shown by Table II. The values obtained for hydrogen adsorption on zinc oxide are higher than those obtained by Taylor and Strother.[15]

TABLE II

ADSORPTION OF HYDROGEN ON ZINC OXIDE AT 85°K.

p, mm.	Cc. N. T. P. H_2/g. ZnO in absence of free radical	p, mm.	Cc. N. T. P. H_2/g. ZnO in presence of equal wt. of free radical
3	0.03	22	0.15
45	.17	38	.23
94	.51	63	.41
151	.73	116	.63
216	.97	157	.79
264	1.13	192	.95
316	1.30	235	1.20
391	1.53	275	1.39
448	1.70	338	1.66
512	1.85	422	1.98
588	2.03	472	2.15
653	2.19	535	2.36
766	2.41	590	2.48
		648	2.72
		694	2.82
		724	2.98

TABLE III

ORTHO–PARA HYDROGEN CONVERSION AT 85°K.

Free radical		Zinc oxide		Free radical on zinc oxide	
1 hr. 45 min.	14%	15 min.	2%	15 min.	84%
2 hr.	13%	35 min.	4%	30 min.	100%
4 hr.	25%	1 hr.	11%	1 hr.	100%
6 hr.	69%	2 hr.	20%		

The ortho–para hydrogen conversion is given in Table III.

It is seen that there is a slow conversion of the hydrogen on the free radical and a similarly slow conversion of the zinc oxide. Intimate mixing of the zinc oxide and the free radical produces a very rapid conversion. This is interpreted to mean that two factors are necessary for the heterogeneous catalysis of ortho to para hydrogen at low temperatures, namely, the existence of an inhomogeneous magnetic field, produced in this case by the free radical, and long contact of the hydrogen with this field, ensured by the van der Waals adsorption of hydrogen on the zinc oxide.

We wish to thank Professor Hugh S. Taylor for his interest in this investigation.

Conclusions

1. The magnetic characteristics of α,α-diphenyl-β-picrylhydrazyl, the corresponding hydrazine, active zinc oxide and ignited zinc oxide were determined.
2. Hydrogen adsorption at liquid air temperatures was determined on α,α-diphenyl-β-picrylhydrazyl, active zinc oxide and on an intimate mixture of the two.
3. Ortho–para hydrogen conversion at liquid air temperatures was found to be slow on zinc oxide and slow on the free radical but very rapid on an intimate mixture of the two.

PRINCETON, N. J. RECEIVED JANUARY 20, 1941

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[15] H. S. Taylor and C. O. Strother, THIS JOURNAL, **56**, 586 (1934).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

The Absorption Spectra of Ions of Europium and the Electric Fields within Some Coördination Compounds

BY SIMON FREED, S. I. WEISSMAN AND FRED E. FORTESS

No one examining the spectra of europium ions whether in solutions or in crystals would question that they represent for the most part the same kind of physical situations. The spectra consist of isolated groups of lines whose numbers, separations, and relative intensities vary with the ionic environment.[1] Not only does there appear a one-to-one correspondence in the groups of all these spectra but the wave lengths of the groups as a whole differ but little. When the crystals are anisotropic, the lines within each group usually possess different polarizations, a definite sign that the ions are oriented by the crystal fields. These fields can be thought of as having brought about a decomposition in the spectra somewhat as an external electric or magnetic field affects the line spectra of gases. As an electric field differs from a magnetic field in the pattern of the group it induces, so crystal fields of different symmetries would be expected, as a rule, to induce different patterns. We are then to ascribe the rather isolated groups appearing in the spectra

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[1] S. Freed and S. I. Weissman, *J. Chem. Phys.*, **6**, 297 (1938); S. Freed and H. F. Jacobson, *ibid.*, **6**, 654 (1938); S. Freed, S. I. Weissman, F. E. Fortess and H. F. Jacobson, *ibid.*, **7**, 824 (1939).

of europium ions to the fields of the environment as they affect the virtual line spectrum of the ions. In agreement with this view is the observation made in some instances that the groups from crystals of the same symmetry consist of the same number of lines but that they consist of different numbers from crystals of different symmetries. However, such is not always to be anticipated theoretically.[2] What determines the number of components into which a particular energy level of the ion will split is the symmetry of the microscopic field about the ion rather than the symmetry of the outer crystalline form. This theory has received quantitative verification.[3] Especially for solutions, it seems worth while to point out that the crystallographic symmetries based upon the outer form do not exhaust the posssibilities of symmetry about the ions, although the two-, three-, four- and six-fold axes of rotations to which the crystallographic groups are restricted may occur in most instances. The same general method[4] employed by Bethe for deriving the numbers of component sub-levels still remains applicable for fields of any symmetry.

It is the extreme sharpness of their spectra which singles out solutions of the europium salts from all others. They are sufficiently sharp that counting the number of components in a group is an experimental possibility, which can scarcely be hoped for in the broad diffuse bands from the solutions of the common colored ions. For this reason, we employ the ions of europium as spectroscopic indicators for the symmetries and, eventually, for the intensities of the fields and we are in position to investigate those configurations of atoms, ions, molecules long recognized by chemists as also present about other central ions.

The spectra of the ions of the rare earths owe their sharpness, it is agreed, to the shielding of an incompletely filled inner electronic shell by two completely filled outer shells.[5] How much more favorable the spectra of europium ions are than those of the common colored ions for the study of ionic environments may be gathered from the following comparison. There are three groups in the visible spectrum of europium ions Eu^{+++} to which we shall refer repeatedly, one in the blue region at about 4650 Å., one in the green at 5250 Å., and one in the yellow at 5790 Å. Table I gives the number of lines in these groups and the total spread, which is a measure of the intensity of the fields in solution.

TABLE I

NUMBER OF COMPONENT LINES IN THREE MAIN GROUPS OF THE SPECTRA OF EUROPIUM IONS IN VARIOUS SOLUTIONS

	Blue		Green		Yellow	
Solution, Europium	No. of lines	Total spread cm.$^{-1}$	No. of lines	Spread cm.$^{-1}$	No. lines	Spread cm.$^{-1}$
Nitrate in water	3	50	2	25	1	
Chloride in water	4	90	3	35	1	
Chloride in alcohol	3	105	2	20	1	
[a]Acetylacetonate in benzene	6	115	4	80	2	3

[a] An unusual example of sharpness is given by the doublet in the yellow. Here the width of the lines is less than 1 Å. and although the separation between the lines is less than 3 Å., they appear completely resolved.

On the other hand, ions of the transition elements, for example, not enjoying the shielding characteristic of the rare earths are very sensitive to their environment. Instead of groups 100 cm.$^{-1}$ wide and less with discrete structure, their spectra consist of continuous bands ranging in width from about 750 cm.$^{-1}$ to 5000 cm.$^{-1}$.[6] It requires little energy to reorganize and re-orient their exposed electrons and form "shared electron bonds" with neighboring systems. Experimentally these disorientations and fresh couplings go hand in hand with changes in color, in magnetic properties, etc., when the environments of these ions are changed. The effects of changing solvents, of adding acids, bases, cyanides, etc., to their solutions are well known. Rather small fluctuations in the force fields such as accompany thermal motion are enough to blur any structures of their spectra into diffuse bands. All the more easily does this occur in the closely spaced complex spectra which result from coupled systems.

Magnetic data and theory[5] have established that the basic state of europium ion Eu^{+++} is $^7F_0$. This state having as its angular momentum $J = 0$ is single; it cannot be decomposed by external fields. Most of the absorption spectrum originates in ions in this state although faint lines originate also in the thermally excited states $^7F_1$ and also $^7F_2$ but these we shall not discuss here. The more intense groups, namely, the three we have already considered, are optical transi-

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(2) H. Bethe, *Ann. Physik*, **3**, 133 (1929).

(3) S. Freed and S. I. Weissman, *J. Chem. Phys.*, **8**, 878 (1940).

(4) E. Wigner, "Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren," F. Vieweg and Sohn, Braunschweig, 1931.

(5) See *e. g.*, J. H. Van Vleck, *J. Phys. Chem.*, **41**, 67 (1937).

(6) H. C. Jones and J. A. Anderson, Carnegie Institution of Washington, Washington, D. C., 1909; H. C. Jones and W. W. Strong, Carnegie Institution of Washington, Washington, D. C., 1910, and 1911.

tions which, beginning at $J = 0$ in each transition, end in the state $J = 0$ for the yellow, $J = 2$ for the green, and $J = 3$ for the group in the blue.[7] The maximum number of lines which can occur in the yellow is one for fields of any symmetry; the maximum in the green is five; and the maximum in the blue is seven. (The number of components upon complete decomposition is given by the expression $2J + 1$ where J is the number of units of angular momentum of the state.) The following Table II gives the number of components induced by fields of several symmetries for some values of J. The optical transition from $J = 0$ to $J = 0$ leads, of course, to but one line at most. We find instead a doublet in the spectrum of the acetylacetonate. It is natural to infer that there are two species present in solution and that the observed spectrum is really the superposition of two separate spectra and confirmation is to be sought in the other groups, in the blue and in the green regions. This brings us to the detailed study of the spectra of europium acetylacetonate and, supplementary to these, the spectra of some related compounds.

TABLE II

NUMBER OF COMPONENT LEVELS

J value of energy level	$J = 0$	$J = 1$	$J = 2$	$J = 3$
Cubic	1	1	2	3
Trigonal	1	2	3	5
Rhombic (and less symmetrical)	1	3	5	7

Astbury[8] has investigated the X-ray diffraction patterns of crystals of a number of acetylacetonates, those of aluminum Al^{+++}, iron Fe^{+++}, gallium Ga^{+++}, scandium Sc^{+++}. The latter is often classed with the rare earths. Figure 1 gives a schematic representation of the structure in the light of the classical work of Werner. Astbury was, however, unable from his data to distinguish the pairing of oxygen atoms required by the structure which corresponds to trigonal symmetry and he assigned the oxygen atoms to equivalent positions at the corners of a regular octahedron.

The acetylacetonates of the rare earths have been the subject of a number of well-known investigations. Biltz[9] has determined their molecular weights by the ebullioscopic method.

As in our previous work, the europium which we employed was generously furnished us by Dr. H. N. McCoy who had separated it from the other rare earths by the methods he has found so effective.[10] We wish to express here our deep gratitude to him.

Our europium acetylacetone was prepared from redistilled Kahlbaum acetylacetone according to the methods of Biltz and of Morgan and Drew.[11] The final products by both methods gave identical results. The crystals obtained after three crystallizations from acetone possessed a spectrum containing one line at 5780 Å., three at 5250 Å., and five at 4650 Å., a set of numbers in agreement with fields of trigonal symmetry about Eu^{+++} and hence conforming to the chelate structure of Fig. 1. It still remains possible that the field of force responsible for the decomposition of the energy levels may well extend beyond the second coördination layer of the ion. However, the inclusion of the second is sufficient to account for trigonal symmetry.

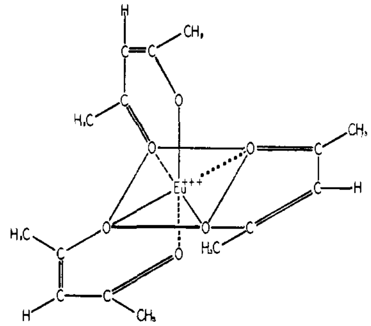

Fig. 1.—Monomer of europium acetylacetonate.

On dissolving the crystals in benzene or in carbon tetrachloride, the resulting spectrum fell into the same distribution of groups as in the spectra from other solutions but the number of the lines within the groups exceeded any previous experience. Indeed they were more numerous than the maxima we have listed. The lines were exceptionally sharp, a consequence presumably of the compact distribution of electron density within the inner shell, its effective shielding, and the short range forces from the molecules of the nonpolar solvent.

Instead of the single line in the yellow, two narrow doublets appeared and at least ten lines stood out in the group in the blue. (The solution in benzene was 0.002 M and the optical path was

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(7) H. Gobrecht, *Ann. Physik*, **28**, 670 (1937); S. Freed and S. I. Weissman, *J. Chem. Phys.*, **8**, 878 (1940).

(8) W. T. Astbury, *Proc. Roy. Soc.* (London), **112**, 448 (1926).

(9) W. Biltz, *Ann.*, **331**, 334 (1904).

(10) H. N. McCoy, THIS JOURNAL, **57**, 1756 (1935).

(11) W. Biltz, *Ann.*, **331**, 334 (1904); G. T. Morgan and H. D. R. Drew, *J. Chem. Soc.*, **119**, 1060 (1921).

90 cm. long.) It was soon noted that the relative intensities of the lines varied with time. After three weeks at room temperature, an equilibrium seemed to have been reached in which six lines remained in the group 4650 Å., four lines in the green, and one close doublet at 5970 Å. The change was regarded as a steady progression of the acetylacetonate toward the equilibrium between its dimeric and monomeric forms. These are schematized in Fig. 1 and Fig. 2.[12]

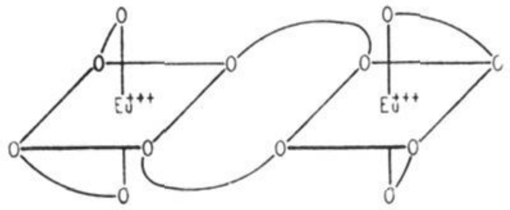

Fig. 2.—Dimer of europium acetylacetonate.

The spectrum first observed was then a superposition of the spectra of both monomer and dimer. Upon evaporating a considerable portion of the solvent, the lines which had faded out began to re-appear all at the same time, becoming visible according to their intensities. They continued to become stronger at the expense of the other lines, finally ending about five times as intense at the new equilibrium. It seems then that as the crystals dissolved, the solute existed principally in the form of dimer even though the amount of solvent was in such abundance as to yield a solution at equilibrium consisting of the monomer almost entirely. The spectrum of the dimer contained the same number of lines in each group as the monomer, six in the blue, four in the green although these were so faint that it was difficult to be certain, and again a narrow doublet in the yellow. Table III gives wave lengths for both monomer and dimer. About a month after the crystals had been prepared, their spectrum was again taken and was found to have changed. We had been impelled to re-examine the spectrum because a solution made by adding a large proportion of solvent to the crystals furnished the spectrum of the monomer, almost exclusively, within only an hour after the crystals had been dissolved.

TABLE III

THREE MAIN GROUPS IN THE ABSORPTION SPECTRUM OF EUROPIUM ACETYLACETONATE

Blue		Green		Yellow	
Wave length, Å.	Relative intensity	Wave length, Å.	Relative intensity	Wave length, Å.	Relative intensity
		Monomer			
4667.6	1	5270.0	Strong	5794.3	Almost equal
4663.3	1	5262.7		5796.5	
4658.7	10				
4651.1	10[a]	5254.3	Weak		
4649.8	10	5249.5			
4644.9	10[a]				
		Dimer			
4665.3	5	5265		5278	Diffuse
4655.1	3	Others weak		5282	Doublet
4651.1	10[a]				
4644.9	10[a]				
4639.9	5 diffuse				
4636.7	5 diffuse				

[a] Lines in common.

The appearance of two lines in the yellow, incompatible with the transition $J = 0$ to $J = 0$, implied the presence of two species and since the components of the doublet were about equally intense these forms, presumably isomers, were present in roughly equal amounts. Optical isomers, according to theory, have identical spectra in regard to the number of components in the groups and their relative intensities; hence the doubling cannot be accounted for by that kind of isomerism. Because a resonance was conceivable between the electronic systems of europium ions in the identical halves of the dimer we added crystals of *colorless* gadolinium acetylacetonate to a dilute solution of the monomer in carbon tetrachloride.[13] The preponderance of the salt of gadolinium was so great and the concentration of both rare earths together was such that about 90% of all the europium would be coupled with the gadolinium in a rare-earth (europium–gadolinium) dimer if free interchange existed on an equivalent basis between the rare earths. If the doubling of the spectrum of the europium–europium dimer depended upon the identity of the electronic structures in the halves of the dimer the spectrum of the dimer should not now make its appearance. In particular, the group in the yellow should not contain more than one line. What transpired was that the spectrum of the

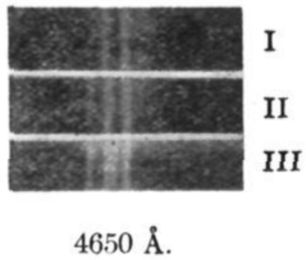

Fig. 3.—The change of the spectrum with time after crystals of europium acetylacetonate are dissolved in water: I, one hour after solution (spectrum of dimer), II, two weeks, III, five weeks (spectrum of monomer).

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[12] Biltz (*loc. cit.*) in his ebullioscopic experiments had discovered the presence of the dimer in addition to the monomer and also the slow attainment of equilibrium. In a solution 0.002 *M* the compound would exist, according to Biltz's results, as at least 90% monomer at equilibrium.

[13] Gadolinium is immediately next to europium in the periodic table and salts of the two are almost inseparable by fractional crystallization. The ionic sizes of the two ions are almost identical.

monomer became fainter and in its place the old spectrum of the dimer showed itself unchanged; in the yellow the doublet was present as before.

The construction of two suitable models for the dimer offers little difficulty. To represent forms with but slight differences in energy as they affect the europium ions, it is sufficient to interchange two terminal positions of neighboring chelate groups. The other terminals of the chelate groups and the rest of the molecule should remain unaltered. The doubling of the line in the yellow region of the spectrum of the monomer cannot be accounted for so simply.

In the hope of resolving this difficulty, we examined the spectra of several derivatives of the acetylacetonate. When the hydrogen on the middle carbon atom of acetylacetone was replaced by a methyl group (3-methylpentanedione-2,4) the spectrum of the resulting europium salt was very similar to that of the simple acetonate. The spectrum of the monomers corresponded line for line.[13a] When acetylacetone was modified so as to be unsymmetrical by replacing a terminal methyl group by a phenyl radical (1-phenylpentanedione-2,4), the spectrum of the europium salt was again practically a copy of that of the acetonate in regard to the wave lengths of corresponding lines. They were more diffuse, however. But now the approximate equality in the intensities of the coexisting spectra was destroyed. The dissymmetry of the compound had as its counterpart the "inequality" in the intensities of the spectra of the isomers. The behavior of the various spectra is summarized in Table IV.

The spectrum both of the monomer and of the dimer was easily partitioned into two spectra each having the same number of lines in the same group and the two component sub-groups from the symmetrical acetone derivative were roughly of equal intensity. In the blue, two sets of three lines, in the green two sets of two and in the yellow two of one line. Such a similarity in the spectra led to our assumption that they originated in isomers. At first glance, one might be inclined to ascribe the existence of two isomers revealed in the spectrum of the monomer to resonance somewhat as in benzene. A shift in the electrons corresponding to a shift in the double bonds would be said to take place in each chelate group. In the case of benzene only states of widely different energies occur. Our states differ however by energies small compared with thermal energy, about 600 cal. per mole since the intensities of the spectra are substantially equal. That such a resonance cannot account for the facts was brought out in the spectrum of the chelate compound when salicylaldehyde took the place of acetylacetone. No shift can occur in the double bonds of the resulting europium structure and yet the same doubling in the spectrum of the monomer appeared. Because of the pronounced dissymmetry in the substituent the relative intensities of the spectra of the two isomers were found very unequal.

If we suppose that the assumption, amply justified in the spectrum of europium fluoride,[3] is also valid in these compounds, namely, that the lines reveal all the sub-levels induced by the fields, we would assign octahedral symmetry to the fields about the europium ions in both isomers of the monomer as well as in both isomers of the dimer (see Table I). In the crystal it may be recalled the number of lines conformed to trigonal symmetry on the same assumption.

TABLE IV

DISTRIBUTION BETWEEN DIMER AND MONOMER IN FRESH AND OLD SOLUTIONS IN DIFFERENT SOLVENTS

Solute, Europium	Solvent	Concn. (molarity)	Type of spectrum
Acetylacetonate	Benzene	0.0045	Mostly dimer fresh soln., 80% monomer old
Acetylacetonate	CCl_4	.0015	All monomer old
-Gadolinium acetylacetonate	Benzene	.003 in Eu .030 in Gd	Mostly dimer 3 months old
Methylacetylacetonate	Benzene	.004	All monomer fresh All monomer old
	Benzene	.020	All monomer fresh All monomer old

As has already been mentioned, the two isomers of the dimer may be represented by models where the first coördination layer is octahedral about the europium ion. The apparent indifference of the patterns in the spectra to the more remote layers, that is, the persistence of octahedral symmetry in all the isomers, may perhaps be related to the solvent. The molecules of the latter may take up positions and orientations to neutralize the stray fields and render the resultant fields about europium more symmetrical. In the crystal, the environment being more nearly fixed in position and orientation acts to decrease the symmetry of the effective fields. The acetyl-

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[13a] The dimer did not seem to be present as the crystals were dissolved and we obtained no spectrum of the dimer of this compound. The salt of the methyl derivative exhibited the sharpest spectrum we have seen from solutions.

acetonates measured by Astbury[8] are rhombic and monoclinic.

That the solvent is of influence may be observed in the spectrum of the monomer. When the solvent is added to the crystals in an amount which is sufficient to form ultimately a dilute solution of the monomer, the spectrum of the monomer as it first appears consists of but one line in the yellow region. As the concentration of the monomer grows with time, the line divides into two of almost equal intensity and the separation continues to increase until it amounts to 3 Å.[14] The delineation of the spectra of the two forms is possible only because of the extreme sharpness of these lines. We are unable to be certain whether similar movements take place in the rest of the spectrum.

To account for the two isomers of the monomer we may proceed from two different points of view. One of these relates to the inequality in the amounts of the two isomers when the substituents in the europium compounds are unsymmetrical. The difference in energy becomes less, the more nearly the two "ends" of the substituents are alike. The intensities of the spectra of the isomers are practically equal when the original diketones are symmetrical. From this one would infer that the energy difference is very slight but nevertheless not zero and that the existence of the two isomers is again bound up with a dissymmetry in the substituent but here induced by the presence of the others. That is, the interaction of the chelate units effects a slight differentiation in the two ends of each unit. Such a differentiation leads at once to two isomers with a slight difference in energy brought about by the two different ways in which the three substituent chelate groups are oriented with respect to each other. Hindered rotation of the methyl groups might be imagined as effecting this unbalance. For example, if the hydrogen atoms of one of the methyl groups are staggered in respect to those of the opposite methyl group in the same chelate unit, a dissymmetry about the hydrogen on the central carbon can result.

One might also ascribe the existence of the two isomers to a distortion in the regular octahedral distribution of the oxygen atoms. Some distortion within rather narrow limits would not markedly influence the decomposition of the energy levels and would be active only within the breadths of the lines. Yet the presence of several isomers would follow from such a structure and any dissymmetry in the substituents might be expected to accentuate the difference in energy between the forms. The origin of the distortion may lie in the higher approximations in the electron density distribution of the europium ion. It has been remarked that the excited states $J = 1$ and $J = 2$ are but little removed in energy from the basic state $J = 0$. The corresponding intervals are actually 350 cm.$^{-1}$ and 1000 cm.$^{-1}$. According to a theorem of Jahn and Teller[15] such states are incompatible with so symmetrical an environment as the octahedral and their contribution to the electron density of the europium ion would probably be a distorting influence. It may be worth while to add that in higher approximation the dissymmetry as discussed in terms of hindered rotation would also be consistent with a slight distortion in any supposed regularity about the europium ion and hence both views should perhaps be taken into account.

Of the existence of the two isomers of the monomer there can scarcely, we think, be any doubt. It seems probable that such pairs of isomers are present also in solutions of the considerable number of coördination compounds which resemble those we have here examined.

We are much indebted to the Penrose Fund of the American Philosophical Society for the support it has given this investigation.

Summary

Because of the sharpness of their spectra, the ions of europium may be employed as spectroscopic indicators for the symmetry and eventually for the intensity of the electric fields of their environment in solution as well as in crystals.

The spectra of some chelate coördination compounds are described and from these are derived the symmetries of the fields about the central ions. The symmetry of the effective fields about the ions in solution differs from that in the crystal.

The process of dimerization of the acetylacetonates of europium and of the dissociation of the dimers can be readily followed spectroscopically.

Both the dimers and the monomers exist in two stereo-isomeric forms. While the structures

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[14] The magnitude of the final separation is somewhat greater when chloroform is employed as solvent.

[15] H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London), **161**, 220 (1937); H. A. Jahn, *ibid.*, **164**, 117 (1938).

of the two dimeric forms are easily accounted for in terms of previous work on coördination compounds, the existence of the two isomers of the monomer brings new isomeric distinctions into this domain of chemistry.

The compounds investigated are those in which one europium ion replaces the active hydrogens of three identical diketones and remains in first coördination with the oxygen atoms of the resulting substituents. The following diketones are employed, acetylacetone (pentanedione-1,4), symmetrical methyl acetylacetone (3-methylpentanedione-2,4), and benzoylacetone (1-phenylpentanedione-2,4). A similar compound is formed with salicylaldehyde. The following serve as solvents: benzene, carbon tetrachloride, and chloroform.

CHICAGO, ILLINOIS RECEIVED DECEMBER 21, 1940

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY]

The Density of Aqueous Solutions of Potassium Hydroxide

BY GOSTA AKERLOF AND PAUL BENDER

Introduction.—The alkali hydroxides exhibit in many respects a very complex behavior of the greatest interest. To get as clear a picture as possible of their thermodynamic properties in concentrated solutions it is our intention to follow up a previous study[1] of sodium hydroxide with a similar one on potassium hydroxide. With this purpose in mind we will present in this paper some measurements of the density of aqueous solutions of the latter. The "International Critical Tables" (I. C. T.) lists a considerable number of references to such determinations but only one of these seems to give data of higher accuracy at a single temperature. The data referred to are those of Pickering[2] at 15°.

Experimental Procedure.—A saturated solution of potassium hydroxide dissolves large quantities of potassium carbonate. The elimination of the carbonate down to the last traces by recrystallization requires an elaborate procedure with a considerable danger that other impurities might be picked up since the hydroxide is extremely reactive. Using as material an analytical reagent of unusually high purity the carbonate present in its saturated solution was precipitated with a slight excess of a warm solution of recrystallized barium hydroxide while the potassium hydroxide solution was being stirred by a strong stream of pure nitrogen. The precipitate was allowed to settle and the excess of barium hydroxide remaining in solution was carefully determined and then removed by mixing the required amount of carbon dioxide gas with a large amount of nitrogen and then letting it bubble through the solution. After the solution had cleared up again it was found by analysis to contain only a faint trace of barium. The ratio of barium hydroxide concentration to that of potassium hydroxide was about 1:7000. The error introduced in the density measurements due to the presence of this trace of barium is for all practical purposes negligible.

The density measurements themselves were carried out in the same manner as previously described for sodium hydroxide and using the same equipment. The corrosive action of potassium hydroxide solutions on the pycnometers was no larger than that of those of sodium hydroxide as found by a recalibration of the pycnometers after the completion of the runs.

Experimental Results.—From the density data the apparent partial molal volume of the hydroxide was first calculated using the values of Smith and Keyes[3] for the specific volume of the solvent. These values, summarized in Table I, were then plotted against the square root of the molality. The resulting isothermal curves, shown graphically in Fig. 1, are continuous without any breaks in contrast to the behavior of the corresponding ones for sodium hydroxide solutions. All the curves approach for the lower third of the concentration range used very closely straight lines while their upper portions accurately follow second order equations. Therefore the data in Table I were divided up in two sections which overlapped each other to some extent. The data in the lower range were least squared linearly and those in the higher one to a quadratic equation. The constants acquired were then least squared against the temperature assuming a third order equation. That the procedure outlined is justifiable is shown by Table II which gives a summary of the final equations and constants obtained. The directly observed and the calculated values for the crossing points of the two sets of curves are practically identical. A comparison of our density data and those of Pickering at 15° shows

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(1) Akerlof and Kegeles, THIS JOURNAL, **61**, 1027 (1939); **62**, 620 (1940).

(2) Pickering, *Phil. Mag.*, [5] **37**, 359 (1894).

(3) Smith and Keyes, *Proc. Am. Acad. Arts Sci.*, **69**, 285 (1934).