On the Molecular Structure of Uranium Hexafluoride

Fausto G. Fumi and Gilbert W. Castellan

On the Molecular Structure of Uranium Hexafluoride

FAUSTO G. FUMI AND GILBERT W. CASTELLAN*
Department of Physics, University of Illinois, Urbana, Illinois
March 16, 1950

RECENTLY S. H. Bauer[1] studied the molecular structure of uranium hexafluoride by means of electron diffraction. The best agreement between calculated and observed intensities is given by Model A_4, obtained by distortion of a trigonal antiprism of symmetry C_{3v}, and by Model C_4, obtained by distortion of an octahedron of symmetry C_{2v}; however, the experimental precision† does not allow a selection to be made between models such as C_4 and C_3, the latter being a rhombic bipyramid of symmetry V_h.

Table I gives the polar coordinates of the bond vectors of the first two models; the bond numbers follow Bauer's enumeration. The configuration of Model C_3 is evident from Bauer's Table III.

All three models involve non-equivalent bonds. The symmetry group of the Model A_4 is C_{3v} and the symmetry group of the Model C_4 is C_2; in both these models the system of six fluorine atoms has a center of symmetry which, of course, does not coincide with the position of the uranium atom. Model C_3, on the other hand, has a center of symmetry.

The possible configurations of the valence electrons of the uranium atom in the models are obtained in Tables II–IV by group theory.

These configurations are:

For the Model A_4: $(sp, sd, pd) + (p^2d^2, d^4)$.
For the Model C_4: $(spd, sd^2, pd^2, d^3) + (pd^2, p^2d)$.
For the Model C_3: d^2sp^3.

Bauer's statement that the hybridization p^3d^3 can lead to a trigonal antiprism with the possibility of two unequal sets of three bonds is not proved in his paper nor included in Kimball's results.[2] Tables II and III show that the hybridization p^3d^3 which is compatible with a regular antiprism (D_{3d}) with all equivalent bonds[2] is also compatible with Models A_4 and C_4.

The hybridization d^3sp^2 is compatible with both the Models A_4 and C_4, while the hybridization d^5s is compatible with the Model A_4 and p^2d^4 with the Model C_4. d^3sp^2, d^5s, and p^2d^4 are the configurations of six valence electrons that Kimball[3] stated could not lead to arrangements with all equivalent bonds, without proving it rigorously since not all the possible arrangements of six equivalent bonds were considered in his paper. It is actually true that d^3sp^2, d^5s, and p^2d^4 necessarily lead to arrangements of coordination number six with some non-equivalent bonds since all the arrangements of six equivalent bonds, except the three considered by Kimball (octahedral O_h; trigonal prismatic D_{3h}; trigonal antiprismatic D_{3d}) and the trigonal trapezohedral $D_3[(s, d) + p + (p^2d^2, d^4)]$ require the use of f orbitals. However, it is interesting to note that d^3sp^2, d^5s, and p^2d^4 are compatible with arrangements which are not general "mixed type arrangements" in the sense implied by Kimball,[2] that is, formed of separate sets of equivalent bonds oriented arbitrarily with respect to one another, lacking any total symmetry. The arrangements with which d^3sp^2, d^5s, and p^2d^4 are compatible are particular mixed type arrangements, having a total symmetry, and thus lie within the scope of group theoretical treatment; they can properly be called "*arrangements with non-equivalent bonds.*"

In general, group theory does not permit one to establish unambiguously the configuration to which a given hybridization will lead.‡ Consequently, it is impossible to state on purely group theoretical grounds which of the compatible hybridizations are operative in the Models A_4 and C_4. It is also impossible to eliminate Model C_3 as a covalent model on the ground that the hybridization d^2sp^3 is known[2] to lead to regular octahedra. Nevertheless, it seems reasonable to argue that the hybridizations d^3sp^2 and d^5s (Model A_4) and d^3sp^2, p^2d^4 (Model C_4) which *cannot* lead to arrangements having six equivalent bonds are more probable.

* AEC Postdoctoral Fellow.
[1] S. H. Bauer, J. Chem. Phys. 18, 27 (1950).
† We are grateful to Professor Bauer for pointing this out to us.
‡ This point will be discussed in a forthcoming publication by F. G. Fumi.
[2] G. E. Kimball, J. Chem. Phys. 8, 188 (1940).

TABLE I. Polar coordinates of the bond vectors.

		Bond number	R(A)	θ	ϕ
Model A_4	·First set	(1)	1.87	62° 46'	0°
		(2)	1.87	62° 46'	120°
		(3)	1.87	62° 46'	240°
	Second set	(4)	2.17	129° 59'	300°
		(5)	2.17	129° 59'	60°
		(6)	2.17	129° 59'	180°
Model C_4	First pair	(2)	1.87	90°	50° 36'
		(5)	1.87	90°	309° 24'
	Second pair	(3)	2.22	90°	139° 23'
		(4)	2.22	90°	220° 37'
	Third pair	(1)	2.12	7° 20'	158° 01'
		(6)	2.12	172° 40'	201° 59'

TABLE II. (Model A_4.)

C_{3v}	A_1	A_2	E
s	1	0	0
p	1	0	1
d	1	0	2
σ	2	0	2

TABLE III. (Model C_4.)

C_2	A	B
s	1	0
p	1	2
d	3	2
σ	3	3

TABLE IV. (Model C_3.)

V_h	A_{1g}	A_{1u}	B_{1g}	B_{1u}	B_{2g}	B_{2u}	B_{3g}	B_{3u}
s	1	0	0	0	0	0	0	0
p	0	0	0	1	0	1	0	1
d	2	0	1	0	1	0	1	0
σ	3	0	0	1	0	1	0	1

The Kinetics of Hydrogen Evolution

J. O'M. BOCKRIS, ROGER PARSONS, AND H. ROSENBERG
Imperial College, London, England
February 27, 1950

CERTAIN conclusions reached by Van Rysselberghe in an interesting recent paper[1] are worthy of comment in the light of data, partly unpublished, obtained by the present authors and their co-workers.

(i) One of the most outstanding facts concerning hydrogen overpotential is its marked dependence on the cathode material most clearly expressed by the relation between overpotential and thermionic work function.[2] Van Rysselberghe suggests that the rate of the discharge of hydrogen ions is not dependent upon the immediate product of this reaction, i.e., whether it results in free atomic hydrogen, adsorbed atomic hydrogen or (by reaction with adsorbed hydrogen) adsorbed molecular hydrogen. The consequence of this view appears to be the prediction of a rate of discharge at high overpotentials (>0.1 v) which is independent of the cathode material, in contrast to the experimental evidence.

(ii) Van Rysselberghe also suggests on theoretical grounds the existence of several "Tafel regions." The experimental evidence for the existence of a different value of the coefficient b of the Tafel equations at low c.d.s. is unsatisfactory. The value of this coefficient for a mercury cathode in $N/10$ HCl was found to be constant at 0.119 v at 22°C from 3.10^{-8} to 10^{-3} amp./cm² by Levina and Sarinsky[3] whose results have been confirmed several times in both HCl and H_2SO_4 solutions at c.d.s. greater than 10^{-8} amp./cm².[4] These measurements are thus directly comparable with those of

Bowden and Grew[5] over the range $3.10^{-8}-10^{-6}$ amp./cm² in which range the results of the latter authors are approximately 0.1 v lower than those of Levina and Sarinsky. Consequently it appears more probable that the measurements of Bowden and Grew are vitiated by the extremely small traces of impurity effective at such low c.d.s. than that they represent a true variation in the coefficient b.

The more important correction to the experimental basis of this suggestion concerns the behavior at high c.d.s. ($>10^{-2}$ amp./cm²) where Van Rysselberghe presumably, mainly on the basis of the work of Hickling and Salt,[6] assumes that the coefficient b approaches zero. It has been shown by one of us[7] that this behavior is not due to errors in the commutator method used by Hickling and Salt. Recently we have observed using a mercury cathode that this effect is removed by extensive electrolytic purification of the solution but reappears on the addition of substances such as H_2S to this purified solution. We conclude that the previously reported approach of overpotential to a constant value at high c.d.s. is due to the presence of those impurities which like H_2S are adsorbed at the electrode only at potentials far from the electrocapillary maximum. In agreement with this Azzam[8] has found that for mercury and several other metals of high overpotential the Tafel equation is applicable to a c.d. of at least 150 amp./cm².

(iii) Van Rysselberghe's theory leads to the results that the overpotential is in the general case independent of hydrogen ion concentration, and in special cases dependent on it. Unpublished data obtained in the authors' laboratory[9] together with the scanty published data[3, 10, 11] obtained under satisfactory experimental conditions indicates that the reverse situation is observed. The overpotential is in fact independent of a pH only for high overpotential metals in solutions of pure acids at low and medium concentrations. For low overpotential metals in pure aqueous acids there is a variation of overpotential with pH even when the acid concentration is as low as $N/100$. In the presence of added salts, the overpotential appears to be a function of pH for both high and low overpotential metals.

[1] Van Rysselberghe, J. Chem. Phys. 17, 1226 (1949).
[2] Bockris, Chem. Rev. 43, 525 (1948).
[3] Levina and Sarinsky, Acta Physicochimica 6, 491 (1937); ibid. 7, 485 (1937).
[4] Agar and Llopis, Anal. fis y quin. 43, 1087 (1947); Ruis and Llopis, ibid. 42, 897 (1946); Béthune, J. Am. Chem. Soc. 71, 1556 (1949).
[5] Bowden and Grew, Trans. Faraday Soc. Discussion 1, 86 (1947).
[6] Hickling and Salt, Trans. Faraday Soc. 36, 1226 (1940).
[7] Bockris, Trans. Faraday Soc. 43, 417 (1947).
[8] Azzam, Thesis, London (1949).
[9] Conway, Thesis, London (1949); Potter (unpublished).
[10] Bockris and Parsons, Trans. Faraday Soc. 45, 916 (1949).
[11] Lukovsev, Levina, and Frumkin, Acta Physicochimica 11, 23 (1939); Legin and Levina, ibid. 12, 251 (1940); Jofa, ibid. 10, 391, 617, 903 (1939); Frumkin, Trans. Faraday Soc. Discussion 43, 57 (1947).

Macroscopic Space Charge in Electrolytes during Electrolysis

WILLIAM SCHRIEVER
Physics Department, University of Oklahoma, Norman, Oklahoma
March 13, 1950

THIS is a reply to the Letter to the Editor, under the same title, by MacInnes, Shedlovsky, and Longworth[1] in which they claim to have shown that the work reported by Reed and Schriever[2] is faulty.

If significant changes in concentration near the current electrodes in our work had taken place, then the potential gradients should have increased as the cathode was approached. In five of the seven electrolytes investigated in the cathode half of the column, the gradients decreased; in the other two they first decreased to below average and then increased as the cathode was approached. Seven of the eight solutions exhibited a decrease in gradient as the anode was approached but one, $Al_2(SO_4)_3$, exhibited a large continuous increase through a distance of 5 cm. It is clear

that ordinary concentration changes cannot account for our data. A more detailed explanation appeared in our original paper.[3]

If, as they claim, "erratically changing concentration differences" had developed then our data should have been erratic. Our data were reproducible and not erratic. This is illustrated by Table I in our original paper. During the 15 minutes that the current passed, in our work, an ion moved only one millimeter. If all the ions in a one-mm layer next to the cathode were swept out, and a full extra set were swept into the one-mm layer next to the anode, the densities of these layers would have changed by only 2 parts in 10,000. Actually, of course, the concentration changes would be much less than this and, in addition, these changes built up from zero to less than 2 parts in 10,000 during the 15 minute interval. Does it not seem a little unreasonable to expect appreciable "erratic" convection to be produced by such small density differences in such a short time?

They also claim that our electrodes were at fault. Again the reproducibility of our data indicates that our electrodes must have been quite satisfactory. Even if the indicated potential differences were in error, as far as absolute magnitude is concerned, such an error would have been the same for all points along the column of electrolyte. This constant error would cause no change in either the calculated potential gradients or in the calculated space-charges. If erratic changes had occurred we could not have achieved reproducibility of data. Any gradual changes in our electrodes were taken into account by the application of our "standard curve" procedure.[4]

Their "admittedly relatively crude" experiment would have been convincing if they had used one of the solutions for which data were reported in our paper, instead of KCl, and if they could have obtained our type of results with their tube horizontal, and their type of results with the tube vertical. They do not describe how they took their "three series of measurements"; if they did not measure their potential differences at all points along the column, for a constant time of current-flow, then their data are not comparable to ours.

It so happens that one of my students has been working since last November with a 0.0024 normal solution of KCl between platinum electrodes, and using the tip of a platinum wire as the exploring electrode. The apparatus and methods are essentially the same as those used by Reed. Our data are not yet complete but they do show that the potential gradient is remarkably constant for most of the length of the 40-cm column. Near the cathode end of the column a small negative space charge is indicated. The data in the anode half of the column are yet too few to make certain that we shall be able to detect a space charge effect there.

Therefore, my guess is that McInnes et al. would get essentially the same kind of results for KCl with their tube horizontal as they would with their tube vertical, if all measurements were carried out with care under exactly the same conditions. Their comments are very much appreciated.

[1] MacInnes, Shedlovsky, and Longworth, J. Chem. Phys. 18, 233 (1950).
[2] C. A. Reed and W. Schriever, J. Chem. Phys. 17, 935–944 (1949).
[3] See reference 2, p. 943.
[4] See reference 2, p. 939.

Further Studies of Hydrocarbon Flame Spectra*

GEORGE A. HORNBECK AND ROBERT C. HERMAN
Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland
March 10, 1950

RECENTLY the authors reported some preliminary investigations of the spectra of stationary hydrocarbon flames, particularly those of ethylene and methane burning with oxygen at reduced pressures ($\sim$50 mm of Hg).[1, 2] These investigations were carried out primarily to examine in greater detail the so-called hydrocarbon or ethylene flame bands. These bands, which