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The Oxidation of Fe++ to Fe+++ by the Irradiation with XRays of Solutions of Ferrous Sulfate in Sulfuric Acid

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The following Raman frequencies were found: 298(4), 394(2), 458(1), 505(0), 559(1), 618(1), 823(10), 848(8), 945(4b), 992(15), 1060(2), 1174(4), 1220(3), 1240(2), 1266(1), 1324(1), 1411(1), 1432(5), 1576(20), 1615(3), 2823(8b), 2864(8b), 2908(4), 2936(8), 3018(5), 3041(10), 3056(7). The figures given in parentheses are visually estimated relative intensities.

The chemical behavior of 1,3-cyclohexadiene is very different from that of benzene or that of cyclohexane as there are two double bonds of distinctly ethylenic character. In view of this fact, it is interesting to note that most of the strong lines in the benzene spectrum have counterparts in the spectrum of 1,3-cyclohexadiene. Because of the lower symmetry, there are more strong lines in the latter spectrum, the number being nearly the same as in the spectrum of cyclohexene which has the same degree of symmetry. The low frequency line at 176 in cyclohexene is not found in the spectrum of 1,3-cyclohexadiene. Two lines are found in this spectrum in the region associated with double bond vibrations both of which have lower frequencies than the lines in this region of the cyclohexene spectrum and are rather close to the positions of the benzene lines in this region. This appears to support the assignments of these benzene lines to vibrations involving double bonds.

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November 26, 1934.

[1] Crossley, J. Chem. Soc. (1904), 1416.
[2] J. W. Murray and D. H. Andrews, J. Chem. Phys. 1, 406 (1933).

The Oxidation of Fe^{++} to Fe^{+++} by the Irradiation with X-Rays of Solutions of Ferrous Sulfate in Sulfuric Acid

In earlier work[1] we have studied the chemical effect of x-rays on ferrous sulfate in 0.8N sulfuric acid. This work has now been extended by a study of the influence of the hydrogen ion in this reaction. Solutions of ferrous sulfate in sulfuric acid, gas-free or containing oxygen at different pressures, were irradiated and analyzed for the ferrous ion, hydrogen and oxygen. The temperature was 30°C. For the wavelength used, the x-ray absorption for all irradiated solutions was practically the same as for water. The ferrous ion concentration was determined by electrometric titration with potassium dichromate. Analysis for hydrogen and oxygen was made by means of a van Slyke apparatus.

In gas-free solutions, hydrogen is produced, the number of moles being slightly larger than one-half the number of ferrous ions oxidized. In solutions containing oxygen, none, or a very small quantity of hydrogen is produced. The number of moles of oxygen consumed is slightly less than one-fourth the number of ferrous ions oxidized. The lack of exact equivalence may be due to the action of the rays on traces of organic impurities in the solutions, resulting in the production of a small quantity of hydrogen and the binding of a small quantity of oxygen.

The number of ferrous ions oxidized per unit of dosage depends on the hydrogen ion concentration, and is within certain limits independent of the concentration of the ferrous and the sulfate ions, and, for solutions containing oxygen, of the oxygen pressure. The ferrous ion concentration has been changed from 50 micromoles per liter to such concentrations as can be obtained in solution, but not over one millimole per liter. In the earlier work[1] at pH equal to 0.5, the independence was established up to 10.0 millimoles per liter of ferrous sulfate. The oxygen pressure has been changed from 70 to 1 cm of mercury. The sulfate ion concentration has been varied by the addition of sodium sulfate in concentrations up to 0.4 molar. The results obtained show that the oxidation of the ferrous ion is due to a primary activation of the water by the x-rays.

The dependence on the hydrogen ion concentration is shown in Fig. 1, where the number of microequivalents of

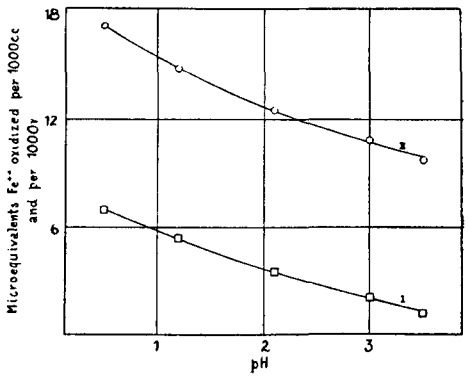

FIG. 1. The oxidation of ferrous sulfate in sulfuric acid as a function of the pH of the irradiated solution. I. gas free; II. oxygen present.

ferrous ion oxidized per 1000 cc of solution and per 1000 r of dosage is given as a function of the pH, for gas-free solutions (I) and for solutions containing oxygen (II). The two curves have a constant difference of 8.8 microequivalents.

The reaction occurring in gas-free solution may be written:

$$Fe^{++}+H^{+}=Fe^{+++}+\tfrac{1}{2}H_2. \qquad (1a)$$

In solutions containing oxygen, it would appear that this same reaction occurs, but the hydrogen evolved is oxidized to water in a secondary reaction, giving as the complete reaction:

$$Fe^{++}+H^{+}+\tfrac{1}{4}O_2=Fe^{+++}+\tfrac{1}{2}H_2O. \qquad (2a)$$

Furthermore, the additional reaction, which is independent of the pH, takes place:

$$Fe^{++}+\tfrac{1}{4}O_2+\tfrac{1}{2}H_2O=Fe^{+++}+OH^{-}, \qquad (2b)$$

this reaction being represented by the difference between curves I and II. The continuous rise of curve I is rather

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surprising, since reaction (1a) is endothermic. Unfortunately, it is not feasible to extend the measurements below the range of pH used.

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[1] Fricke and Morse, Phil. Mag. 7, 129 (1929).

A New Approximation Method in the Problem of Many Electrons

The principles of an approximation method have been recently published by the author for systems consisting of closed shells and of valence electrons.[1] The method consists in treating simultaneously the atom kernels according to Thomas-Fermi and the valence electrons according to Schroedinger. It is possible to obtain an approximated Schroedinger equation for the valence electrons from the variation principle for the whole energy. There are no additional exclusion conditions for the valence electrons, arising from the states occupied by paired electrons. But the potential field for the valence electrons contains, besides the familiar electrostatic action of the charge of closed shells on the valence electrons, an additive term of the form $\partial T/\partial\rho$, where T is the kinetic energy per unit of volume of the paired electrons, ρ their density. (The theory of Thomas-Fermi gives $\partial T/\partial\rho=(h^2/8m)[(3/\pi)\rho]^{2/3}$.)

There is nothing to prevent the use of better distributions of electrical density ρ than those obtained from the Thomas-Fermi method. But even the use of the latter gives the right order of magnitude, e.g., for a univalent ion the potential function is, in the region from $r=\infty$ to $r=r_0(=4.6\text{A})$, the pure Coulomb potential, i.e., $-e^2/r$, and then the value $eV+\partial T/\partial\rho$ is constant, being equal to $-e^2/r_0$.[2] If we put the valence electron into this potential hole, then its energy will be somewhat higher than the potential $-e^2/r_0$ at the bottom of the hole, namely, -3.1 volts. For caesium, where the application of the Thomas-Fermi solutions for the atomic kernels is better justified than in other cases, the experimental value is -3.9 volts. Without an additive potential and without the exclusion principle the valence electron would fall into the K-shell with many thousand volts of ionization energy.

The practical value of the method lies in that it allows us to obtain the entire potential function $eV+\partial T/\partial\rho$ from experimental data. The potential field and the corresponding eigenfunctions of the valence electrons can be obtained from the spectra so that the lowest state of the valence electrons corresponds to the lowest level obtained in the potential field without any additional conditions. These data enable us to enter upon the problem of boundary. Thus both the electrostatic and the exclusion principle influences of the atomic kernels on all the valence electrons are taken into consideration and the Ritz method may be used for the valence electrons alone.

For potassium a preliminary calculation suggested the expression $-1/r+(2.74/r)e^{-1.16r}$ for the complete potential for the valence electron, and the corresponding eigenfunction $\psi\sim e^{-0.39r}$ (approximated by means of the Ritz method expressed in atomic units). Then the Heitler-London method will give for K_2 an equilibrium distance of about 4A (exp.: 3.9A) and an energy of about 37 percent of the experimental value. It is this result which agrees very well with the results obtained by James[3] for Li_2 who considered the effects produced by closed shells in detail. We must also assume, that the greater part of the binding energy appears first in higher approximations. The accordance of the results of Rosen and Ikehara[4] and of others with experimental data must be ascribed to their being arbitrary assumptions. The decrease in the value of the triplet under the influence of the closed shells, emphasized by James, comes quite naturally in our calculation, for the additional potential changes not only the Coulomb interaction but also the exchange integrals. A diminution in the exchange integrals produces an increase in the singlet and a decrease in the triplet term. However, our having obtained more favorable results than may have been expected from James's calculations may be explained first by our having omitted the mutual interaction between atomic kernels and, secondly, by our having partially included the polarization forces with the closed shells in our empirical potential function.

For KH a rough approximation including, however, the homopolar and ionic states gives an equilibrium distance of about 2A and an energy of -0.8 volt. The share of the ionic state in the molecule is 80 percent. The difference as compared with the experimental value of -2.06 volts must be again explained by polarization forces. In the extreme case of pure ionic binding we can avail ourselves of the result of Hylleraas[5] for the internal polarization interaction of H^-. Then, in the subsequent calculation, only the resulting density (not the eigenfunctions) of the H^- atom plays a part. This was assumed approximately as $\sim e^{-11r/8}$. Thus we find an equilibrium distance of 1.9A and a binding energy of 1.95 volts.

A detailed account of the subject will shortly appear in the *Acta Physicochimica U. R. S. S.* The approximation method is being further elaborated for the alkaline molecules and its hydrides in this institute. The method shall be extended for polyvalent atoms.

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November 26, 1934.

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