TABLE III

RATE OF METHANOLYSIS OF *n*-PROPYL PROPIONATE

Initial mmoles of reactants					
MeOH	*n*-ProPro	MeOH/*n*-ProPro	Mole % HCl	Temp., °C.	Mean rate constant × 10⁴ and σ[a]
909	60.8	15:1	1.28	20.0	$k_1' = 2.18 \pm 0.08$
902	60.2	15:1	1.27	30.0	$k_1' = 4.5 \pm .3$
906	75.2	12:1	0.99	30.0	$k_1' = 3.7 \pm .1$
906	75.2	12:1	2.52	30.0	$k_1' = 9.6 \pm .1$
903	113	8:1	0.82	30.0	$k_1' = 3.1 \pm .2$
903	113	8:1	2.67	30.0	$k_1' = 9.0 \pm .1$
246	245	1:1	4.28	20.0	$k_2' = 0.32 \pm .01$[b]
245	245	1:1	4.19	25.0	$k_2' = .41 \pm .01$[b]
244	244	1:1	4.20	30.0	$k_2' = .60 \pm .01$[b]

[a] Units of pseudo-first-order kinetics, sec.$^{-1}$; second-order kinetics, l. mole^{-1} sec.$^{-1}$. [b] Mean value for the first 40% of reaction only.

methanolysis of *n*-propyl propionate were determined at 20.0, 25.0 and 30.0°. Each sample was analyzed at intervals of approximately 17 min. by gas chromatography with the rapid 4-ft. TCP-Carbowax column. The apparent second-order rate constants were calculated for each point along the decay curve by equation 3. The calculated rate constants were found to decrease by as much as 12% as the reaction approached equilibrium. This decrease in the apparent rate of alcoholysis may be caused by: (1) the change in solution composition during reaction; (2) the reduction in the concentration of the hydrogen chloride catalyst by side reactions (the halogenation of the alcohols as well as the formation of hydronium ion from the water formed in the halogenation reaction) which proceed at a significant rate at the catalyst concentrations used in these experiments. Nevertheless, essentially constant values were obtained for the rate constant during the first 40% of the reaction. The apparent second-order rate constants for the first 40% of the reaction were found to be $(3.2 \pm 0.1) \times 10^{-5}$, $(4.1 \pm 0.1) \times 10^{-5}$, and $(6.0 \pm 0.1) \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ at a catalyst concentration of *ca.* 4.2 mole % hydrogen chloride (see Table III) and temperatures of 20.0, 25.0 and 30.0.°, respectively.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF KANSAS]

The Dissociation Energy of Fluorine and the Magnetic Deflection of its Molecular Beams[1,2]

BY THOMAS A. MILNE AND PAUL W. GILLES

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A molecular beam of fluorine atoms and molecules issuing from a furnace passed through an inhomogeneous magnetic field and impinged on a detector of thin tellurium metal. It was shown that the detector responded to atoms alone. Two kinds of measurements of the atomic beam were made. They were absolute intensity measurements at two different temperatures and relative intensity measurements at several different temperatures. Dissociation energies obtained from the two kinds of measurements are in good agreement, and the average of six determinations by the second method is $D_0 = 41.3 \pm 0.5$ kcal./mole.

Previous work with fluorine has not established an entirely certain value for its dissociation energy. Some estimates and measurements, mostly early ones, led to values of about 60 kcal./mole,[3] or higher while others of a more direct nature strongly favor a value in the range 35 to 40 kcal./mole.[4]

The fractional dissociation of fluorine, α, is a sensitive function of the dissociation energy D_0. Doescher,[4g] Gilles and Margrave,[4h] and Wise[4k] attempted to establish α and hence D_0 by measuring some property of fluorine, such as a pressure or rate of effusion. They assumed that the difference between the measured and expected values was caused by the presence of atoms in the equilibrium gas. Their results indicate a low value but have been criticized[3j] because of possible errors arising from impurities and corrosion of the furnace.

The present work is an attempt to establish α and D_0, but it involves a unique feature designed to

[1] Presented at the Symposium on High Temperature Chemistry before the Division of Physical and Inorganic Chemistry at the 126th meeting of the American Chemical Society, New York, September 13, 1954.

[2] Taken in part from the Ph.D. thesis of Thomas A. Milne, University of Kansas, 1954.

[3] (a) H. V. Wartenberg, G. Sprenger and J. Taylor, *Z. physik. Chem.* **Bodenstein-Festband** 61–68 (1931); (b) E. Angerer and A. Mueller, *Physik. Z.*, **26**, 643 (1925); (c) E. Lederle, *Z. physik. Chem.*, **B17**, 353 (1932); (d) M. S. Desai, *Proc. Roy. Soc.* (*London*), **A136**, 76 (1932); (e) G. Glockler, *Phys. Rev.* **46**, 111 (1934); (f) M. Bodenstein, H. Jockush and S. H. Chong, *Z. anorg. allgem. Chem.*, **231**, 24 (1937); (g) V. M. Dukelskii and N. J. Ionov, *J. Exptl. i Teoret. Fiziik*, **10**, 1248 (1940); (h) E. Wicke, *Angew. Chem.*, **A60**, 65 (1948); *Z. Elektrochem.*, **53**, 212 (1949); (i) A. D. Caunt and R. F. Barrow, *Nature*, **164**, 753 (1949); (j) R. T. Sanderson, *J. Chem. Phys.*, **22**, 345 (1954); (k) A. F. Kapustinskii, *Trudy Moskov. Khim.-Tekhnol. Instit. im. D. I. Mendeleeva*, **22**, 17 (1956).

[4] (a) A. L. Wahrhaftig, *J. Chem. Phys.*, **10**, 248 (1942); (b) H. Schmitz and H. J. Schumacher, *Z. Naturforsch*, **2a**, 350 (1947); (c) M. W. Nathans, *J. Chem. Phys.*, **18**, 1122 (1950); (d) R. Mulliken, Abstracts, 117th Meeting of the American Chemical Society, 31-c (1950); (e) H. J. Schumacher, H. Schmitz and P. H. Brodersen, *Anales Asoc. quimi. argentina*, **38**, 98 (1950); (f) H. J. Schumacher, *ibid.*, **38**, 113 (1950); (g) R. N. Doescher, *J. Chem. Phys.*, **20**, 330 (1952); (h) P. W. Gilles and J. L. Margrave, *ibid.*, **21**, 381 (1953); (i) A. D. Caunt and R. F. Barrow, *Proc. Roy. Soc.* (*London*), **A219**, 120 (1953); *Trans. Faraday Soc.*, **46**, 154 (1950); (j) E. Wicke and H. Friz, *Z. Elektrochem.*, **57**, 9 (1953); (k) H. J. Wise, *J. Phys. Chem.*, **58**, 389 (1954); *J. Chem. Phys.* **20**, 927 (1952); (m) J. L. Margrave, *ibid.*, **22**, 636 (1954); (n) I. N. Bakulina and N. I. Ionov, *Doklady Akad. Nauk S.S.S.R.*, **105**, 680 (1955); (p) K. L. Wray and D. F. Hornig, *J. Chem. Phys.*, **24**, 1271 (1956); (q) A. L. G. Rees, *ibid.*, **26**, 1567 (1957); (r) T. L. Bailey, *ibid.*, **28**, 792 (1958); (s) T. G. Stamper and R. F. Barrow, *Trans. Faraday Soc.*, **54**. 1592 (1958); (t) R. Thorburn, *Proc. Phys. Soc.* (*London*), **73**, 122 (1959); (u) R. P. Iczkowski and J. L. Margrave, *J. Chem. Phys.*, **30**, 403 (1959).

eliminate the possible sources of error inherent in previous experiments. Measurements are made on the atomic species alone, rather than on the combined properties of atoms and molecules.

The experiments consisted of heating fluorine at a pressure of a few tenths mm. Hg in a Monel oven to such a temperature that appreciable dissociation occurred, and allowing the beam of atoms and molecules issuing from an orifice to pass through an inhomogeneous magnetic field. The Stern–Gerlach effect served to deflect the atoms because they are paramagnetic, but the molecules, having no electronic moment, were undeflected. The beam was allowed to strike a thin tellurium film which had been evaporated onto a glass slide. The molecules caused no effect on the film, but the atoms reacted to produce a volatile fluoride, thus effecting a removal of the film. From the transmissivity of the slide after physical development the intensity of the atomic beam was inferred.

Two modifications of the experiment were employed. In the first modification the absolute intensity of the atomic beam was measured. This value was combined with the geometric factors of the system to obtain the pressure of atoms in the furnace and the dissociation equilibrium constant K. The heat of dissociation was obtained from K and free energy functions. In the other method, the relative intensities of the atomic beam were measured at several furnace temperatures. These then were related to values for K from which D_0 was determined by a sigma treatment.

Experimental

The apparatus required for these measurements consisted of a fluorine handling system, a molecular beam and magnet system, and a detecting device.

The fluorine used in this work was supplied by the Pennsylvania Salt Manufacturing Company and was guaranteed to have a purity of 96% or greater. The fluorine was passed through a NaF trap to absorb HF and allowed to leak slowly into a reservoir which was connected directly to the end of the furnace as shown in Fig. 1.

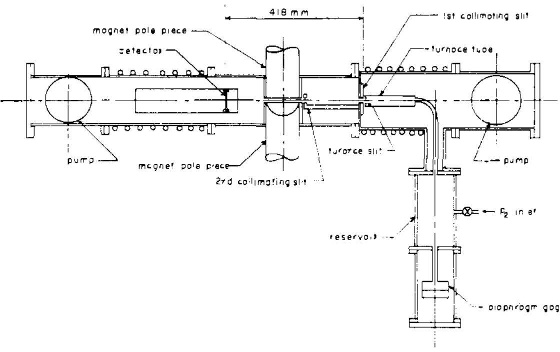

Fig. 1.—Stern–Gerlach apparatus showing fluorine reservoir and pressure gauge at lower right, furnace at upper right, magnet and deflection tube in center and detector chamber at left.

Apparatus.—The fluorine pressure in the reservoir was measured by means of a diaphragm gauge similar to that described in Dibeler and Cordero and by Greenough and Williams.[5] The position of a 0.001″ Al diaphragm, which separated the fluorine in the reservoir from a high vacuum surrounding the gauge, was fixed by the fluorine pressure. As the position of the diaphragm changed, the mutual inductance of a nearby air core transformer was changed. A variable mutual inductance micromanometer circuit was used to indicate the position of the diaphragm and, hence, the pressure of fluorine.[6] The pressure in the system was sufficiently high so that the pressure indicated by the micromanometer was that existing in the furnace. The gauge was calibrated against a McLeod Gauge with an inert gas.

The molecular beam apparatus, shown schematically in Fig. 1, was composed of segments of 7″ o.d. brass tubing having $^1/_8$″ walls. The segments were flanged together with rubber "O" ring gaskets. The furnace chamber with the attached reservoir is shown on the right, the collimating chamber in the center and the detector chamber on the left. Oil diffusion pumps, connected to the system through CO_2-refrigerated traps, were used at each end of the apparatus. The beam was conducted through the inhomogeneous magnetic field in an elliptical brass tube, 0.3 × 0.9 cm., connecting the collimating and detector chambers. The beam passed through a furnace orifice, a first collimating slit in the wall between the furnace and collimating chambers, and a second collimating slit near the entrance to the elliptical tube.

The magnet pole pieces were 4″ in diameter and were situated outside the vacuum. Their shape was that suggested by Stern and Gerlach.[7] The angle of the point was 70° and the slot was 0.3 cm. wide and 3 cm. deep. The point and slot face were 0.29 cm. apart. The position of the beam could not be determined during an experiment. When the apparatus was dismantled it was estimated that the beam had been 0.45 cm. from the point, that is, 0.16 cm. into the slot. Field gradients up to about 4×10^4 gauss/cm. were obtained by passing up to 10 amp. through about 1800 turns.

The furnace was constructed from one-inch o.d. Monel tubing 8″ long. The ends were also of Monel. It was held by two collar clamps so that it could be rotated about its axis. Each collar rested on legs that were adjustable in height. These legs were soldered to a movable platform, adjustable from outside the vacuum by a micrometer-driven bellows arrangement.

Resistive heating of the furnace was accomplished by two separate nichrome windings. Two chromel–alumel thermocouples were used. One was placed in a hole drilled radially to a depth of $^3/_8$″ into the furnace end plate holding the orifice slit. The other was placed against the outside of the furnace about an inch away from the slit. The thermocouples were calibrated at the melting point of aluminum.

All the slits were constructed of Monel. Each was rectangular with edges ground to a knife edge. The furnace slit was 0.002″ wide and $^1/_4$″ high. The first collimating slit was about 0.015″ wide, the second slit about 0.005″ wide.

Beam Detection.—Detection of the beam was accomplished by a method used by Simons and Glassner.[8] They found that a thin film of tellurium metal was responsive to atoms of Cl and Br but not to their molecules. The films were effective because a volatile tellurium halide was formed.

For the present work, thin, invisible films of tellurium were prepared on microscope slides by high vacuum evaporation. Preliminary experiments indicated that such a detector distinguished between the fluorine atoms and molecules. After exposure to the beam, the detector was immersed for 10 to 20 minutes in a developing solution suggested by Odell[9] which contained Na_2SO_3, $AgNO_3$ and $Na_2S_2O_3$. During this interval silver was precipitated preferentially on the remaining tellurium. The plate then was washed with distilled water. After this development of the image, it was visible. The developed images were scanned with a recording Leeds and Northrup densitometer.

The detector holder was mounted on a movable platform similar to that holding the furnace. The plate could there-

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[5] V. H. Dibeler and F. Cordero, *J. Research Natl. Bur. Standards*, **46**, 1 (1951); M. L. Greenough and W. E. Williams, *ibid.*, **46**, 5 (1951).

[6] We are greatly indebted to Drs. Donald G. Wilson and William P. Smith, and Mr. David Seamans of the University of Kansas Department of Electrical Engineering who designed and constructed the micromanometer circuit. The details of its operation appear in an appendix to the thesis of Thomas A. Milne.

[7] W. Gerlach and O. Stern, *Ann. Physik*, **74**, 673 (1924).

[8] J. H. Simons and J. Glassner, *J. Chem. Phys.*, **8**, 547 (1940).

[9] A. F. Odell, *British J. Photog.*, **84**, 310 (1937).

by be moved without a vacuum break allowing a number of images to be formed on a single plate.

The response of this detector to atoms alone was shown by two different techniques. One employed the molecular beam apparatus with the magnet off; the other with the magnet on. With the magnet off, no beam trace appeared when the furnace was cold, yet when the furnace was sufficiently hot to produce an appreciable number of atoms, a trace appeared. When the magnet was on, the beam image was a doublet with no observable intensity at the undeflected position.

Identification of the Beam.—Proof that the component of the beam responsible for the image consisted of F atoms was provided by examination of both the position and the shape of the image.

In F the ground state, $2p^5\ ^2P^0_{3/2}$, lies 404 cm.$^{-1}$ below $2p^5\ ^2P^0_{1/2}$. The Stern-Gerlach pattern to be expected in an experiment employing a velocity selector consists of three components lying at relative displacements of 1/3, 2/3 and 6/3 on each side of the undeflected position. In the present experiments no such selector could be used, and the distribution of velocities in the beam caused broadening.

Stern[10] considered this effect of the distribution of molecular velocities and obtained equations that relate the intensity of a beam to the displacement. His equations were used to calculate the relative intensities of each component of the beam at different distances from the undeflected position. Figure 2 shows the results of the calculation. Data used for these calculations included: (1) width of undeflected beam = 0.2 mm.; (2) temperature = 893°K.; (3) field gradient = 3.76×10^4 gauss/cm.; (4) length of path in the field = 10 cm.; and (5) distance between end of field and detector = 12.8 cm. Since the magnetic field removes the degeneracy of the states, the statistical weights for the component curves were the same.

One important feature shown in Fig. 2 is that resolution of the hot beam into its components is impossible without a velocity selector. The combined intensity of the components appears as a smooth curve with a single maximum.

It was not feasible to measure the field gradient in the apparatus. Instead, calibration runs were performed with 99.99% Ag in the same apparatus. A cold rolled steel furnace replaced the Monel one, and was heated by a 0.010" Mo winding. The furnace was insulated by 0.002" Mo radiation shields, and operated at 1380°K. The Ag was condensed on a glass plate, the image being developed and read by the same techniques used for the F detector. The field gradient was calculated from the position of the maximum intensity of the Ag beam.

Table I contains the data relating to the first proof that F is the component of the beam responsible for Te removal.

TABLE I

FIRST PROOF THAT BEAM CONSISTED OF F

T (°K.)	$\partial H/\partial z \times 10^4$ (gauss/cm.)	$S\alpha$ (calcd.) (mm.)	Sm (calcd.) (mm.)	Sm (obsd.) (mm.)
893 ± 3	3.8 ± 0.2	0.84 ± 0.10	0.49 ± 0.08	0.54 ± 0.02
		1.7 ± .2		
		5.0 ± .6		
954 ± 10	3.0 ± .1	0.62 ± .06	.34 ± .05	.44 ± .01
		1.2 ± .1		
		3.7 ± .4		
937 ± 3	2.0 ± .1	0.42 ± .05	.32 ± .05	.31 ± .03
		0.85 ± .10		
		2.5 ± .3		

Values in the second column were obtained from the Ag experiments. Values in the third column $S\alpha$ represent the deflections suffered by molecules with the most probable velocity. Each of the three values at one temperature is for one of the three P states of the fluorine atom. They were obtained from T, $\partial H/\partial z$, geometry and magnetic moments. Values in the fourth column represent the calculated position of the maximum intensity in the composite beam. They were obtained from those in the third column in the same way that Fig. 2 was obtained. Values in the last column were measured from the densitometer record. The agreement between the measured and calculated values is satisfactory.

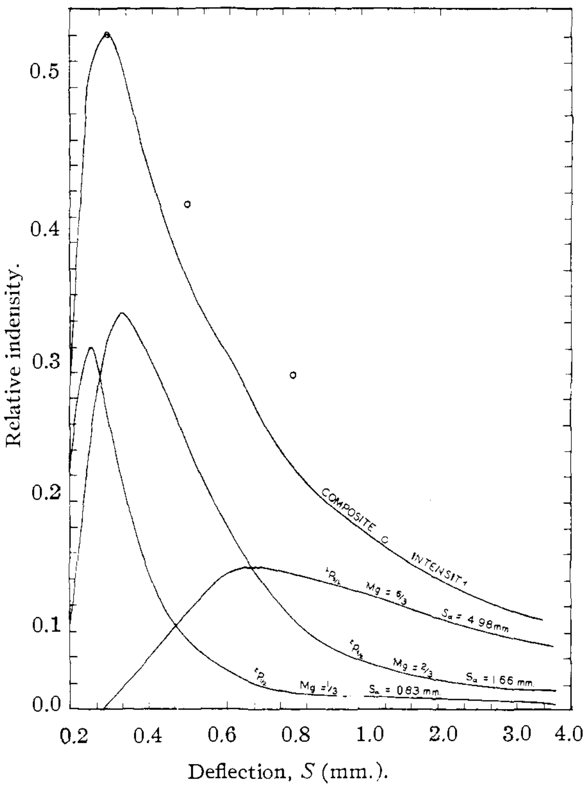

Fig. 2.—Relative intensity of deflected atomic fluorine beam at 893°K. *versus* displacement from undeflected position in a Stern-Gerlach experiment. The four curves are calculated ones. The lowest three are for the different magnetic states of the atoms as labeled. The fourth, the sum of the other three, predicts the pattern and indicates that the different states cannot be resolved. The four circles are experimental points whose agreement with the uppermost curve indicates that the beam consisted of fluorine atoms. The quantity $S\alpha$ is the deflection experienced by atoms with most probable velocity in the furnace.

The nature of the second proof that the image is caused by F is indicated in Fig. 2. The plots show that the shape of the composite beam is broader than any of its components. Measurements were made of the deflected fluorine beam intensity at various deflections, and the results were compared with the calculated values obtained from Fig. 2. After normalization of the results so that the calculated and observed deflections corresponding to maximum composite intensity coincided, the measured deflections at 3/4, 1/2 and 1/4 the maximum intensity are plotted also on Fig. 2. It is seen that the measured shape is also in agreement with prediction.

Procedure.—Experiments were performed in the following general manner. The entire system was evacuated to a pressure of about 2×10^{-6} mm. and the Monel tube furnace was heated to the temperature to be used in the run. A shutter protected the detector plate from any material effusing from the furnace. Fluorine was admitted to the furnace and allowed to flow for about 10 to 20 minutes before the first run. The detector slide was held on a movable platform which was set at a known position by a micrometer adjustment. With the furnace at the desired temperature and the fluorine at the desired pressure the shutter was opened, exposing the plate to the narrow beam of fluorine coming through the slits. The slits previously were aligned by a simple optical procedure.

After a definite period of time, the shutter was closed. The temperature of the furnace was adjusted to a new value, and the detector platform was moved to expose a fresh portion of the tellurium film to the beam. Four to eight such exposures could be made on a single plate with or without

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(10) O. Stern, *Z. Physik*, **41**, 563 (1927).

TABLE II

THIRD LAW DETERMINATION OF DISSOCIATION ENERGY OF F_2

	Run No. 1			Run No. 2		
Temp., °K.	893 ± 5			830 ± 5		
Total pressure, μ	344 ± 40			225 ± 40		
Time for remov. of Te, sec.	2100 ± 300			4080 ± 300		
Orifice area, cm².	$(2.1 \pm 0.2) \times 10^{-3}$			$(2.4 \pm 0.2) \times 10^{-3}$		
Length of beam, orifice to detector, mm.	418 ± 5			418 ± 5		
Mass Te per 3.14 mm². of detector, g.	$(23.9 \pm 10) \times 10^{-9}$			$(24.5 \pm 10) \times 10^{-9}$		
Assumed reaction product	TeF_6	TeF_4	TeF_2	TeF_6	TeF_4	TeF_2
Partial pressure of F, μ	98.4	65.6	32.8	44.6	29.8	14.9
α	0.167	0.106	0.0502	0.110	0.0714	0.0342
Log K	−4.285	−4.688	−5.342	−4.838	−5.216	−5.858
ΔH_0^0 kcal./mole (±2.5)	42.0	43.6	46.3	41.0	42.4	44.8

the deflecting field so that a number of runs could be performed consecutively.

When the exposures were completed the plate was removed, developed and recorded on the microphotometer. The optical densities were converted to relative thicknesses of absorbing material and hence gave a measure of the amount of tellurium removed by the impinging fluorine.

Results

Since it had been shown previously that the detector responded to atoms alone, the experiments were performed without a magnetic field. This procedure simplified intensity measurements. Measurements of the intensity of the atomic beam of fluorine may be utilized in two ways to obtain information about $D_0(F_2)$.

Absolute Intensity Method.—First, if the absolute intensity of the beam of fluorine atoms can be measured, one may calculate the partial pressure of fluorine inside the furnace by means of the Knudsen equation for molecular effusion

$$P_F = (m_F/CKkat)(T/M)^{1/2} \qquad (1)$$

Here m_F is the number of grams of gas effusing in time t from a furnace orifice of area a and hitting a collector which intercepts a fraction k of the total fluorine atoms which effuse. The quantities T and M are the temperature and atomic weight of the effusing gas; K is a factor which corrects for the fact that the orifice has a finite thickness; and C is a numerical constant whose value depends on the units of the other quantities.

If the rate of effusion is sufficiently slow, then P_F is the equilibrium partial pressure of F inside the furnace. A measurement of P_T, the total pressure in the furnace, thus permits a calculation of P_{F_2} and hence of the equilibrium constant for the reaction

$$F_2(g) = 2F(g)$$

The equilibrium constant is related to the dissociation energy of fluorine by the relation

$$\Delta H_0^0 = -T\Delta\left[\frac{F^0 - H_0^0}{T}\right] - RT \ln K \qquad (2)$$

The quantity in brackets, the free energy function change, has been calculated and tabulated for atomic and molecular fluorine by Haar and Beckett[11] whose values have been used here.

Experimentally, the various factors on the right-hand side of equation 1 were determined as follows. The temperature of the gas, which is assumed to be in temperature equilibrium with the furnace walls, was measured by means of calibrated chromel-alumel thermocouples situated as described above. The area of the orifice and the factor k are calculated from the geometry of the system. The correction factor K has been discussed by Clausing[12] and in the present case is essentially unity. The quantity of atomic fluorine hitting the detector in a time t was determined by depositing a known mass of tellurium metal on a microscope plate and then making a series of exposures of varying lengths. From graphs of the intensity of the tracings *versus* the time of exposure, all at the same total pressure and temperature, one can calculate the time required for essentially complete removal of the tellurium film. To relate the mass of tellurium lost to the amount of atomic fluorine impinging, an assumption must be made as to the product of the reaction between Te and F. The compounds TeF_6, TeF_4 and TeF_2 are all volatile at room temperature and 10^{-5} mm. pressure, so that different partial pressures of atomic fluorine and hence different calculated ΔH_0^0 will be obtained depending on the assumed reaction products.

Two runs at different temperatures were made according to this first method. The data and results of these runs are presented in Table II. The probable errors listed are calculated from the uncertainties in the various factors according to the law of the propagation of errors. The principal assumption made is that all of the fluorine atoms which strike the surface of the Te react, and that none of the molecules do. It would be expected that if this were not true then the reaction probability would increase with increasing temperature. This would lead to smaller calculated values of ΔH_0^0 the higher the experimental temperature. No such effect is apparent in the two experiments recorded in Table II. In fact, the apparent variation is in the opposite direction although the two values of ΔH_0^0 are consistent for a given assumed reaction product of Te plus F, within the calculated uncertainties.

These results indicate a low value for the dissociation energy of fluorine and can in no way be reconciled with ΔH_0^0 of 60 kcal./mole.

Relative Intensity Method.—The second method of utilizing the atomic beam intensity data is to measure the change in beam intensity as a function of temperature. In order to make accurate com-

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[11] L. Haar and C. W. Beckett, NBS Report 1435, 1952.

[12] P. Clausing, *Ann. Physik*, **12**, 961 (1932).

parisons of intensities at different temperatures, the times of the runs were empirically adjusted so that a whole series of exposures at different temperatures produced tracings of very nearly uniform intensity, all on a single detector plate. Thus the quantities measured experimentally were the times of the the runs t, the temperatures T, the total pressures P_T, and the relative intensities of the tracings X. The quantity X is simply the height of the developed tracing as measured by the microphotometer. It was shown that these heights gave a true indication of the relative intensity of the fluorine atomic beam by performing several runs of differing lengths, but at the same temperature, and comparing the resulting X values with the times of exposure.

These four measured quantities enable one to calculate ΔH_0^0 in the following way. At small degrees of dissociation the total pressure P_T is approximately the pressure of F_2 so that the dissociation equilibrium constant may be written as

$$\ln K = \ln (P_F)^2/P_{F_2} = \ln (P_F)^2/P_T \qquad (3)$$

From equation 1 the partial pressure of fluorine atoms is

$$P_F = k' X(T/M)^{1/2}/C\text{K}\, kat \qquad (4)$$

in which k' is a constant relating the relative intensity measurement X to the mass of F which strikes the detector.

The substitution of equation 4 into 3 and thence equation 3 into 2, followed by rearrangement and separation of terms, produces the equation

$$\begin{aligned}\Sigma' &= \ln X^2T/t^2\, P_T + \Delta[(F^0 - H_0^0)/RT] \\ &= -\Delta H_0^0/RT - \ln (k'/C\text{K}\, ka)^2/M \qquad (5)\end{aligned}$$

in which Σ' is defined by the first two terms.

If the quantities k', C, K, k and a are independent of temperature over the experimental range, then a plot of Σ' *versus* $1/T$ gives a straight line whose slope is $-\Delta H_0^0/R$.

The assumption that $P_{F_2} = P_T$ may be checked by using the derived value of ΔH_0^0 to calculate the degree of dissociation at the various experimental temperatures. This degree of dissociation permits a calculation of P_{F_2} which then may be substituted in equation 5 in place of P_T. Each new ΔH_0^0 obtained may be used to correct the value of P_{F_2} until the assumed and calculated values of ΔH_0^0 agree within any prescribed limits.

Six series of exposures were made according to the second scheme described above. The range of pressures, times, temperatures and X's for these six runs are presented in Table III, together with the calculated and assumed values of ΔH_0^0 and the range of calculated α's, the degrees of dissociation of fluorine. The ΔH_0^0 values were obtained from a least squares analysis of plots of Σ' *versus* $1/T$. Probable errors were calculated for each least squares fit by standard statistical methods. The final $\Delta H_0^0 = 41.28 \pm 0.48$ kcal./mole is obtained from an average of the six values, weighted in the standard fashion according to the square of the reciprocal of their probable errors. The probable error of this weighted average is 0.476 by the method of external consistency, and 0.356 from internal consistency. The larger is used.

Aside from errors in measuring the quantities X, t, T and P_T, which should not greatly affect the ΔH_0^0 values, the other source of possible error lies in the assumption that the constants k', k, K, a and C are not functions of temperature. It can be shown that no significant temperature dependence of k, K, a or C exists in these experiments. The constant k', however, which relates the response of the detector to the intensity of the impinging beam, might well be temperature dependent. Such a dependence, if of an appreciable magnitude, should make itself apparent as a deviation from a straight line in the plot of Σ' *versus* $1/T$. One exception is if k' varies as $1/T$. In this case the slope would be changed but the plot of Σ *versus* $1/T$ would still be a straight line. In either event, any large temperature dependence would produce noticeably different values for ΔH_0^0 from those obtained from the two experiments shown in Table II. The plots of the six runs do not show any deviation from straight line behavior, and the results of the two runs shown in Table II preclude any large temperature dependent error.

TABLE III

SECOND LAW DETERMINATION OF DISSOCIATION ENERGY OF FLUORINE

$P(\mu)$	T(°K.)	α	ΔH_0^0 (kcal./mole) Input	Calcd.	Chosen	Prob. error
296–311	651–849	0.0015–0.081	42.45	42.61	42.53	±0.64
324–355	689–895	.015–0.40	38.65	38.77	38.71	±0.86
285–322	967–754	.63–0.01	39.73	39.62	39.68	±3.61
330–366	794–1009	.015–0.35	44.57	44.64	44.60	±1.33
329–344	1024–739	.74–0.02	40.90	40.81	40.85	±0.59
251–268	989–749	.61–0.022	41.40	41.23	41.32	±1.32
			Weighted av.		41.3	±0.5

A comparison of the results shown in Tables II and III leads the authors to choose a value of ΔH_0^0 of 41.3 ± 0.5 kcal./mole or 1.79 ± 0.02 e.v., the value obtained from the second type of experiment. The most consistency between the results of the two methods is obtained if it is assumed that all of the fluorine atoms hitting the detector react to produce TeF_6.

Discussion

The method employed here seems particularly well adapted to minimizing the effects of corrosion of the furnace by hot fluorine. It was observed that at even the highest temperatures the corrosion of the Monel furnace tube was not extensive. A compact, coherent white layer adhered to the walls of the Monel furnace and prevented further corrosion. In contrast, in an experiment with chlorine gas, also held in a Monel tube, the corrosion reaction product volatilized, permitting very extensive attack of the Monel tube. The furnace tube used in the runs from which the data of Tables II and III were taken had been exposed to fluorine at high temperature for many hours previously and should have been quite well coated. No clogging or widening of the furnace slit was observed in any of these runs.

Recently, the vapor pressure of NiF_2 has been measured by two methods[13] and the results lend support to the assumption that gaseous corrosion

(13) M. Farber, R. T. Meyer and J. L. Margrave, *J. Phys. Chem.*, **62**, 883 (1958).

products will have an insignificant effect in this work and in the work of Doescher and Wise.[4g,k]

The recent direct determinations of the electron affinity of fluorine[4n,r] when combined with other thermochemical data yield a $D_0(F_2)$ of 37 ± 2 kcal./mole. A third law interpretation[4s] of Doescher's and Wise's results yields a value of 36.7 ± 0.1 kcal./mole, and the value deduced from the continuous absorption spectra[4q] of F_2 plus a knowledge of certain ground state parameters is 37.8 ± 0.85 kcal./mole. In addition, Iczkowski and Margrave[4u] have reported a direct spectroscopic determination of $D_0(F_2)$, involving a vibrational analysis of transitions from the ground state to a stable upper state, which gives $D_0(F_2) = 37.5 \pm 2$, depending on the upper state dissociation products.

In view of this evidence there may be unknown systematic errors that tend to make the present results a few kilocalories too high. Nevertheless, these results leave no doubt that the dissociation energy of fluorine is low, in fact between that of Br_2 and I_2. The electron affinity of F is nearly that of Br.

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Some Studies in Molecular Orbital Theory. I

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A simple interaction theory based on the single configuration LCAO MO method is applied to the problem of the ionization potentials and the near ultraviolet absorption spectra of mono-substituted benzenes with special reference to the evaluation of the empirical parameters. Both conjugative and inductive effects are included. To estimate parameters, only interactions between the highest occupied and the lowest vacant molecular orbitals of benzene and the occupied π-orbital of the substituent are considered, but the theory predicts the perturbed orbital energies with reasonable accuracy. General principles for parameter determination are given and three separate methods are applied to halogen monosubstituted benzenes. Parameters obtained in the three ways are found to reproduce the observed spectroscopic data quite satisfactorily. Extensive further applications of the theory are shown to be possible.

1. Introduction

There are two main ways in which a substituent containing π-electrons may affect the electronic structure of an aromatic hydrocarbon. One of these is the conjugative effect or charge transfer effect, in which the π-electrons of the substituent enter into conjugation with the aromatic system. The other is involved when the substituent to some extent perturbs the potential acting on the π-electrons of the hydrocarbon; it is known as the inductive effect. In substituted benzenes it would be particularly desirable to have available a systematic treatment of the electronic structure which would allow one to estimate to what extent the two effects interact or coöperate.

Therefore the electronic structures of substituted benzenes have been treated by several authors by the semi-empirical LCAO MO approximation, with special reference to the question of how to estimate the integral values entering the molecular computations as parameters. Wheland[2a] has first introduced the method of calculation and estimated parameters using the directing properties in chemical reactivity, and Robertson and Matsen[2b] have evaluated parameters from the observed spectral shifts of the near ultraviolet absorption spectra of the substituted benzenes relative to benzene (and the corresponding intensities). Recently, Knipe[3] has employed a similar method in discussing the dipole moments of some halogen-substituted benzenes and compared his results with the other authors.

The most important problem is the difficulty of determining the energy parameters, which involve in most cases atomic integrals or coulomb integrals for heteroatoms, resonance integrals for heteropolar bonds, and coulomb integral contribution due to the inductive effect. The parameters determined up to date[4] often depend upon too arbitrary assumptions for them to be usable in computations including nearest neighbor overlap integrals. In this paper an interaction theory based on the molecular orbital method is presented to estimate parameters and three methods of parameter determination are given which involve the use of experimental data on ionization potentials and near ultraviolet absorption spectra. Several applications to halogen-substituted benzenes are made, and the results of applying the three methods of parameter evaluation are compared.

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(2) (a) G. W. Wheland, THIS JOURNAL, **64**, 900 (1942); (b) F. A. Matsen, *ibid.*, **72**, 5243 (1950); W. W. Robertson and F. A. Matsen, *ibid.*, **72**, 5252 (1950).

(3) R. H. Knipe, *J. Chem. Phys.*, **23**, 2089 (1955).

(4) Other works not cited above are: C. Sandorfy, *Bull. soc. chim France*, **16**, 615 (1949); H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953).