reproducibility and

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[1] This communication embodies parts of the experimental material presented by James R. White (1944) and James S. Smith (1943) to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] "The International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1931, pp. 24–26.

[3] P. Chappuis, *Trav. et Memoires Bur. International Poids et Mesures*, **13**, D40 (1907).

[4] M. Thiesen, K. Scheel and H. Diesselhorst, *Wiss. Abhandl. physik-tech. Reichsanstalt*, **3**, 67 (1900) 1–70.

[5] M. Thiesen, *ibid.*, **4**, 30 (1904).

[6] L. W. Tilton and J. K. Taylor, *J. Research Natl. Bur. Standards*, **18**, 205 (1937). The density is expressed as grams per milliliter.

better temperature control above 65°. Series S serves, within its range and accuracy, to confirm the results of series W and as a source of information about the volumetric behavior of Pyrex vessels.

Experimental

Water.—Since the density of natural water expressed to one part per million is subject to change with repeated distillation because of changes in the isotopic ratio,[7] it is necessary for practical purposes to limit as well as describe the purification of the water. We employed "conductivity water" such as is available in any well-equipped laboratory. Natural water from the New Haven city supply was first distilled from a steam-heated tin-lined still which supplies the laboratory. Then, after addition of 0.25% of solid sodium hydroxide and 0.05% of potassium permanganate, it was redistilled once from an electrically heated 200-liter Barnstead still. A middle fraction was collected in Jena glass bottles and protected by suitable traps from carbon dioxide and ammonia. The specific conductivity of the water samples used was about 10^{-7} mho for series W and about 2×10^{-7} mho for series S.

Mercury.—Two liters of mercury distilled several times during earlier work in this Laboratory was sprayed through a four foot column containing 10% nitric acid. It was then distilled twice in air, rejecting the first 100 cc. and last 200 cc. of distillate each time. The still was dismantled and cleaned between distillations. The bulk of this air-distilled mercury was then redistilled twice[8] in vacuum, rejecting the first and last fractions as before. The resulting pure mercury (about 700 cc.) was stored in glass stoppered bottles kept under a bell jar. Small samples were withdrawn, as needed, by a suction tube thrust well below the surface.

Dilatometers.—Two series of ten Pyrex dilatometers were constructed according to the designs shown in Fig. 1. Their volumes ranged from 105 to 125 ml. each. The internal diameters of the side-arm capillaries were about 1 mm. The positions of the stopcocks in series S and W necessitated some differences in the filling techniques, but once filled with mercury and water their operation was identical and made use of a simple but precise method of determining the volume changes of expansion. Through the wide side arms, platinum-tipped pipets (P) withdraw the displaced mercury from the capillaries completely submerged in the thermostat. This avoids emergent stem corrections. The pipets, one for each dilatometer, were made by sealing a platinum tube (0.5 mm. o.d.) into a thin-walled Pyrex glass tube (7 mm. o.d.) and firmly cementing a hard rubber collar (C) in place. This collar governs the depth to which the platinum tube enters the capillary portion of the side arm and determines the position of the meniscus each time mercury is withdrawn. The rims of collars and side arms are ground 90° to their axes.

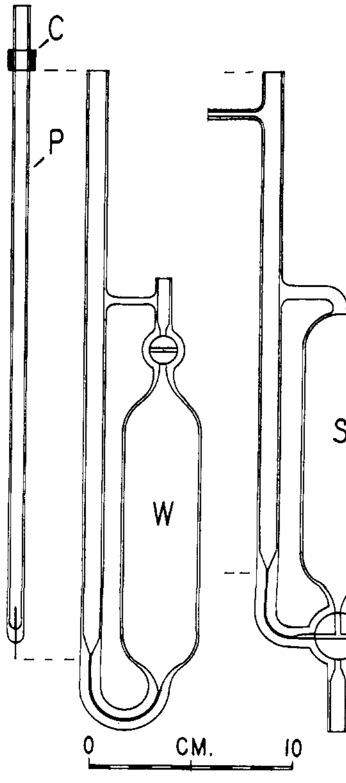

Fig. 1.—The dilatometers.

The precision with which the position of the meniscus is thus defined was determined by the use of a "side arm" which was similar in all respects to those attached to the dilatometers except that it was sealed off and closed about 1 cm. below the position of the meniscus. The capillary of this side arm was filled with mercury, the excess withdrawn to a fixed level with one of the pipets described above, and the side arm was weighed. Proceeding in this manner for over 20 weighings, it was found that the surface of the mercury in the capillary could be broken dependably and reproducibly within a precision of 0.2 mg. of mercury. This means that the volume of water and mercury in a 100-ml. dilatometer can be defined to 2 parts in 10 million by the use of a withdrawal pipet if no other uncertainties are involved. To ensure reproducibility of withdrawal, a constant suction of about 150 mm. of mercury was always used.

Thermostat.—To maintain dilatometer temperatures constant to within 0.001° for an hour, we constructed a thermostat within a thermostat. The outer thermostat contained about 300 liters of water, and its temperature was regulated to within 0.01° over the range 5 to 85°. The inner thermostat, in which the dilatometers and the platinum resistance thermometer were immersed, contained about 30 liters of distilled water. It was well stirred but was not supplied with a thermoregulator. It was heated, or cooled, by conduction through its walls, which were constructed of 16 gage copper and insulated from the outer bath and metal supports by $^3/_{16}''$ transite wallboard. It was covered with transite and $^1/_2''$ plywood arranged in three sections for easy access to the tops of the dilatometer arms. The cover extended down along the sides of the inner thermostat to a point below the water level of the outer thermostat. Two metal propellers with bakelite shafts served to stir the distilled water circulating among the dilatometers so that except for the thermometer leads there was no metal-to-metal contact between the inner thermostat and its environment. Both thermostats were protected from drafts by a layer of felt.

Temperature Measurement.—An Eppley Model 460 Bridge was used to measure temperature by means of Leeds and Northrup platinum resistance thermometer (#166026 and #400320). On the basis of calibrations of the bridge, of standard resistors, of the thermometers before and after the two sets of measurements and a check against the sodium sulfate decahydrate transition[9] (32.383°), we believe that the agreement between our temperature scale and that of the National Bureau of Standards is everywhere better than 0.002° and that the error in any nominal 10° interval is less than 0.001°. In the range 0 to 40° the outmoded International Hydrogen Scale, used by Chappuis in his measurements on water, coincides with the present International Temperature Scale, as defined by platinum resistance thermometer, within the accidental errors of comparison.[10]

Filling and Weighing the Dilatometers.—The water samples were degassed by boiling for 10 minutes in a quartz flask at 60° under reduced pressure and then cooled *in vacuo* to about 35°. By means of a stainless steel-tipped glass syringe, this air-free water was rapidly injected into the dilatometers containing about 7 ml. of weighed mercury. The dilatometers were then weighed in a room maintained at constant temperature and humidity. Pressure, tem-

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[7] N. E. Dorsey, "Properties of Ordinary Water-Substance," Reinhold Publ. Corp., New York, N. Y., 1940, p. 198, *et seq.*

[8] Relative density measurements performed on the mercury before and after the first vacuum distillation indicated that the second vacuum distillation was unnecessary for the determination of volumes to one part per million.

[9] T. W. Richards and R. C. Wells, *Z. physik. Chem.*, **43**, 465 (1903).

[10] J. Busse, "Temperature; Its Measurement in Science and Industry," American Institute of Physics, 1941, p. 229.

perature and humidity were taken into account in applying vacuum corrections and an empty dilatometer was used as a tare. Weighing was one by interchange of weights and load to give equal arm rest-points.[11] The independent weight calibrations used in the series S and series W measurements differed by less than 0.04 mg.

Following weighing, the dilatometers were enclosed in the inner thermostat, nominally at 5°. After 3 or 4 hr., the temperature in this thermostat became constant (drift about 0.001°/hr.) and the first withdrawal of mercury was made. The temperature was then raised 10°, and another withdrawal made after temperature equilibrium. Proceeding in this manner, mercury was withdrawn at 10° intervals from 5 to 85°.

Treatment of the Results.—The weights of withdrawn mercury and the original weights of mercury and water were combined with the known (or assumed) densities of mercury and water to calculate $\Delta V/\Delta t$, the expansion of the dilatometers per degree over the various 10° intervals. For this calculation, the density of water (5 to 45°) was derived from eq. 1, and the density of mercury (5 to 85°) was interpolated from a table in the Handbook of Chemistry and Physics.[12] This tabulation of mercury densities, based upon a compilation by Fowler,[13] was selected because it is closest in accord with the density scale chosen by Chappuis in his measurements of the density of water and is therefore consistent with eq. 1.

Plots of $\Delta V/\Delta t$ against t, the average temperature of the interval Δt, are illustrated in Fig. 2 for representative dilatometers of series W. The dashed lines are drawn through the data of the range 5 to 45° and can be represented by the equations

$$\Delta V/\Delta t = a + b(t - 25) \qquad (2)$$

and

$$V = V_{25^\circ} + a(t - 25) + b/2\,(t - 25)^2 \qquad (3)$$

Treating each dilatometer independently, these equations were then used to evaluate V_t, and hence d, over the range 45 to 85°. Since this range constituted an extrapolation and was as great as that used in the evaluation of a and b, the values of d derived from different dilatometers at a given high temperature differed considerably from their means.

TABLE I

SERIES W

t	1st Approximation d (av.)	1st Approximation $10^6\,\Delta d$ (av.)	2nd Approximation d (av.)	2nd Approximation $10^6\,\Delta d$ (av.)	Eq. 1 d	Eq. 1 $\delta \times 10^6$
5	0.9999919	0.0	0.9999919	0.0	0.9999919	0.0
15	.9991284	.3	.9991280	.6	.9991286	− 0.6
25	.9970759	.6	.9970752	.6	.9970751	+ 0.1
35	.9940635	.4	.9940633	.4	.9940635	− 0.2
45	.9902436	.2	.9902437	.2	.9902435	+ 0.2
55	.9857214	1.3	.9857213	.7	.9857164	+ 4.9
65	.9805764	2.3	.9805774	.6	.9805529	+ 24.5
75	.9748712	2.9	.9748704	1.0	.9748042	+ 66.2
85	.9686335	4.0	.9686348	1.7	.9685077	+127.1

SERIES S

t	1st Approximation d (av.)	1st Approximation $10^6\,\Delta d$ (av.)	2nd Approximation d (av.)	2nd Approximation $10^6\,\Delta d$ (av.)
0			0.9998689	1.1
5			.9999923	1.0
15			.9991290	1.2
25			.9970751	0.0
35			.9940642	.5
45			.9902438	.6
55	0.9857216	2.0	.9857222	.7
65	.9805763	3.2	.9805772	1.6
70[a]	.9777906	4.4	.9777918	2.3
75	.9748678	3.7	.9748090	2.1

(All densities expressed as g./ml.)

[a] By eq. 1, d = 0.9777491 at 70°.

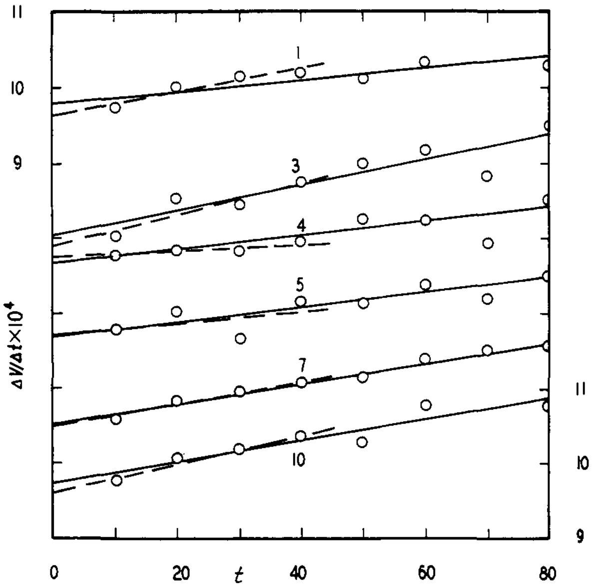

Fig. 2.—Expansion of the dilatometers.

The mean values of d so determined, and Δd, the average deviations from them (for the dilatometers represented in Fig. 2), are recorded in Table I as "first approximation." Using the mean values of the first approximation densities described above, values of $\Delta V/\Delta t$ for the dilatometers were recalculated for the four 10° intervals between 45 and 85° The complete curves for $\Delta V/\Delta t$, second approximation, are represented in Fig. 2 by the solid straight lines. Then, using all values of $\Delta V/\Delta t$ from 5 to 85°, new values of the parameters of eq. 2 were determined by the method of least squares. These new values of a and b were used to calculate a second set of values of the dilatometer volumes and of the density of water. The new mean values for d are given in Table I as "second approximation" and agree to better than 1 part per million with the "first approximation" mean value. As expected, the deviations from the means are much less for the second approximation than for the first and represent more nearly the expected normal scattering. Convergence has been secured, since a third similar approximation produced no significant changes in the means or in the deviations.

Since the Tilton and Taylor equation was based upon very numerous data below 45°, we have adopted the plan of calculating densities at all temperatures by eq. 1 and representing graphically our experimental results above 45° by the difference between them and values of d calculated from eq. 1. This difference, defined by

$$\delta = d(\text{exp.}) - d(\text{eq. 1})$$

was used to obtain smoothed values of δ and the temperature coefficient, $d\delta/dt$. Table II contains values of δ derived from both series S and series W dilatometers, as well as our smoothed values.

TABLE II

t	$\delta \times 10^6$ Series S	$\delta \times 10^6$ Series W	$\delta \times 10^6$ Plot	d Plot	$d\delta/dt \times 10^6$	$\alpha \times 10^6$	$d\alpha/dt \times 10^6$
85		127.1	127.1	0.9686348	7.10	669.93	5.614
80			93.9	.9718163	6.17	641.67	5.690
75	64.8	66.2	65.4	.9748696	5.19	613.02	5.772
70	42.7		42.2	.9777913	4.08	583.92	5.878
65	24.3	24.5	24.7	.9805776	2.94	554.16	6.040
60			12.7	.9832233	1.93	523.44	6.262
55	5.8	4.9	5.4	.9857218	1.07	491.46	6.538
50			1.7	.9880650	0.48	457.98	6.864
45	0.3	0.2	0.2	.9902437	0.14	422.73	7.248
40			0	.9922473	0	385.40	7.698

Because of the practical importance of having values of α, the coefficient of expansion of water, the smoothed values of δ were adjusted by the Stirling interpolation formula[14] so

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(11) Method recommended in "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1931, Vol. I, p. 74.

(12) "Handbook of Chemistry and Physics," 27th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1943, p. 1619. We were aware of the fact that the unit of volume used in this table should have been ml. not cu. cm., as written in the column headings. This error has been corrected in the 35th edition (1951).

(13) F. E. Fowler, "Smithsonian Physical Tables," Smithsonian Institution, Washington, D. C., 1933, p. 169.

(14) J. B. Scarborough, "Numerical Mathematical Analysis," Johns Hopkins Press, Baltimore, Md., 1950, p. 70.

as to avoid any discontinuity[15] in α and $d\alpha/dt$ within the range 40 to 50° where our results begin to depart from eq. 1. Table II contains our final smoothed values of d, α and $d\alpha/dt$, obtained in this manner. Both α and $d\alpha/dt$ are recorded to two more figures than are physically significant to allow exact interpolation and reproduction of our results.

TABLE III

PARAMETERS OF EQUATION 5

Dilatometer	$A \times 10^6$	$B \times 10^9$	Dilatometer	$A \times 10^6$	$B \times 10^9$
9W	9.469	4.33	2S	9.755	3.59
2W	9.424	4.57	6S	9.714	3.92
10W	9.394	6.06	7S	9.668	4.89
6W	9.388	8.79	4S	9.668	3.01
7W	9.369	6.49	9S	9.666	5.85
5W	9.367	4.81	10S	9.606	8.13
4W	9.354	4.06	3S	9.597	4.26
8W	9.287	6.66	1S	9.596	5.08
1W	9.286	3.26	8S	9.578	5.47
3W	9.105	8.03	5S	9.564	3.97

The Expansion of Pyrex Vessels.—As a result of our measurements the volumes of the dilatometers can be represented by the equation

$$V_t = V_{25}[1 + A(t - 25) + B(t - 25)^2] \qquad (5)$$

The parameters A and B, calculated from our final values of a and b (second approximation) of eq. (2), appear in Table III. In this table the dilatometers of each series are arranged in the order of decreasing values of A, the coefficient of expansion at 25°. Although the Pyrex used in constructing series W and series S was from different stock, dilatometers within a given series were made from common stock, and a particular piece of tubing served as the source of glass for two or three dilatometers. As expected, these group themselves into two's or three's with closely agreeing values of A, but it is surprising that the values of B should exhibit such wide variations between the individual dilatometers making up these groups. These differences in B point up what may be a serious weakness in the experimental method usually employed for precise measurement of the expansibilities of liquids. Customarily, the expansibility of the dilatometer is represented as a function of temperature by equating it to three times the linear coefficient of expansion of a cylindrical segment cut from the dilatometer or the tubing from which it was made. Our experience indicates that inaccuracies may result from this procedure, for Table III leaves no doubt that the act of fabrication introduces noteworthy variations into the volume coefficient of expansion. For example, among the five pairs of dilatometers, 7W-5W, 8W-1W, 7S-4S, 4S-9S and 3S-1S, the differential coefficients, $A(dV/dt)V_{25}$, differ by only 0.02%, while the corresponding integral coefficients, $(V_{75} - V_5)/70\,V_{25}$, differ by as much as 1%. This makes it probable that the discrepancies between our densities and those reported by Jones, Taylor and Vogel[16] result from the use by those authors of a single parameter, $A = 9.66 \times 10^{-6}$, to describe the expansion of their two Pyrex dilatometers between 20 and 80°.

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[15] Discontinuities have sometimes been reported in density–temperature curves for pure liquids. See, for example, G. Antonoff and R. J. Conan, *Z. Naturforschg.*, **4a**, 156 (1949). The temperature intervals in the present measurements are too great to detect discontinuities if present, so continuity has been assumed as the only practical basis for estimating expansibilities from our results.

[16] G. Jones, E. F. Taylor and R. C. Vogel, THIS JOURNAL, **70**, 966 (1948).

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE INORGANIC AND PHYSICAL CHEMISTRY LABORATORIES, AND THE INSTITUTE OF SCIENCE, GUJARAT COLLEGE]

The Action of Dinitrogen Tetroxide on Hyponitrites, Nitrites and Oxides. The Induced Decomposition of Hyponitrites

BY TRAMBAKLAL MOHANLAL OZA AND VASANTRAI TRAMBAKLAL OZA

RECEIVED JULY 29, 1955

The action of dinitrogen tetroxide and nitrogen dioxide for 0.5 hr. on $Ag_2N_2O_2$, $SrN_2O_2 \cdot 5H_2O$ and SrN_2O_2, on $AgNO_2 \cdot Ca(NO_2)_2 \cdot H_2O$ and $Ca(NO_2)_2$, approx. $^1/_4$ H_2O and on Ag_2O and CaO has been studied. The products of the reaction, both solid and gaseous, have been analyzed quantitatively. The results show that (i) the hyponitrites seem to suffer induced decomposition even at 0° according to equations (1) $M_2N_2O_2 = M_2O + N_2O$ and (2) $3M_2N_2O_2 = 2M_2O + 2MNO_2 + 2N_2$, which occur in their thermal decomposition,[1] (ii) hydrated nitrites and nitriles which decompose below 140° react and (iii) the primary product, nitrite, nitrate or both, of the action of N_2O_4 or NO_2 on oxides seems to be dependent on the nature of the oxide.

The action of dinitrogen tetroxide on hyponitrites of sodium and silver has been studied by Addison and the co-workers.[2] They identified in the products two oxyhyponitrites, which were oxidized ultimately to $M_2N_2O_6$; formation of $M_2N_2O_4$ and $M_2N_2O_5$ was also reported. The action of N_2O_4 and NO_2 on nitrites and oxides has been studied by many investigators. This has been reviewed by Addison and Lewis,[3] who found that sodium nitrite underwent no change in contact with dinitrogen tetroxide and its thermal dissociation products up to 100°, while CaO and Na_2O_2 formed only nitrate below 124°. Ferraro and Gibson[4] found formation of nitrates or addition compounds with oxides of Ag, Mg, Ca, Sr and Hg.

The present work was undertaken mainly to elucidate the effect of nitrogen dioxide on oxides, nitrites and hyponitrites, all of which are present in the system when the thermal decomposition of hyponitrites is studied. The complete system has been examined both before and after the reaction. The results show that (i) nitrogen of the hyponitrite molecule does not remain intact, (ii) water exercises a profound influence on the reactivity of nitrites, hydrated nitrites reacting even at 0° and silver nitrite, which is anhydrous, reacting only at 120°, (iii) in the case of CaO, which contains fixed oxygen, the primary product of the action of N_2O_4 or NO_2 is the nitrate, but in the case of Ag_2O, which has its oxygen not so firmly fixed, both ni-

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[1] T. M. Oza and V. T. Oza, *J. Phys. Chem.*, **60**, 192 (1956).

[2] C. C. Addison, G. A. Gamlen and R. Thompson, *J. Chem. Soc.*, 346 (1952).

[3] C. C. Addison and J. Lewis, *ibid.*, 1874 (1953).

[4] J. R. Ferraro and G. Gibson, THIS JOURNAL, **75**, 5747 (1953).