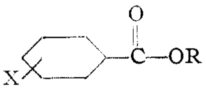
TABLE I

BENZOIC ACID ESTERS



R	X	R. I., $n^{75}D$	M. p., °C.	B. p., °C.	Mm.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found
o-Allylphenyl	Hydrogen	1.5675		118	0.5	$C_{16}H_{14}O_2$	80.65	80.87	5.92	5.97		
o-Allylphenyl	p-Chloro	1.5789		149	1	$C_{16}H_{13}ClO_2$					13.49	12.98
2-Allyl-6-s-butylphenyl	Hydrogen	1.5497		161–162	2	$C_{20}H_{22}O_2$	81.59	81.63	7.53	7.48		
o-s-Butylphenyl	p-Chloro	1.5610		145–146	1.4	$C_{17}H_{17}ClO_2$					12.28	12.47
p-s-Butylphenyl[a]	p-Chloro		54–55			$C_{17}H_{17}ClO_2$					12.28	12.35
m-Tolyl[a]	m-Chloro		51–52			$C_{14}H_{11}ClO_2$					14.38	14.40
m-Tolyl[a]	p-Chloro		95–96			$C_{14}H_{11}ClO_2$					14.38	14.25
p-Tolyl[a]	p-Chloro		99–100			$C_{14}H_{11}ClO_2$					14.38	14.35
2,4,5-Trichlorophenyl[a]	p-Chloro		152.5–155			$C_{13}H_8Cl_4O_2$					42.21	42.09

[a] Recrystallized from methanol.

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Oxidation of Some Rare Earth Oxides with Ozone

BY SHERMAN RABIDEAU[1] AND GEORGE GLOCKLER

The possible oxidation states of the lanthanide series of elements has evoked considerable interest, not only for the bearing this information may have upon the placement of these elements in a periodic arrangement, but also because of the chemical relationship to the actinides. A valence greater than four has not been established for praseodymium, and it appears that the trivalent state is the maximum for neodymium, samarium and gadolinium.

Gruen and Katz[2] have reported that the oxidation of the sesquioxide of praseodymium to the dioxide occurs with the use of atomic oxygen at a reduced pressure and at elevated temperatures, but no change in the compound Pr_6O_{11} was found under similar conditions. Also with regard to the oxides of neodymium, samarium and gadolinium, atomic oxygen was apparently without effect.

In an attempt to produce the maximum oxidation state for praseodymium, neodymium, samarium, and gadolinium, the dry oxides were subjected to the action of ozone at room temperature and at atmospheric pressure.

Experimental.—The rare earth oxides were obtained from the collection of Professor L. Rolla and the purity was stated to be greater than 99.9%. The sesquioxide of praseodymium was obtained by reduction of the higher oxides in a stream of hydrogen at 950°. The compound Pr_6O_{11} was prepared by ignition in air. The ozone was produced with the use of three Berthollet tubes connected in series as described by Greenwood[3] with the exception that ground glass standard taper joints were used to join the tubes instead of mercury seals. The oxygen was prepared from the reaction of distilled water with C.P. sodium peroxide to avoid the interference from the nitrogen present in U.S.P. tank oxygen. Rather large weight increases in the rare earth oxides were noted when tank oxygen was used in the ozonizer. By sealing some of the gadolinium oxide exposed to ozone prepared from commercial oxygen into a tube connected to a vacuum line and then heating the sample, brown fumes were evolved which attacked the mercury in the McLeod gage. This weight increase was not observed when purified oxygen was used in the ozonizer. The oxygen was dried with concentrated sulfuric acid, solid potassium hydroxide, and barium oxide before entering the ozonizer. The ozone concentration produced by a silent electrical discharge was approximately 9% by weight.

Only in the case of the oxides of praseodymium was an oxidation by ozone observed. Both the sesquioxide and the higher oxide, Pr_6O_{11}, reacted with ozone to form the dioxide. In Table I are given the results of the oxidations of the two oxides of praseodymium with ozone.

TABLE I

OXIDATION OF PRASEODYMIUM OXIDES WITH OZONE

Oxide	Wt. of oxide, g.	Reaction time, hr.	Wt. gain on oxidation, g.	Wt. loss on reduction, g.	Moles O_2 gained/mole oxide	PrO_2, %
Pr_2O_3	2.3644	13	0.0936	0.0936	0.409	81.6
Pr_6O_{11}	2.5442	6.5	.0283	.1071	.355	89.5

The weight loss of the oxidation product was determined by reduction of the rare earth to the sesquioxide in a stream of purified hydrogen at a temperature of 950°. Indicative of a reaction were the change in color, the evolution of heat upon exposure to ozone, and the increase in weight. The green sesquioxide of praseodymium rapidly became cocoa-brown in color, and became black after a reaction period of several hours. Further evidence of the oxidation of the praseodymium oxides by ozone was obtained from an observed decrease in the paramagnetic susceptibility.

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[1] Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

[2] D. M. Gruen and J. J. Katz, A. E. C. D. 1892, March, 1948.

[3] F. L. Greenwood, *Ind. Eng. Chem., Anal. Ed.*, **17**, 446 (1945).

The Conductivity Measurements of the Aqueous Solutions from the Sulfates of Bivalent Metal and Titanium

BY S. R. PATEL

The compounds $RSO_4 \cdot Ti(SO_4)_2$ described previously[1] are hydrolyzed, by boiling with distilled water, according to the expression

$$RSO_4 \cdot Ti(SO_4)_2 + 4H_2O \longrightarrow Ti(OH)_4 + RSO_4 + 2H_2SO_4$$

The electric conductivity of the solutions so obtained has been measured and compared with that of similar solutions containing the calculated quantity of the bivalent metallic sulfate and sulfuric acid.

The general procedure and the data obtained for the compound $ZnSO_4 \cdot Ti(SO_4)_2$ taken for illustration are given below.

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[1] Mehta and Patel, THIS JOURNAL, **72**, 224 (1950).

A weighed quantity (0.2 g.) of $ZnSO_4 \cdot Ti(SO_4)_2$ was boiled with distilled water (350 cc.), the metatitanic acid filtered off and the sp. conductivity in mhos./cm. of the filtrate (made to 100 cc.) was determined by the method of Kohlrausch. This filtrate was again diluted with an equal volume of distilled water and sp. conductivity measured. This operation was repeated thrice. Similar measurements were made with soutions prepared from the calculated amount of zinc sulfate and sulfuric acid. The values thus obtained which are reported in Table I, are very close to each other showing thereby that the hydrolysis takes place according to the expression given before and the substance $ZnSO_4 \cdot Ti(SO_4)_2$ behaves as a double sulfate.

TABLE I

SPECIFIC CONDUCTIVITY OF HYDROLYZED SOLUTIONS AND SYNTHETIC SOLUTIONS OF SAME CONCENTRATION

Solution	Sp. conductivity, mhos. $\times 10^{-4}$				
$ZnSO_4 \cdot Ti(SO_4)_2$	5.61	3.05	1.76	0.91	0.48
$ZnSO_4 + H_2SO_4$	5.48	2.94	1.67	0.89	0.46

The other compounds of the type $RSO_4 \cdot Ti(SO_4)_2$ were also examined and showed similar behavior.

Acknowledgment.—The author wishes to thank Prof. S. M. Mehta for his interest and encouragement in this work.

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Elastic Constants of Gelatinous Substances

BY ARVIND MOHAN SRIVASTAVA

The importance of measurement of elastic constants of gels is threefold, *viz.*, (1) it provides a basis for comparison with other substances; (2) it furnishes a criterion for studying the semi-solid nature of gels, and (3) it affords a basis to understand the ultimate mechanical behavior of gels. From the knowledge of variation of these quantities with frequency, temperature and other factors, conclusions may be drawn to elucidate the mechanism of gel formation and the internal structure of the gel.

The method[1] is an adaptation of the ultrasonic technique developed by Pellam and Galt,[2] modified by Teetar[3]; it is based on the theory of Knott.[4] Ultrasonic waves are generated by a suitable pulse transmitter, impinged upon a slab of gel, received by a quartz crystal and detected after proper amplification on a cathode-ray tube. The rotation of the slab in a vertical plane changes the angle of incidence of these waves and in two positions sharp minima in the transmitted intensity are observed due to the total reflection of the two waves set up in the gel. These two waves are due to the resolution of the incident beam into longitudinal and transverse components.

From the two critical angles, θ_e and θ_s, the velocity of the waves V_e and V_s can be computed. A knowledge of these and the density ρ of the gel gives the elastic constants from the relationships

$$V_e = \frac{V_{\text{water}}}{\text{Sin }\theta_e}; \quad V_s = \frac{V_{\text{water}}}{\text{Sin }\theta_s}$$

$$V_e/V_s = k; \quad \sigma = \frac{k^2 - 2}{2(k^2 - 1)}$$

$$V_s = \sqrt{\frac{S}{\rho}}; \quad E = 2(1 + \sigma)S$$

where σ, E, S are the Poisson ratio, Young modulus and Shear modulus.

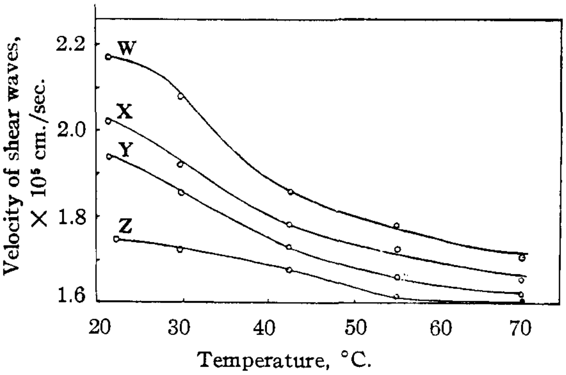

Fig. 1.—Iron silicate gel: velocity-temperature relationships: W, 2.500 ml./s; X, 2.250 ml./s.; Y, 1.250 ml./s.; Z, 0.625 ml./s.

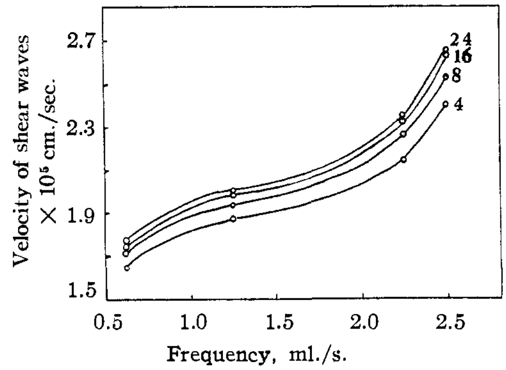

Fig. 2.—Iron silicate gel: velocity-frequency relationship at 30°; 4, 8, 16 and 24 hours.

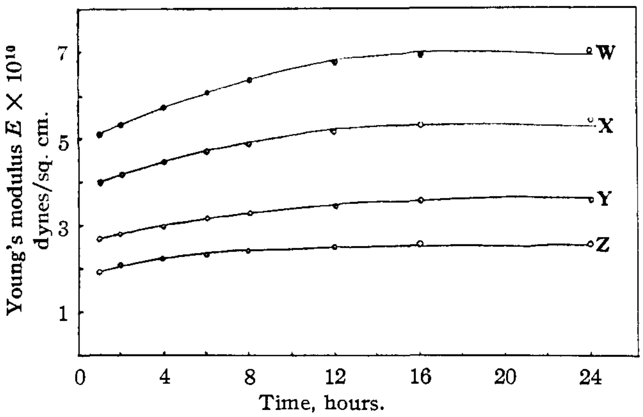

Fig. 3.—Iron silicate gel showing variation of E with time at 30°: W, 2.500 ml./s.; X, 2.250 ml./s.; Y, 1.250 ml./s.; Z, 0.625 ml./s.

The values obtained for the various constants are plotted in Figs. 1–3. The four frequencies used were, 0.625, 1 250, 2 250 and 2.500 Mc./sec.

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(1) A. M. Srivastava, *Proc. Nat. Acad. Sci., India*, **18A**, 51 (1949).

(2) J. R. Pellam and J. K. Galt, *J. Chem. Phys.*, **14**, 608 (1946).

(3) C. E. Teetar, *J. Acc. Soc. Am.*, **18**, 488 (1946).

(4) C. G. Knott, *Phil. Mag.*, **48**, 64 (1899).