A Reinvestigation of the Hydrolysis of Pentavalent Vanadium

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The hydroxo complexes of pentavalent vanadium in a 1 M perchlorate medium have been reinvestigated by UV-visible spectrophotometric techniques. The acid and alkaline regions were treated separately. The experimental data in the acid region were explained in terms of the following equilibria:

In the alkaline region:

The numerical work was done by factor analysis and least squares refinements, and in addition to the equilibrium constants, molar absorptivities of the individual species have been calculated.

The water chemistry of Group VB metals has been known to be rather complicated. Quite complete discussions of the earlier investigations may be found in the papers by Rosotti and Rosotti,² and Ingri and Brito.⁴ Several workers have attempted to explain the behaviour of vanadium(V) in water, and very early the existence of poly-ions was claimed. However, there was very little agreement be-

tween the workers until the late fifties. Britton and Robinson³ have claimed the existence of the complex $\text{V}_{10}\text{O}_{27}^{4-}$. Several workers have assumed the degree of polymerization to be lower. For instance Düllberg⁵ chooses the formula $\text{HV}_6\text{O}_{17}^{3-}$. At present the model of Rosotti and Rosotti¹ is generally accepted for the pH-range concerned. These authors have made a study of the system in the acid range by titration curve methods, and explain their data in terms of the equilibria:

In addition to the potentiometric work, absorption spectra in highly acid vanadium solutions were also measured. At the hydrogen ion concentrations in question, VO_2^+ is found to be the only species of significant concentration.

In nearly neutral vanadium solutions, very slow reactions are found to take place. Ingri and Brito⁴ denote this region "the instability gap". The heavy polyvanadates are believed to be broken down to less condensed species in this region. The work of Ingri and Brito is the most important investigation of alkaline vanadium solutions. The following reactions are assumed to take place:

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Titration curve techniques were applied to obtain these stoichiometries and stability constants, and the investigation mainly covers the pH-range 7.5 to 11. More alkaline solutions have been studied by Newman *et al.*⁵ by spectrometric methods. The presence of HVO_4^{2-} , $\text{V}_2\text{O}_7^{4-}$ and VO_4^{3-} is claimed. For the equilibrium $\text{VO}_4^{3-} + \text{H}_2\text{O} = \text{HVO}_4^{2-} + \text{OH}^-$ a K -value of 0.097 ± 0.005 is given.

EXPERIMENTAL

The present investigation utilizes UV-visible absorption spectrophotometric data. For reasons caused by the "instability gap" mentioned above, measurements were performed in the acid and alkaline ranges separately. The initial concentrations of the solutions are presented in Tables 3 and 7. Attempts were made to measure the spectra of solutions in the "unstable" range, but these data were not treated quantitatively.

For the measurements in the acid region a Perkin Elmer 137 UV spectrophotometer was utilized. In the alkaline region a Spectronic 710 spectrophotometer was used. In order to perform a proper factor analysis of the absorbance data, the precision of the instruments had to be evaluated. The spectra of acid potassium bichromate solutions of different concentrations were recorded and the residual absorbance errors of the spectrophotometers were estimated using Wernimont's procedure.¹⁰ The investigations showed that the concentration factor was responsible for 99.995 % of the total variance for the Perkin-Elmer instrument, and 99.997 % for the Spectronic instrument, in the range of 0–1.5 absorbance units. The residual 0.005 % and 0.003 %, respectively, were caused by other factors. This corresponds to instrumental residual errors of 0.0034 and 0.0028 absorbance units for the Perkin-Elmer and the Spectronic instrument, respectively. Systematic error sources, like cell imperfections, multiple reflections, imperfect monochromacy and imperfections in the photomultiplier module all contribute to these deviations. We are, however, aware of the fact that the instrumental precision is not invariant. If measurements are made of solutions of high absorbance the error will be greater because of the decreased throughput of light. The refractive index of the liquid and hence the reflectance of the surfaces between the quartz walls and the solutions will be dependent on the wavelength. Such effects will cause the instrumental performance to vary within certain limits. These effects cause difficulties in selecting the number of absorbing components by factor analysis.

In both regions a number of solutions with different $[\text{H}^+]$ and $[\text{V}]$ were prepared, and

their spectra were recorded. The ionic strength for all solutions was kept constant at 1.0 M by adding an appropriate amount of sodium perchlorate, and thus all equilibrium constants evaluated in this investigation are practical constants referring to this ionic strength. In order to avoid interference no buffers were used. $[\text{H}^+]$ was adjusted by addition of HClO_4 and NaOH only, thus assuring the absence of other ions than H^+ , Na^+ , OH^- and ClO_4^- in addition to the several vanadate ions. The perchlorate medium was chosen since the ClO_4^- -ion is known to be a poor complexing agent. The hydroxo complexes are thus assumed to be the only complexes in the solutions. The hydrogen ion concentrations were measured by an Orion 801A pH-meter using a glass electrode in combination with a special reference electrode designed for minimizing the liquid junction potential. This electrode is in principle the same as the one used by Rosotti and Rosotti¹ for measurements in 1 M NaClO_4 -medium:

The inner and outer solutions were connected by a porous glass sinter.

The relation between the measured potential and the hydrogen ion concentration was obtained by titration of NaOH and HClO_4 at ionic strength 1 M, *i.e.* the potentials were measured on solutions with known concentrations of H^+ and OH^- . Certain deviations from Nernst equation behaviour were observed as expected when using a glass electrode. For high and low values of $-\log h$ non-linearity was found, and in the linear range the slope was slightly different from the value predicted from the Nernst equation. At $-\log h = 1.0$ the deviation from the straight line was approximately 12 mV. At $-\log h = 13.0$ a deviation of -20 mV was found. Since this relation is empirical, it is assumed to involve the liquid junction potential and other disturbing factors, and a closer analysis of these phenomena is therefore thought to be unnecessary. It may, however, be mentioned that in the neutral range ($-\log h \approx 7$) the liquid junction potential for an equivalent nitrate electrode is estimated to be 0.06 mV,¹⁴ but that it will increase as $[\text{H}^+]$ or $[\text{OH}^-]$ increases. The titrations were reproducible within limits indicated by a standard deviation of 0.3 mV.

Stability of the solutions was checked by measuring the spectra at intervals of 24 h and comparing the results. In the alkaline range, the solutions were heated to 80 °C for 90 min. This caused the yellow colour of the solution to disappear.⁴ After this all solutions were found to be stable apart from those in the instability gap where the spectra were continuously changing even after two weeks.

INTERPRETATION OF THE DATA

Factor analysis in combination with least squares fitting was used for the interpretation of the experimental data. The basic problem has been to find a model of the system which fits the measured data as well as possible, *i.e.* a least squares fit was performed. For given values of wavelengths and initial concentration, the residual error may be expressed as:

$$s = A - \sum C_i \alpha_i$$

Here A denotes the observed absorbance value while C_i and α_i denote calculated values of concentrations and molar absorptivities. The C_i and α_i values are dependent on certain parameters, *i.e.* the equilibrium constants, and the s -value is then in turn a function of these parameters. Consequently, the sum of squares of residual errors is a function of the equilibrium constants, and may be minimized with respect to these constants. In matrix notation the sum of squares may be expressed by the formula:

$$t = \text{tr}[(A - EC)^T(A - EC)]$$

A is the matrix of observed absorbances, E is the matrix of molar absorptivities and C is the concentration matrix. The E and C matrices may both be unknown. In some cases, however, either the E -matrix or the C -matrix will be known, or perhaps one or more vectors of the E -matrix. In such cases it is desirable to be able to keep the parameters in question invariant during the minimization process. Once the minimization is performed, it may be of interest to obtain a measure of the goodness of the fit. The sum of squares is not very well suited since its numerical value is dependent on the dimensions of the matrices involved. The root mean square (RMS) is, however, better suited. In many cases it may also be of interest to find the standard deviation for each of the single solutions involved. These values should be comparable with the instrumental error. If this is not the case, it is probable that the model chosen is incomplete, or that a false minimum is encountered.

In this work, we have applied, in addition to the least squares fitting, the method of factor analysis.⁷ The essence of this method is

the evaluation of the eigenvalues and eigenvectors of the second moment matrix:⁶

$$M = \frac{1}{n_s} AA^T$$

n_s is the number of solutions investigated. The number of nonzero eigenvalues of this matrix corresponds to the number of linearly independent vectors of the A -matrix. When the necessary allowance is made for experimental error, this number corresponds to the number of absorbing components in the system investigated. This number is naturally of great interest when studying systems where the parameters are generally unknown.

In practice, one eigenvector is assumed initially. The residual standard deviation is then calculated. If the residual standard deviation is greater than the computed instrumental error, one more vector is introduced, and the corresponding residual standard deviation is found. This cycle is repeated until the residual standard deviation is comparable with the instrumental error. The number of eigenvectors needed for this is assumed to be the number of absorbing components in the system. Keeping this in mind, it is clear that uncertainties in the numerical value of the instrumental error will cause problems. Several workers have sought alternative criteria for the vanishing of an eigenvector.^{15,16} Rummel¹⁹ suggests a rather primitive method which, however, has proved to give a fairly correct picture of the systems examined in this work. The point is simply found where the eigenvectors no longer change appreciably as the number of components is increased.

In this work we have made use of two different program systems for the numerical treatment. The first one, MUCO01, is developed by Kankare⁶ and makes use of factor analysis in addition to the least squares techniques. This program has proved to be especially useful when investigating a system where none, or but a few parameters are known beforehand as it has proved to have a quite wide range of convergence with respect to trial parameters. The second program, SQUAD, is designed by Leggett and McBryde.⁸ This program turned out to be superior to MUCO01 on the final refinement stages. Both programs have been modified for the UNIVAC 1108 computer by

the authors. Generally the modifications are minor. A change of a certain importance is, however, applied to SQUAD, where dynamic dimensioning of the matrices has been implemented (Appendix A). The basic principles of the programs are, however, left unchanged, and the reader is referred to the original program descriptions. The well-known program, HALTAFALL, of Ingri, Kakolowicz and Silén,⁹ designed for calculations of equilibrium concentrations has also been used. This program has, however, much wider applications than what has been used in this work. HALTAFALL has also been adapted for the UNIVAC 1108 computer by the authors, and the input structure modified for convenience of use.¹¹ It should be noted that the non-linear refinement routines of the programs MUCO01 and SQUAD require initial guesses of the equilibrium constants and assumptions must be made as to the stoichiometries of the equilibrium systems. The stoichiometric coefficients cannot be determined directly, and difficulties in finding these coefficients are quite common. In practice attempts are made to minimize the RMS-value with respect to stoichiometry as well as the numerical values of the equilibrium constants. In spite of the difficulties, this procedure may be successful in many cases. If the stoichiometries assumed are incorrect, divergence of the refinement may be the result. The method is used with greatest success if a large amount of data of high precision is accessible. In this study, the instruments used have a limited precision, and work is proceeding in this laboratory to develop a high precision computer-controlled spectrophotometer and titration system.

Table 1. Analysis of the second moment matrix for acid vanadate solutions. Instrumental standard deviation is assumed to be 0.0035.

	ROOT	RES.TRACE	RES.S.D.
1	71.194879	.080955	.076043
2	.064320	.016635	.035771
3	.011429	.00506	.020828
4	.003097	.00218	.013844
5	.000862	.001246	.011163
6	.000591	.000655	.008534
7	.000377	.000279	.005904

RESULTS AND DISCUSSION

In the acid range, the analysis of the second moment matrix indicated the presence of two absorbing components in the system assuming the standard error of the spectrophotometer to be 0.0034 absorbance units. This can be seen from Table 1 where the residuals due to increasing numbers of components are presented. In this connection it must be pointed out that for a large part of this investigation 1 mm quartz cells were used. In order to obtain the true absorbance values, it has therefore been necessary to multiply the measured values by 10. Consequently we have had to work with standard errors 10 times as large as the instrument error. On this background it will be seen that two absorbing components are indicated by the factor analysis. However, experience from similar investigations (to be published) has shown that in many cases the model is improved by increasing this number, especially if two or more components resemble each other. This proved to be the case for this set of data where smooth absorbance curves were obtained for four components. It may also be seen from Fig. 3 that four components are indicated by the method of Rummel¹⁹ for the acid vanadium solutions.

After several other attempts, the model of

Table 2A. Calculated values for practical equilibrium constants of the system vanadium (V)–H₂O at ionic strength 1.0. (The constants of Rosotti have been expressed as formation constants).

	This work		Rosotti and Rosotti	
	log K	$\sigma(\log K)$	log K	$\sigma(\log K)$
K_1	-7.63	0.14	-6.75	0.15
K_2	-11.57	0.34	-10.35	0.3
K_3	-17.40	1.0	-16.15	0.1

Table 2B. Correlation matrix for the equilibrium constants in the acid range.

	1	2	3
1	1.000	-0.0459	0.6850
2	-0.0459	1.000	-0.1800
3	0.6850	-0.1800	1.000

Rosotti and Rosotti,¹ which corresponds to four absorbing components, was finally assumed, and the corresponding equilibrium constants were calculated. The program systems are so designed that the equilibria most conveniently are presented as follows:

The computed constants are given in Table 2 and compared with the constants of Rosotti and Rosotti. In Table 3 the residual standard deviations of the solutions in question based on this model are presented. A first glance on Table 2 may give an impression of poor agreement between the two investigations. We shall, however, show that differences in the measurement of $[\text{H}^+]$ will cause considerable discrepancies in the calculated constants. The equilibrium

has been examined using HALTAFALL. The connection between the concentration of $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ and $[\text{H}^+]$ has been calculated for a series of numerical values for the equilibrium constant. The result is displayed in Fig. 1. Fig. 2 is based upon this set of graphs. It shows that a change of 0.1 in $-\log h$ will cause a cor-

Table 3. Calculated residuals based upon the best model.

pH	Total conc. of V(V)	Residual standard deviation
1.75	0.00012	0.0204
2.49	0.00012	0.0093
3.00	0.00012	0.0489
3.18	0.00012	0.0592
3.50	0.00012	0.0766
4.10	0.00012	0.0217
4.46	0.00012	0.0132
5.16	0.00012	0.0342
6.12	0.00012	0.0776
1.68	0.001	0.0158
2.54	0.001	0.0454
2.88	0.001	0.0360
3.05	0.001	0.0706
3.63	0.001	0.0213
4.18	0.001	0.0401
4.76	0.001	0.0397
5.57	0.001	0.0524

Fig. 1. Relation between $-\log h$ and $\alpha(\text{H}_2\text{V}_{10}\text{O}_{28}^{4-})$ for different values of K_1 . The α -value for a complex is defined as the fraction of the total quantity of vanadium present in the complex. $\alpha = 0.5$ is indicated by the dotted line $a-a'$. Compare Fig. 3B and Fig. 5B.

responding change of approximately 1.4 in the logarithm of the complex constant in the range of main importance. (h denotes hydrogen ion concentration.) The conclusion is that even though an appreciable numerical difference is found between this work and that of Rosotti, the actual concentration distributions are very nearly the same. Besides it might be pointed out that the K -values for the dissociation reactions

Fig. 2. The uncertainty in the equilibrium constant as a function of the uncertainty in $-\log h$. These values are derived from the line $a-a'$ in Fig. 1.

Fig. 3. Eigenvalues of the second moment matrices of the data measured in the acid region (open circles) and in the alkaline region (black dots).

being K_2/K_1 and K_3/K_1 , respectively, agree quite well with the values found by Rosotti. Our values are 3.94 and 5.83, and Rosotti gives the values 3.60 and 5.80, respectively.

In Fig. 4 the connection between $-\log h$ and concentration for the single species is given. The graphs are plotted with aid of HALTAFALL. It may be noted that the concentration of $V_{10}O_{28}^{6-}$ is low within the range studied. This gives as a result a relatively low accuracy of K_3 and the molar absorptivity of the compound. In Table 4 and Fig. 5 the calculated molar absorptivities are presented. VO_2^+ is found to absorb considerably less than the dekanavanadates. Consequently one will expect highly acid solutions to have a weaker colour than solutions of higher $-\log h$. The spectra of $H_2V_{10}O_{28}^{4-}$ and $HV_{10}O_{28}^{5-}$ resemble each other. This may be a source of uncertainty in the values of the complex constants. It should also be pointed out that the values of $\log K_1$ and

Table 4. Calculated molar absorptivities for the vanadates in acid solutions.

$\lambda(\text{nm})$	VO_2^+	$H_2V_{10}O_{28}^{4-}$	$HV_{10}O_{28}^{5-}$	$V_{10}O_{28}^{6-}$
250	2273	69410	74850	37770
260	2013	65440	67620	47090
270	1963	57120	56090	55570
280	1774	46270	45590	46510
290	1565	37270	37390	34270
300	1314	30820	29840	28510
310	1015	26120	25740	25980
320	798	23300	22620	25510
330	691	21740	20450	17850
340	581	21000	18660	16810
350	432	19930	17910	12360
360	311	18430	17590	10050
370	238	17240	16550	6739
380	174	15870	16300	1787
390	144	14580	14810	0

$\log K_3$ are highly correlated, but the refinement converges satisfactorily, nevertheless.

For $-\log h$ -values between 5.5 and 8 instability, or very slow reactions has made numerical work difficult. From $-\log h=8$ and upwards stability was attained, but these solutions had to be heated in order to establish equilibrium. The heating resulted in complete disappearance of the clear yellow colour of the fresh solutions. The same effect could be obtained by storing the solutions for several days. It is reasonable to believe that this fading corresponds to a breakdown of dekanavanadates or other heavy vanadium complexes to more simple species.

The result of the factor analysis of the data obtained in this region is shown in Table 5.

Table 5. Analysis of the second moment matrix for alkaline solutions. Instrumental standard deviation is assumed to be 0.0028.

	ROOT	RES.TRACE	RES.S.D.
1	577.240814	5.404732	.547962
2	5.210184	.194548	.106977
3	.169226	.025322	.039782
4	.017836	.007486	.022340
5	.006976	.000510	.006037
6	.000447	.000063	.002201
7	.000046	.000017	.001188
8	.000017	.000000	.000050

Fig. 4A. Distribution of the dekanadates as a function of hydrogen concentration and vanadium concentration. This presentation is similar to the one used by Atkinson and McBryde¹⁷ for portraying the distribution of aquo-complexes of Fe(III).¹⁸ This diagram and those of Figs. 3B, 5A and 5B are calculated by means of HALTAFALL.

Fig. 4B. Distribution of the dekanadates as a function of $-\log h$, the total concentration being kept constant at $10^{-3} M$.

Table 6A. Calculated values for equilibrium constants of the alkaline range of the system vanadium(V)–H₂O.

	This work log K	$\sigma(\log K)$	Ingri and Brito log K	$\sigma(\log K)$	Newman <i>et al.</i> log K	$\sigma(\log K)$
K_4	11.69	0.09	10.82	0.05	—	—
K_5	33.51	0.01	31.78	0.04	—	—
K_6	–12.09	0.01	—	—	–12.99	0.00

Table 6B. Correction matrix for the equilibrium constants in the alkaline range.

	1	2	3
1	1.000	–0.0216	0.2794
2	–0.0216	1.000	–0.1664
3	0.2794	–0.1664	1.000

Assuming the standard error of the instrument to be 0.0028 three absorbing components are indicated, noting that only 1 mm cells have been used for obtaining the data in this region. However, it proved necessary to increase this number by one. Four components are also

Table 7. Residual errors of alkaline vanadium solutions based upon the best model.

pH	Initial conc. of V	Res. error
7.94	0.001	0.0078
8.13	0.001	0.0193
8.52	0.001	0.0098
9.02	0.001	0.0174
9.41	0.01	0.0212
9.68	0.001	0.0114
10.34	0.001	0.0208
10.76	0.001	0.0153
11.15	0.001	0.0198

Fig. 5. Spectral characteristics of the species found in acid vanadium solutions. Wavelength range is 250–390 nm.

indicated by Fig. 3. An attempt of fitting a model with five absorbing components (VO_4^{3-} , HVO_4^{2-} , H_2VO_4^- , $\text{HV}_2\text{O}_7^{3-}$ and $\text{V}_3\text{O}_9^{3-}$) failed completely. When trying to interpret these data, the first assumption was based upon the work of Ingri and Brito.⁴ Since our data covered a greater range of $[\text{H}^+]$ than the data of Ingri and Brito, it was, however, necessary to specify an additional equilibrium for the most alkaline part. We were not able to fit the equilibrium

to the data. The following set of equilibria was found to give the best fit:

The constants calculated are given in Table 6, and the residual errors of the single solutions in Table 7. Comparison is made with the results of Ingri and Brito and Newman *et al.*⁵ In order to make comparison easy, all constants are given as formation constants according to the above equilibria.

Fig. 6A. Distribution of the alkaline vanadates as a function of $-\log h$ and total concentration of vanadium.

Fig. 6B. Distribution of the alkaline vanadates as a function of $-\log h$. Total vanadium concentration in 10^{-3} M.

Even in this case, the disagreement between this work and that of Ingri and Brito is less than what might be the first impression. It is very important to note that one component

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is left out. In order to check the agreement between the two investigations, we have theoretically calculated a titration curve (by means of HALTAFALL) and compared it with the

Fig. 7. Spectral characteristics of the alkaline vanadates. Wavelength range is 210–350 nm.

experimental titration curves given in the article of Ingri and Brito. The agreement is, as shown in Fig. 8, satisfactory, taking into ac-

Fig. 8. Theoretical "titration" curve, i.e. the average number of protons set free per vanadium, Z , versus $-\log h$ (fully drawn curve). Comparison is made with one experimental titration curve from the work of Ingri and Brito⁴ (open circles).

count that such curves prove sensitive to the species present.

The disagreement between this work and that of Newman *et al.* cannot be readily explained. It should be pointed out, however, that the accuracy of the least squares methods is likely to be higher than that of the simple extrapolation method. This has strikingly been demonstrated by Childs¹² in a recent study. On the other hand the work of Newman *et al.* is based upon a larger amount of data in the $-\log h$ -range in question.

The connection between $-\log h$ and concentration in the alkaline range is presented in Fig. 6. HVO_4^{2-} is found to be the most important component over a large part of the range in fair agreement with Ingri and Brito.

The molar absorptivities for the complexes are presented in Table 8, and graphically in Fig. 7. The spectra are quite different, this being of great advantage when using these methods. It will be seen that none of the species present absorbs appreciably in the visible region, this being the reason for the lack of colour of the solutions.

CONCLUSION

The method of spectrophotometry is well suited for the study of complexation equilibria

Table 8. Calculated molar absorptivities for the vanadates in alkaline solutions.

$\lambda(\text{nm})$	$\text{V}_3\text{O}_9^{3-}$	$\text{HV}_2\text{O}_7^{3-}$	HVO_4^{2-}	VO_4^{3-}
210	30830	28110	9045	8379
220	31770	29460	8302	8555
230	35860	30960	7568	8346
240	38500	30550	6827	7349
250	31140	20920	6219	6758
260	22270	9524	6979	7442
270	19230	5387	7451	8001
280	18930	10570	5806	6151
290	17260	14630	3598	3891
300	12690	14040	2136	2211
310	8658	9948	1462	1501
320	6038	6797	1086	1106
330	4548	5258	748	769
340	3320	3476	431	357
350	2178	2680	178	147
360	1248	1931	701	58
370	524	1445	295	0
380	263	965	85	0
390	114	519	139	0

even in the case of complicated hydrolysis reactions. The least squares techniques represent a powerful tool for the reduction of the relatively large amount of numerical material produced in spectrophotometry. Solutions of relatively low concentrations can be successfully examined by these methods.

In the special case of the hydrolysis of pentavalent vanadium the agreement with the results of potentiometric methods is found to be satisfactory. Moreover it provides valuable information about the absorption characteristics of the individual species present in the solutions.

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APPENDIX A.

DYNAMIC DIMENSIONING OF THE ARRAYS OF SQUAD

The program, SQUAD, is written in FORTRAN IV, and is so constructed that the arrays must be of the exact size required. In the original user's manual for the program, which may be obtained from the authors,⁸ this problem is solved by the method of reassembling the program each time necessary. This step will, however, be inefficient, time-consuming and expensive, especially if the program is often used, with different systems. In our case this solution was unsatisfactory. Fortunately our UNIVAC 1100 computer system permits the use of ALGOL where dynamic dimensioning is performed. Besides, it is permitted to call FORTRAN routines from an ALGOL program, and this is the key to our solution of the problem. A small ALGOL main program is written, whose only task is to dimension the necessary arrays correctly. When the actual main program is called, it is formally treated as an EXTERNAL FORTRAN SUBROUTINE. The small ALGOL "superprogram" has the following form (In the NU ALGOL dialect¹³).

```
BEGIN
EXTERNAL FORTRAN PROCEDURE
SQUAD;
INTEGER NUMPH, NBA, NTS, NCV;
INTEGER III, JJJ, NNN;
READ (NUMPH, NBA, NTS, NCV);
III = NBA * NUMPH; JJJ = NCV * 2; NNN =
NTS + 4;
BEGIN
REAL2 ARRAY EQ (1:NNN, 1:NBA), Q(1:
NUMPH, 1:NNN), TS(1:NUMPH, 1:NBA),
SP2(1:III, 1:JJJ), EC(1:4, 1:NBA), STD(1:4, 1:
NBA), B(1:NUMPH, 1:NBA); REAL ARRAY
SPEC(1:NUMPH, 1:NBA), SS1(1:III), SSRSOL
(1:NUMPH);
SQUAD(EQ, Q, TS, SP2, EC, STD,
B, SPEC, SS1, SSRSOL, III, JJJ, NNN, NUMPH,
NBA); END;
END;
```

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