

**157. Nuclear Magnetic Resonance Study of Polyvanadate Equilibria by Use of Vanadium-51.**

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Nuclear magnetic resonance of the  $^{51}\text{V}$  nucleus has been used to study aqueous polyvanadate equilibria. The results confirm the existence of the ions  $\text{VO}_4^{3-}$ ,  $\text{VO}_4\text{H}^{2-}$ ,  $\text{V}_2\text{O}_7^{4-}$ ,  $\text{VO}_4\text{H}_2^-$ , and also strongly support that of  $\text{V}_2\text{O}_7\text{H}^{3-}$ ,  $\text{V}_3\text{O}_9^{3-}$ ,  $\text{V}_{10}\text{O}_{28}^{6-}$  and its protonated forms, and  $\text{VO}_2^+$ . No other ion is observed with the possible exception of  $\text{V}_4\text{O}_{12}^{4-}$ . The results also give information about the stereochemistry of the various ions, and about the kinetics of some of their interchanges.

INGRI and BRITO <sup>1</sup> have surveyed most of the recent work on polyvanadates and conclude that only the species of nominal formulæ  $\text{VO}_4^{3-}$ ,  $\text{VO}_4\text{H}^{2-}$ ,  $\text{V}_2\text{O}_7\text{H}^{3-}$ ,  $\text{V}_3\text{O}_9^{3-}$ ,  $\text{VO}_3^-$ ,  $\text{V}_{10}\text{O}_{28}^{6-}$ ,  $\text{HV}_{10}\text{O}_{28}^{5-}$ ,  $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ , and  $\text{VO}_2^+$  exist. The methods which have been applied to study this system so far have been mainly spectrophotometry and electrometry. The purpose of the present work is (a) to confirm the conclusions of Ingri and Brito; (b) to decide whether the dimeric species is  $\text{V}_2\text{O}_7^{4-}$  or  $\text{V}_2\text{O}_7\text{H}^{3-}$ , or whether both occur; (c) to obtain further information about the stereochemistry of the various species, and about the kinetics of their interchange; (d) to explain the transient orange colour produced when a small proportion of acid is added to an alkaline polyvanadate solution; and (e) to elucidate the structure of the orange species which is stable in solutions having pH values between 7 and 2.

Information on all these problems has been obtained from a study of the  $^{51}\text{V}$  nuclear magnetic resonance spectra of aqueous polyvanadates. The  $^{51}\text{V}$  signals may be as narrow as 0.02 gauss, with a signal-to-noise ratio in normal solution of fifty to one. This means that many chemical shifts, line widths, and amplitudes can be measured accurately. Further, most of the polyvanadate species exchange sufficiently slowly with each other, and are sufficiently separated in chemical shift, to appear as distinct lines in the nuclear resonance spectrum.

**EXPERIMENTAL**

The spectra were measured at 14.542 Mc./sec. on a Varian Associates V4200B wide-line spectrometer using a variable temperature accessory. The wide-line spectrometer has been modified to permit the spectrum to be scanned by varying the frequency of the spectrometer, holding the magnetic field stable. The frequency of the oscillator is compared with an accurate standard frequency, using a Venner counter, thereby permitting the frequency to be measured to the nearest cycle per second.<sup>2</sup> A twelve-inch Varian magnet was used with a super-stabiliser to hold the magnetic field constant, and the inhomogeneity of the magnetic field over the sample was 10 milligauss. Chemical shifts were reproducible to  $\pm 0.2$  p.p.m. for the narrower lines over a wide range of different samples, and line widths under 0.1 gauss were reproducible to  $\pm 0.002$  gauss. The relative areas of two narrow separate lines in the same sample could be determined to  $\pm 5\%$  and those of two broader, overlapping lines to  $\pm 10\%$ .

Chemical shifts at 23° were measured relative to vanadium oxychloride,  $\text{VOCl}_3$ . This was prepared by the method of *Inorganic Syntheses*,<sup>3</sup> and, being a pure liquid, gave an extremely strong signal. All the vanadium compounds used showed large variations of chemical shift with temperature, and so care was taken to maintain both the samples and the standard at the probe temperature when they were not in actual use. For variable temperature work, the  $^{23}\text{Na}$  resonance was used as an internal standard because, although it is less convenient, it does not shift with temperature.

Stock solutions were made from AnalaR ammonium metavanadate, which was dissolved in water containing 5/4 equiv. of AnalaR sodium hydroxide, and boiled to remove ammonia. The

<sup>1</sup> Ingri and Brito, *Acta Chem. Scand.*, 1959, **13**, 1971; see also Schiller and Thilo, *Z. anorg. Chem.*, 1961, **310**, 261.

<sup>2</sup> Richards and Yorke, *Mol. Phys.*, 1963, **6**, 289.

<sup>3</sup> *Inorg. Synth.*, 1960, **6**, 119.

acid used was AnalaR 6.5N-perchloric acid, and the alkali AnalaR 6.5N-sodium hydroxide. The ionic strength was kept approximately constant by adding AnalaR 6.5N-sodium perchlorate so that the volume of perchlorate plus that of acid or alkali was always 3 ml., in 20 ml. stock. Changes in ionic strength were found, in fact, to have very little effect on the observed spectra. pH measurements were done on a Pye pH meter using a glass electrode.

RESULTS

*Alkaline Solutions.*—1.0 Gram-atom of vanadium per litre stock solution. The results obtained in alkaline solution are illustrated in Fig. 1. (The Varian wide-line spectrometer presents resonances in "derivative" form.) The width of the first line is 0.019 gauss, and its shift is 536.2 p.p.m. from  $\text{VOCl}_3$ . Between pH 13.4 and 12.8 this line shifts to 533.0 p.p.m. and widens to 0.042 gauss. At pH 13.4 a second line also appears, of shift 556.2 p.p.m. and width 0.045 gauss. Below pH 12.8 this line remains in approximately constant proportion to the 533.0 line, until at pH 11.5 it starts to broaden and becomes asymmetric. At this pH the

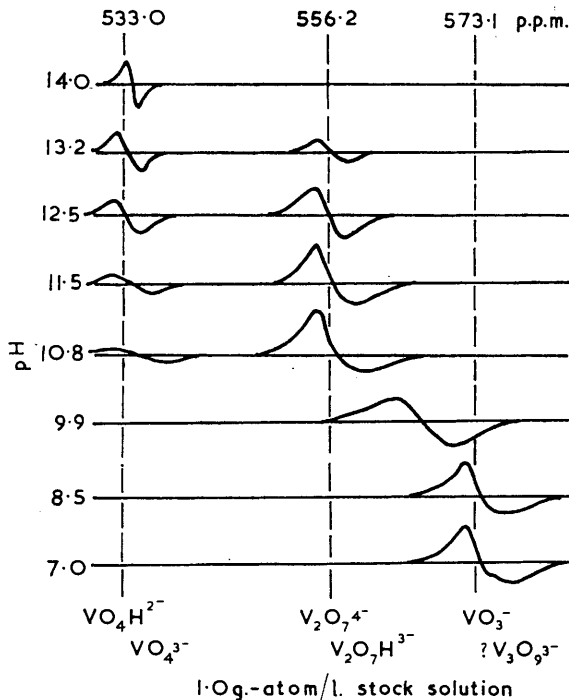


FIG. 1. Vanadium resonances in solution of different pH.

533.0 line also broadens, symmetrically, and shifts somewhat upfield. The asymmetry of the line originally at 556.2 p.p.m. is most marked at pH 10.8, but below pH 10.3 there remains only a single line of width approximately 0.12 gauss.

Between pH 10.3 and 8.8 only one line is observed, whose shift is almost linear with pH. Below pH 8.8 this line shifts no further, but becomes asymmetrical and at pH 7.0 can just be resolved into two components, one of width 0.059 gauss and shift 573.1 p.p.m. (ca. 10%), and a second of width 0.14 gauss and shift 576.8 p.p.m. (ca. 90%).

*2.0 Gram-atom per litre stock solution.* The results obtained are the same as with the 1 g.-atom/l. stock, except that no asymmetries are observed. From the chemical shifts, it can be shown (see below) that the 556.2 and 576.8 species increase in concentration relative to the 533.0 and the 573.1 species.

*0.5 Gram-atom per litre stock solutions.* The results obtained from these solutions are illustrated in Fig. 2. In general, double lines are resolved at the lower concentration, presumably because of a slower rate of exchange among the different species. The first equilibrium,

between the 536.2 and the 533.0 species, is not observably affected. The second equilibrium, however, shifts in favour of the 533.0 species, while retaining its pH independence. At pH 11.5 the previous asymmetry in the 556.2 line is seen to be due to a separate species, which at pH 10.8 is present in 50% proportion, with a shift of 562 p.p.m. and width 0.14 gauss. At pH 9.9 the line again becomes asymmetrical and shifts linearly with pH down to pH 9.2, after which it splits into the same two components as before, with the same shifts and widths but with the narrower line now in *ca.* 30–40% proportion. Unfortunately this last increase in percentage (from 10% in the normal solution) is not sufficiently reproducible to distinguish for certain whether it is a 3- or a 4-fold increase for a 2-fold change in concentration.

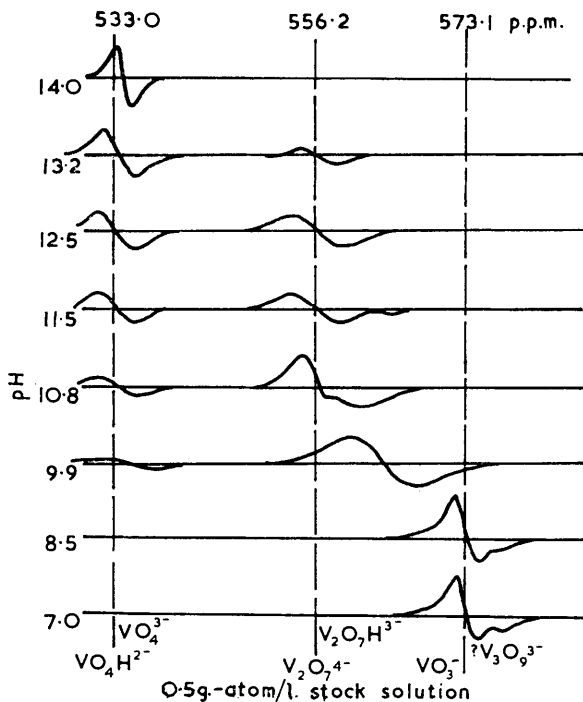


FIG. 2. Vanadium resonances in solutions of different pH.

*Lower concentrations.* A special study was made of the 533.0 and 556.2 p.p.m. lines with 0.5, 0.25, and 0.125 g.-atm l. stock. It was possible to work reproducibly at such low concentrations because of the narrowness of the two lines involved. The quantity

$$\frac{(\text{Area of } 556.2 \text{ line})}{(\text{Area of } 533.0 \text{ line})^2 \times \text{total V molarity as } \text{VO}_4^{3-}} = R \text{ (say)}$$

was calculated for six solutions between pH 11.5 and 12.3, and came to 0.062, 0.053, 0.046, 0.046, 0.043, 0.045. The approximately constant value of this quantity indicates that the equilibrium involves two species in one of which there are twice as many vanadium atoms as in the other.

*Effect of varying temperature.* This was studied on selected samples. Large linear changes of chemical shift were observed over a range from 0 to 60°. The observed changes of chemical shift against temperature were, in p.p.m. per 10°: 536.2, 0.72; 533.0, 1.05; 556.2, 1.05; 573.1, 0.4; 576.8, 0.7;  $\text{VOCl}_3$ , 0.4. The positions of equilibria were not detectably affected. The general effect of raising the temperature was to merge all double lines, except at pH values greater than 12.0, and the effect of lowering the temperature was to emphasise all the splittings observed at 0.5 g.-atm l. without producing any further ones. No appreciable narrowing of already narrow lines was observed on raising the temperature.

*Acid Solutions and Transient Species.*—When acid is added to the alkaline solutions of polyvanadates, a russet coloured precipitate forms which soon redissolves to an orange solution. The

orange colour is stable for several hours, but fades rapidly on boiling, with the liberation of protons.<sup>4</sup> It forms homogeneously in about 5 min. at room temperature in a rapidly cooled solution 2.0 g.-atom l. in vanadate at pH 6.9. At a given pH an unstable orange solution gave the "colourless" spectrum expected as above, plus three new lines (Fig. 3) whose shifts, widths, and magnitudes are, respectively: 510.3 p.p.m., 0.1 gauss,  $20 \pm 5\%$ ; 498 p.p.m., 0.03 gauss,  $62 \pm 10\%$ ; 420 p.p.m., 0.3 gauss,  $18 \pm 5\%$ . These quantities remain unaffected except in total amplitude down to pH 5.8, and are thus common to both the unstable (pH > 7.0) and part of the stable (pH < 7.0) region for orange colours. They are apparently unaffected by a wide range of concentration changes. Below pH 5.8 all three lines begin to shift upfield; for example at pH 3.2 the shift values are 519 (+9), 510 (+12), and 422 (+2) p.p.m. The central component also narrows somewhat, with a corresponding gain in amplitude.

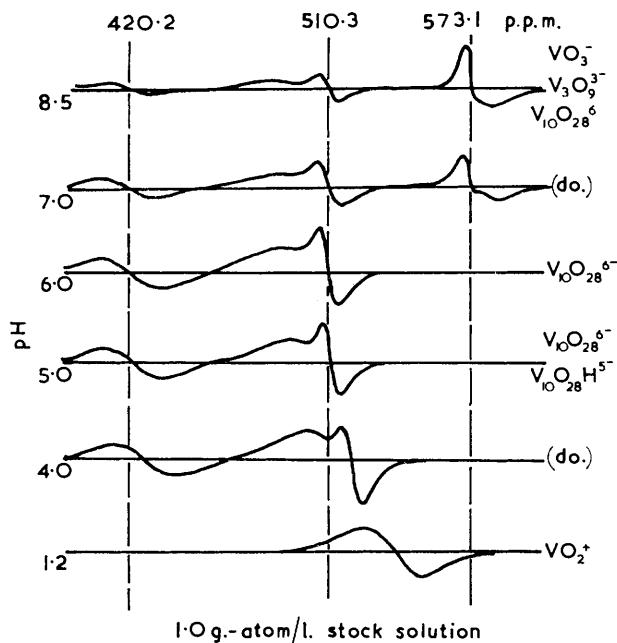


FIG. 3. Vanadium resonances in solutions of different pH.

Below pH 6.0 all freshly prepared solutions contained much colloidal red precipitate which on boiling became mostly an insoluble form of  $V_2O_5$ . This ruled out any meaningful measurements between pH 3 and 1.2. Below pH 1.2 the precipitate redissolved to give a yellow solution, and only one line was observed, always at 543.1 p.p.m. and always 0.29 gauss wide.

The effect of raising the temperature was to reduce the width of the wider lines by about 10% for every  $10^\circ$  rise. The temperature coefficients of the chemical shifts which were observed were: lines at 510.3, 498, 420 p.p.m., 1.4 p.p.m./ $10^\circ$ ; line at 543.1 p.p.m., 2.25 p.p.m./ $10^\circ$ .

#### DISCUSSION

*Alkaline Region.*—The  $^{51}\text{V}$  nucleus (99.75% abundant) has a spin quantum number of 7/2 and an electric quadrupole moment of  $7.3e \times 10^{-27}$  cm.<sup>2</sup> When the vanadium atom is in a symmetrical electrical environment the quadrupole coupling constant is small, quadrupole relaxation is inefficient, and a narrow nuclear resonance line is expected. If the electrical environment of the vanadium atom is unsymmetrical, however, there will be strong quadrupole coupling at the vanadium nucleus, resulting in a very short spin-lattice relaxation time and a broadened nuclear resonance line.

The 536.2 p.p.m. line clearly corresponds to the ion  $\text{VO}_4^{3-}$ . This ion is known to be tetrahedral and the very narrow line width supports this symmetry. The 533.0 p.p.m.

<sup>4</sup> Britton and Welford, *J.*, 1940, 895, and previous references quoted therein.

line is therefore presumably due to  $\text{VO}_4\text{H}^{2-}$ . The intensities of the lines at 533.0 and 556.2 p.p.m. vary with concentration but not with pH. It is therefore probable that there is an equilibrium between the two species giving rise to these lines. If this equilibrium was  $2\text{VO}_4\text{H}^{2-} \rightleftharpoons \text{V}_2\text{O}_7^{4-} + \text{H}_2\text{O}$  we should expect the ratio  $R$  (p. 866) to be constant. This ratio is indeed found to be approximately constant as indicated in the results (lower concentrations). We therefore assign the line at 556.2 p.p.m. to  $\text{V}_2\text{O}_7^{4-}$ . Just before the  $\text{VO}_4\text{H}^{2-}$  line disappears it becomes broader and shows a chemical shift. This suggests that in these conditions the exchange between this and the  $\text{V}_2\text{O}_7^{4-}$  species is becoming faster and this may be because the dimerisation is acid catalysed.

The 562 p.p.m. line is not observably favoured or disfavoured in magnitude relative to the 556.2 line by any change in concentration between the rather narrow limits within which it may be distinguished. In view of this, and of the chemical shifts discussed below, it seems to be due to the species  $\text{V}_2\text{O}_7\text{H}^{3-}$ .

The behaviour of the 573.1 and 576.8 p.p.m. lines, in particular their change in relative magnitude with concentration but not with pH, suggests that the narrower line corresponds to either  $\text{VO}_3\text{H}_2\text{O}^-$  or  $\text{VO}_2(\text{OH})_2^-$ , and the wider one to  $\text{V}_3\text{O}_9^{3-}$ . However because the accuracy with which the intensities of the lines could be measured could not for certain distinguish between a 3- and a 4-fold increase, the possibility of  $\text{V}_4\text{O}_{12}^{4-}$ , or even of a mixture where both species have very similar chemical shifts, cannot be ruled out. Some further support for this equilibrium may be obtained from a consideration of the variation of chemical shift with pH in the three solutions made from 2.0, 1.0, and 0.5 g.-atom/l. stock. In each of these solutions the resonance near 562 p.p.m. shifts linearly with pH to a value of about 575 p.p.m. as the pH changes from 10 to 9.2. If the shift of the resonance with pH is interpreted in terms of an equilibrium between  $\text{V}_2\text{O}_7\text{H}^{3-}$  and a  $\text{V}_3$  or  $\text{V}_4$  species, the linear plots of chemical shift against pH may be used to determine the equilibrium at any fixed value of pH in the three solutions of different concentrations. From the concentration of species obtained an equilibrium constant can be evaluated and the results obtained are in best agreement within a  $\text{V}_2\text{-V}_3$  equilibrium. The accuracy of the results is low, however, and a  $\text{V}_2\text{-V}_4$  equilibrium cannot be ruled out.

The resonances at 573.1 and 576.8 p.p.m. are most clearly separated at low pH. This suggests that the exchange rate between the two species involved is slowest at low pH and it may be that the exchange process involves an intermediate which has greater charge per vanadium atom than unity, and which is therefore in small concentration at the low pH.

*Acid Solutions.*—The three resonances observed at  $\text{pH} > 5.8$  have chemical shifts and relative intensities (1 : 3 : 1) which appear to be quite independent of pH or of concentration. This strongly suggests that they are caused by different vanadium atoms in the same ionic species, and fits very well with the widely proposed existence of  $\text{V}_{10}\text{O}_{28}^{6-}$ .<sup>5</sup> If this assignment is assumed to be true, it is possible to deduce new information about the structure of this ion. The ten vanadium atoms appear to be divided into like groups of two, two, and six atoms. The first two atoms must be in a rather symmetrical environment as the width of the 510.3 p.p.m. line is only 0.1 gauss. The next two atoms are in an unsymmetrical environment and are distinguished by their large low-field chemical shift. The other six atoms have a chemical shift closer in value to the other species which have been observed, and are also in a relatively unsymmetrical environment.

The observed shifts with pH below 5.8 may be explained by postulating a rapid reversible protonation at many alternative sites. This is equivalent to postulating the presence of species such as  $\text{V}_{10}\text{O}_{28}\text{H}^{5-}$  and  $\text{V}_{10}\text{O}_{28}\text{H}_2^{4-}$ , in accord with many published results.<sup>5</sup>

The crystal structure of “ $\text{K}_3\text{V}_5\text{O}_{14}$ ” has been studied by Bystrom and Evans.<sup>6</sup> It consists of complex tessellated sheets of vanadium atoms linked by oxygen atoms, three

<sup>5</sup> Rossotti and Rossotti, *Acta Chem. Scand.*, 1956, **10**, 957; Schwarzenbach and Geier, *Helv. Chim. Acta*, 1961, **44**, 859.

<sup>6</sup> Bystrom and Evans, *Acta Chem. Scand.*, 1959, **13**, 377.

out of five vanadiums being in a square-pyramidal environment and the other two being in an approximately tetrahedral environment. The idea of the existence of vanadium atoms in sites of different symmetry in the related anion is therefore by no means unreasonable.

The line at 543.1 p.p.m., found in very acid solutions, is almost certainly due to  $\text{VO}_2^+$ .<sup>5</sup> As the shift and width are unaffected even in extremely acid solution, the once suggested existence of  $\text{VO}^{3+}$  seems rather unlikely. Indeed, the width of 0.29 gauss suggests that the oxygen atoms may well surround the vanadium atom unsymmetrically.

The observed narrowing of some of the broad resonances when the temperature is raised may be due partly to a decrease in the viscosity of the solution, with a consequent decrease in the correlation time, and partly to an increase of symmetry caused by excitation of low frequency vibrations.

The shift of point 8 is estimated after the following argument: Almost all the work

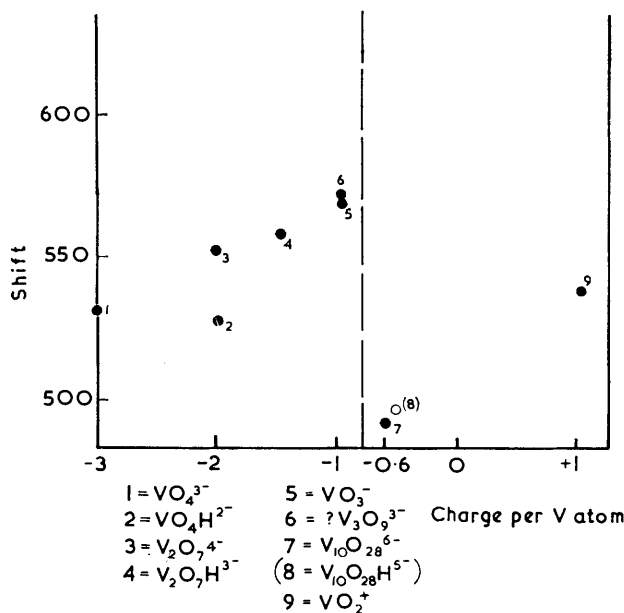


FIG. 4.

done in the region pH 7—4 confirms the existence of three species only, namely,  $\text{V}_{10}\text{O}_{28}^{6-}$ ,  $\text{HV}_{10}\text{O}_{28}^{5-}$ , and  $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ . For a series such as this it is almost certain that the shift of "pure  $\text{HV}_{10}\text{O}_{28}^{5-}$ " is almost the same as that of  $\text{HV}_{10}\text{O}_{28}^{5-}$  partly disproportionated into  $\text{V}_{10}\text{O}_{28}^{6-} + \text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ . But from the amount of acid added it is possible to estimate fairly accurately where the orange solution would have been "pure  $\text{HV}_{10}\text{O}_{28}^{5-}$ " if this were not partly disproportionated. Its shift is thus readily estimated.

*General.*—The plot of chemical shift against charge per vanadium atom is interesting (Fig. 4). The chemical shifts fall approximately into two separate straight lines, dividing the species into two regions which have already been characterised by the line widths of the resonances and the colours of the solutions. Within each region equilibria are attained fairly rapidly, but across the discontinuity exchange is slow. For each of the two types of resonance there is a general upfield shift with decreasing charge per vanadium atom. This is in accordance with the theory of chemical shift due to Ramsey<sup>7</sup> and the spectroscopic observations of Carrington and Schonland.<sup>8</sup> The removal of charge from the oxygen atoms

<sup>7</sup> Ramsey, *Phys. Rev.*, 1950, **78**, 699.

<sup>8</sup> Carrington and Schonland, *Mol. Phys.*, 1960, **3**, 331.

in the complex discourages transitions of electrons from an oxygen  $t_1$  to vanadium  $e_g$  orbital.

It is surprising that the exchange between  $\text{VO}_4^{3-}$  and  $\text{VO}_4\text{H}^{2-}$  at pH 13 is apparently more rapid than the exchange between  $\text{V}_2\text{O}_7^{4-}$  and  $\text{V}_2\text{O}_7\text{H}^{3-}$  at pH 11. This may be due to the kinetic stabilisation of the  $\text{V}_2\text{O}_7\text{H}^{3-}$  ion by intramolecular hydrogen bonding.

*Conclusions.*—(a) The conclusions of Ingri and Brito<sup>1</sup> are broadly confirmed by the n.m.r. data; (b) There is evidence for the simultaneous existence of both the  $\text{V}_2\text{O}_7^{4-}$  and the  $\text{V}_2\text{O}_7\text{H}^{3-}$  ions in certain solutions; (c) In the very symmetrical  $\text{VO}_4^{3-}$  ion the vanadium resonance is extremely narrow. In all the other colourless species the resonances are only slightly broader and so it seems very probable that the basic unit in these ions is a  $\text{VO}_4$  tetrahedron. The coloured species have broader resonances, which is consistent with a less symmetrical electrical environment for the vanadium nucleus. It has been possible to observe varying exchange rates between the different species in the solutions; (d) The transient orange colour produced by adding acid to an alkaline solution is probably  $\text{V}_{10}\text{O}_{28}^{6-}$ ; (e) In this ion there are three distinguishable types of vanadium atoms in the proportions of 2 : 2 : 6.

Much preliminary work, including an exhaustive literature survey, was done by Dr. E. J. Wells.<sup>9</sup> We acknowledge discussions with Dr. L. M. Venanzi and Dr. F. J. C. Rossotti and thank the Hydrocarbon Research Group of the Institute of Petroleum for financial assistance, and the D.S.I.R. for grants and for a Maintenance Grant (to O. W. H.)

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<sup>9</sup> Wells, D.Phil. Thesis, Oxford, 1961.

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