

in the determination of 0.01 *M* lead solutions, and 0.01 *M* in alkali nitrate in the titration of 0.001 *M* lead solutions, to suppress the migration current of lead. Other conditions were the same as in the titration of oxalate with lead. The titration of 0.01 *M* lead was found accurate to within 0.2% and that of 0.001 *M* lead to within 0.5%.

**Ferrocyanide with Lead.**—Solutions which were about 0.005 *M* in potassium ferrocyanide were titrated under the conditions described above with 0.1 *M* lead nitrate solutions. The end-point corresponded to a composition of the precipitate of  $Pb_2Fe(CN)_6$ .

**Lead with Potassium Iodate.**—Since iodate yields a reduction wave with a diffusion current which is about three times as great as that of an equimolecular lead solution, the amperometric titration of lead with iodate has been investigated in detail. The potentials at which iodate yields reduction waves depend upon the *pH* of the medium when the latter is smaller than 7. Dependent upon the *pH* it was possible to titrate lead with iodate at potentials at which lead yielded a diffusion current, and at which iodate either was not reduced or also yielded a diffusion current. Solutions which were 0.01 *M* in lead nitrate and 0.1 *M* in potassium nitrate were titrated with 0.2 *M* solutions of potassium iodate in neutral media and in the presence of acetic acid at various potentials. Under all conditions the end-point

(point of intersection of precipitation and reagent lines) was found about 3% before the equivalence point. Upon further investigation it appeared that the deviations were due to the tenacious tendency of lead iodate to stay in supersaturated solution. Addition of solid lead iodate was not of sufficient aid to make the titration practicable. Titrations have been carried out in a medium of 30% ethanol to decrease the solubility of lead iodate and to overcome supersaturation. However, again the results were found to be low, as a result of coprecipitation of lead nitrate with lead iodate. A detailed account of all the experiments is given in the thesis of the junior author,<sup>1</sup> and is not reported here, especially since we found that the simple iodometric back titration of an excess of standard iodate solution added to the lead solution yielded accurate results.

#### Summary

1. Sulfate has been titrated amperometrically with lead nitrate in concentrations between 0.01 and 0.001 *M* in the presence of various indifferent electrolytes. Conditions have been described under which these titrations yield accurate results.

2. Results of the amperometric titrations of lead with sulfate, oxalate, and iodate, and titrations of oxalate and ferrocyanide with lead have been reported.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## Adsorption of Vapors at Solid Surfaces and the Change of Surface Electrical Potential<sup>1</sup>

BY ARTHUR A. FROST AND VICTOR R. HURKA

It is well known that adsorbed gases affect the thermionic work functions and photoelectric thresholds of metals. Therefore it would be expected that Volta potentials or surface potentials in general would also depend on the extent of adsorption. Measurement of changes in surface potential would be an indirect measurement of adsorption. Dean, Gatty and Rideal<sup>2</sup> have recently discussed various sources of potential at phase boundaries and have used the term *adsorption potential* to denote a potential difference arising from the formation of an adsorbed layer.

It was with the purpose of studying such adsorption potentials at solid surfaces that the present work was begun. This paper is of the nature of a survey and deals with methods of measurement and a discussion of typical results.

Two experimental methods have been employed. The first method was direct but only semi-quantitative. The second method, involving a vibrating electrode, proved to be more satisfactory. A third possible method<sup>3</sup> depending upon ionization of vapor was not tried because it was felt probable that ionization of the vapor

(1) A portion of this paper was presented at the Cincinnati meeting of the American Chemical Society, April, 1940.

(2) Dean, Gatty and Rideal, *Trans. Faraday Soc.*, **36**, 181 (1940).

(3) Such a method has been used for observing potential changes due to monomolecular films on water. See for example, Harkins and Fisher, *J. Chem. Phys.*, **1**, 852 (1933).

would cause formation of foreign molecules which would be adsorbed and so vitiate the results.

### Direct Method

**Apparatus.**—This method made use of a cell of two electrodes connected directly to an electrometer. Detail of the cell is shown in Fig. 1. The electrodes were concentric cylinders of brass, each  $1\frac{1}{2}$ " (3.7 cm.) long. The outer cylinder was gold-plated and  $\frac{3}{8}$ " (9 mm.) outside diameter. The inner cylinder of  $\frac{1}{4}$ " (6.2 mm.) diameter was easily removable and could be coated with thin films of various substances such as paraffin or collodion. The clearance between the two cylinders was approximately  $\frac{1}{32}$ " (0.8 mm.). Air, dried and passed through activated charcoal, was drawn between the two electrodes. Vapor-saturated air was then introduced and the change in electrometer reading observed.

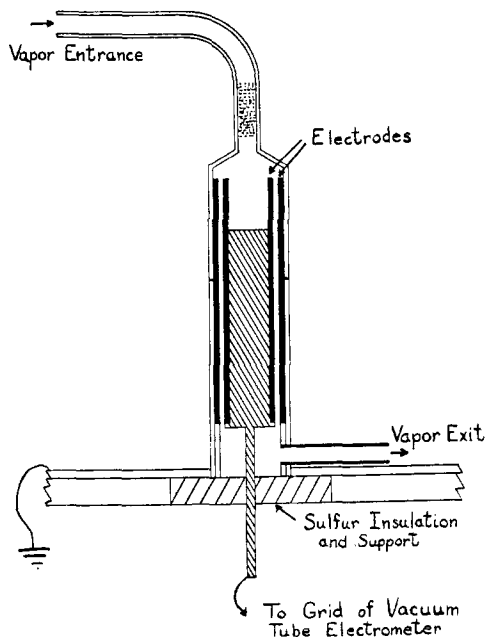


Fig. 1.—Cell for use in direct method.

The electrometer consisted of a type 32 radio tube operated at low voltage and having the grid current balanced by a current through a high resistance according to a circuit of Nottingham.<sup>4</sup> A type 30 tube was used as an amplifier, the output being read on a milliammeter. The instrument was calibrated for direct reading in millivolts. Because of leakage currents of the order of  $10^{-13}$  ampere, the reading had to be taken within a few seconds after introducing or removing the vapor.

(4) Nottingham, *J. Franklin Inst.*, **209**, 287 (1930).

**Results.**—Typical results with this apparatus are shown in Table I. The values given are in each case maximum reversible changes in potential, *i. e.*, the change in potential as shown in the table is reversed when the vapor is removed from the cell. Occasionally the reversible change was superimposed on a more permanent change, which, however, could not be measured with this apparatus. A positive sign indicates that the inner, coated, electrode increases in potential with respect to the outer gold-plated electrode. The actual potential difference before admitting vapor could be adjusted at will and was found to have no effect on the observed changes in potential. Values quoted are reproducible only to within 10–20 mv. with this apparatus.

TABLE I  
POTENTIAL CHANGES IN MILLIVOLTS

Vapor	Surface of inner electrode Paraffin	Collodion
H <sub>2</sub> O	0	- 75
NH <sub>3</sub>	+150	-100
C <sub>2</sub> H <sub>5</sub> OH	+ 50	-400
(CH <sub>3</sub> ) <sub>2</sub> CO	+100	-400
CHCl <sub>3</sub>	-120	-250
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	+100	-300
Camphor	+ 50	-100
CCl <sub>4</sub>	0	-100
C <sub>6</sub> H <sub>6</sub>	0	-120

The potential changes are probably principally due to oriented dipoles in the surface. It is interesting to note that symmetrical molecules such as carbon tetrachloride and benzene can give an effect despite their lack of dipole moments in the molecules as a whole. In such cases it would be supposed that there are induced dipoles formed when adsorption takes place.

### The Vibrating Plate Method

**Apparatus.**—This set-up was designed for more quantitative measurements and control of the pressure of the vapor being adsorbed. The apparatus was modeled after that used by Zisman,<sup>5</sup> Porter,<sup>6</sup> Fink and Dehmel<sup>7</sup> and others. It consists essentially of: (1) A parallel-plate condenser, one plate of which can be rapidly oscillated so that an alternating current is produced if the potentials near the surfaces of the two plates are not the same. (2) A source of audio-frequency alternating current together with a constant magnetic field to produce the oscillation of the condenser plate. (3) An amplifier for detecting the alternating current from the condenser. (4) A potentiometer system of such a nature that a potential equal and opposite to the surface potential difference at the plates may be

(5) Zisman, *Rev. Sci. Instruments*, **3**, 7 (1932).

(6) Porter, *THIS JOURNAL*, **59**, 1883 (1937).

(7) Fink and Dehmel, *Trans. Electrochem. Soc.*, **70**, 281 (1936).

imposed upon the condenser so as to give a null effect in the amplifier. (5) A means of evacuating the condenser system and for introducing therein the vapor under consideration at a known pressure.

A mathematical analysis of our electrical circuit may be found in a paper by Porter.<sup>8</sup> Figure 2 shows the important features of the unit containing the parallel plate condenser and accessories. The unit is mounted on a brass plate A fitted with a bell jar J. A loud speaker magnet and coil assembly M cause vibration of the upper condenser plate  $P_1$  which is connected with the coil by a Pyrex rod. The lower condenser plate  $P_2$  may be adjusted in position with the aid of the screw S acting through metal bellows. The two plates may be adjusted parallel to each other by means of nuts on the three supports, N, of the magnet and coil assembly. L is the lead from the highly insulated vibrating plate to the amplifier. Part of the electrical and magnetic shielding is shown at T. The bell jar may be evacuated through V and filled with vapor from a supply bulb B. A mercury manometer was used to measure the pressure of the vapor.

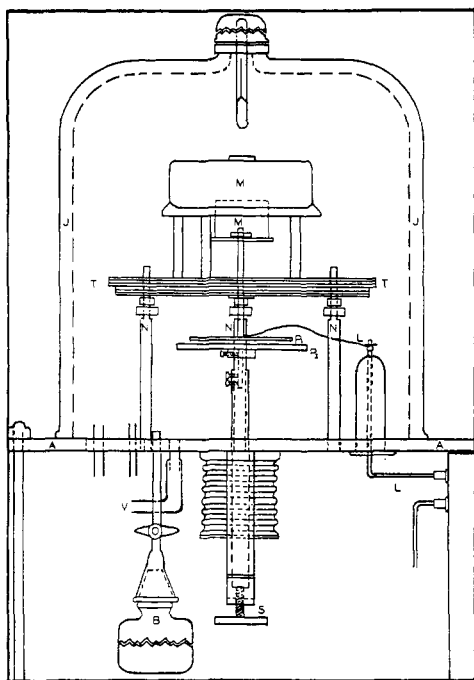


Fig. 2.—Vibrating plate and accessories.

The source of oscillating current for the loud speaker coil consisted of a well-shielded and sound insulated buzzer suitably altered so as to interrupt a direct current. The frequency was about 200 cycles per second.

The amplifier consisted of three stages with capacity coupling. The resistance in series within the potentiometer and vibrating condenser and across which the amplifier was placed was 20 megohms.

The two parallel plates  $P_1$  and  $P_2$  were of gold-plated brass, respectively 5 and 6 cm. in diameter. The amplitude of vibration of  $P_1$  amounted to about 0.5 mm. With the lower plate adjusted as closely as convenient without touching the upper plate and with the individual parts of

the apparatus well shielded a potential difference of 1 millivolt could be detected.

In making a determination of adsorption potential the lower plate, which was easily removed, was coated with a thin film to form the desired surface. The upper plate was carefully kept free of dirt and foreign matter by washing with ether. Neglecting this careful cleansing made detection of a null extremely difficult since a heterogeneous surface was then presented.<sup>8</sup> The technique of measurement consisted in varying the potentiometer setting until a minimum response was heard in the phones connected to the amplifier. With adequate shielding a null effect was nearly obtained. Upon introducing vapor into the system a different setting of the potentiometer indicated the new potential, the difference in potential depending upon the adsorption at the surface. The electrical connections were such that a positive value of the potential  $V$  indicates that the lower electrode was positive with respect to the vibrating electrode when the null was obtained.

The paraffin surface was usually obtained by melting a small amount of paraffin (Parowax) on the plate. The thickness of these films was of the order of 0.1–0.2 mm. *p*-Nitroaniline surfaces were produced by evaporation of a solution of *p*-nitroaniline in ethyl acetate. An analogous technique also was used occasionally for paraffin surfaces.

**Results.**—Figures 3, 4 and 5 show in graphical form some of the results obtained by this method. In each case the potential  $V$ , as read on the potentiometer, is plotted against  $P$  the pressure of the vapor in mm. of mercury. In all cases the gold-plated upper electrode is the reference electrode. The temperature was always 25° to within

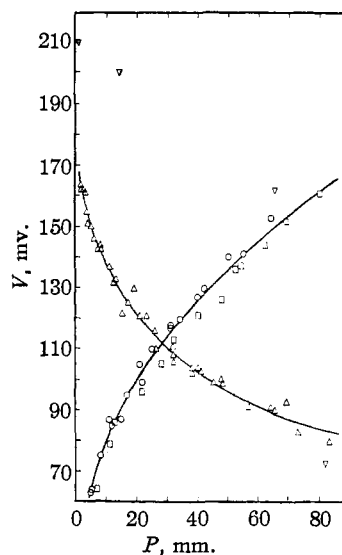


Fig. 3.—Ethyl acetate adsorption:  $V$ , potential in millivolts;  $P$ , pressure in mm.;  $\nabla$  and  $\Delta$  *p*-nitroaniline surface,  $\nabla$  four points taken as the vapor was first introduced,  $\Delta$  points showing reversible adsorption;  $\circ$  and  $\square$  points for two different paraffin surfaces.

(8) Yamins and Zisman, *J. Chem. Phys.*, **1**, 657 (1933).

a few degrees. Any effect due to variation of temperature was found to be small compared with various irreversible effects apparently due to changes in the nature of the surface film.

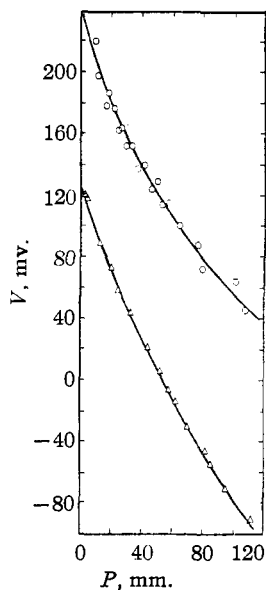


Fig. 4.—Chloroform on paraffin: O and Δ results for two different paraffin surfaces.

Results for ethyl acetate adsorption are shown in Fig. 3, the curve with positive slope being for a paraffin surface and the curve with negative slope being for a *p*-nitroaniline surface. It is interesting to note that the adsorption potentials for ethyl acetate at these two surfaces are opposite in sign and approximately equal in magnitude at corresponding pressures. Values shown for the paraffin surface include results obtained with two different surfaces, both surfaces being produced by melting of the paraffin on the plate.

Two different runs for chloroform on paraffin are shown in Fig. 4. The two curves differ by an approximately constant potential and were obtained using two different paraffin surfaces, both prepared in the same way, namely, by melting the paraffin on the plate. These results are typical of many which show that the absolute potentials as observed are quite sensitive to the preparation of the surface whereas the changes in potential are reasonably consistent.

Benzene on paraffin, in Fig. 5, gives results similar to chloroform except that the reversible effect is relatively small. In the particular run shown the reversible effect was approximately reproducible below about 50 mm. pressure. When the pressure of the benzene was raised above that value a permanent potential change was imposed of the order of +220 mv. A decrease in the pressure then showed a reversible change analogous to that observed in the original potential range.

Cyclohexane on paraffin showed a permanent change of potential similar to that observed with benzene. In this case, however, the surface actually changed visibly to have the appearance of a liquid solution at about the same time the permanent change of about +85 mv. was observed. These more permanent potential changes can be accounted for by assuming a penetration of the paraffin surface at high vapor concentrations and a subsequent potential change at the gold-paraffin interface. This assumption is given considerable weight by the experimental observation that a paraffin surface prepared by the evaporation of a benzene solution of paraffin has an original potential of about +150 mv. which undergoes no permanent change even on long standing in contact with relatively high pressures of benzene vapor.

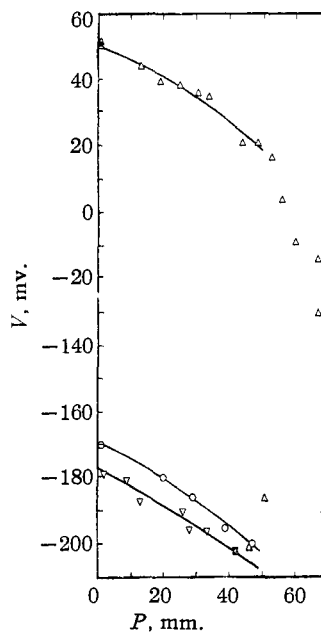


Fig. 5.—Benzene on paraffin: O, vapor first introduced; ∇, reversible adsorption below 45 mm.; \*, last point before permanent potential change starts taking place; Δ, measurements during and after the permanent change.

### Discussion

Results obtained by the two methods may be compared if it is assumed that air has no reversible effect. The comparison may be made when it is realized that what is measured in the direct method is the reversible change in potential corresponding to nearly complete saturation of the air with vapor. Comparable results for adsorption at a paraffin surface are as follows, the first value in each case being obtained by the direct method and shown in Table I and the second value being read off from the appropriate graph as the maximum change in potential observed by the vibrating plate method: for ethyl acetate +100 mv., +110; chloroform -120, -210; ben-

zene 0, -30. The values in each case agree as to sign and order of magnitude which is all that could be expected considering the more qualitative nature of the results of the direct method. The fact that the potential changes observed with the direct method are smaller (disregarding the sign) probably results from incomplete saturation of the air with the vapor.

The curves shown in Figs. 3, 4 and 5 are most easily interpreted if it is assumed that the change in potential is proportional to the surface concentration of adsorbed molecules, in which case the curves are then equivalent to adsorption isotherms. That this is a reasonable approximate assumption is indicated by the fact that potential changes due to monomolecular films on water are nearly proportional to the surface concentration in the film.<sup>9</sup> Whether the adsorption potential is positive or negative depends on the orientation of the dipoles in the adsorbed film.

The greatest difficulty in interpretation is that the observed change in potential may be composed of an effect at the upper electrode surface as well as at the lower surface. Gold was chosen for the surface of the upper or reference electrode because of its chemical stability and therefore constancy of surface condition. However, it is known that adsorption potentials may be set up at a gold surface. Ouellet and Rideal<sup>10</sup> measured such changes in potential by observing the shift of photoelectric threshold as various gases or vapors were introduced into a photon counter tube in which a gold surface acted as cathode. They found that oxygen and iodine caused an increase in work function while ethyl ether, ethyl alcohol or acetone caused a decrease, and petroleum ether, carbon tetrachloride, benzene or chloroform had no effect. If their observation of no change of work function for benzene or chloroform holds for our gold surface also, then we can conclude that our measured potential changes for benzene and chloroform really represent adsorption potentials of these vapors at the paraffin surface, and from the sign of the reversible adsorption potential conclude that the reversibly adsorbed molecules have dipoles oriented with the positive charge away from the paraffin surface. It is proposed to carry out future experiments to decide just how much potential change, if any, occurs at the gold surface under our conditions.

(9) See for example reference in note 3.

(10) Ouellet and Rideal, *J. Chem. Phys.*, **3**, 150 (1935).

Although adsorption potentials can be measured by the photoelectric technique the vibrating plate method is much simpler. Furthermore, the latter method has the advantage of being able to measure adsorption potentials at insulating surfaces such as paraffin, whereas the surface whose photoelectric properties are to be observed must be conducting. The photoelectric method used by Ouellet and Rideal may be objected to in general on the basis that the slight ionization of the vapor (which is necessary for the measurement) may cause the formation of foreign molecules which can be adsorbed strongly and thus create a false adsorption potential.

The fact that there are two dielectrics, the vapor and the paraffin or other film, does not require a modification of the theory of the vibrating plate measurement. When the null is obtained, no electric field exists across the vapor between the plates so the observed potentiometer reading gives the algebraic sum of all potentials in the circuit, including potential differences across the various surfaces and also possibly within the paraffin. If the paraffin is a perfect insulator, a potential difference could exist across the paraffin film. Such a potential difference caused by adsorbed ions or electrostatic charge would probably be dissipated slowly. In this work no effect has been found which requires such a potential difference for its explanation. It is supposed that such a potential is absent or at least constant.

Although it is well known that high vacuum technique is important for preparing surfaces for photoelectric threshold measurements,<sup>11</sup> such technique was not used in the present work. The surfaces used by us were all exposed to the atmosphere and may very well have strongly adsorbed molecules on them during the course of the measurements. Such contaminating molecules would probably cause a constant shift of the potential differences, but apparently do not appreciably affect observed changes in potential when a vapor is adsorbed reversibly. It is these changes of potential, or adsorption potentials, corresponding to easily reversible van der Waals adsorption that is of primary interest to us in this investigation. A more careful technique of preparation of surfaces would no doubt be necessary for a study of less reversible adsorption.

The measurement of adsorption potentials can be considered an indirect or supplementary

(11) Cashman and Huxford, *Phys. Rev.*, **48**, 734 (1935).

method for studying adsorption. Although the interpretation of results is complicated as mentioned above, it has one definite advantage over conventional methods for investigating adsorption in that only a relatively small amount of surface (a few square centimeters) is required.

The authors are grateful to Professor Malcolm Dole for discussions of various aspects of this work.

### Summary

The change of surface electrical potential of various surfaces as caused by the adsorption of

vapors of inorganic and organic substances has been observed by two different methods. The first apparatus, making use of a vacuum tube electrometer, gives direct qualitative observations of the effect. The second apparatus using a vibrating electrode, potentiometer, amplifier set-up yields quantitative observations of the change of potential with pressure of vapor. The observed potential changes vary from 5 to 500 millivolts. It is believed that the technique will be useful as a method for studying adsorption.

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[CONTRIBUTIONS FROM THE DEPARTMENTS OF CHEMISTRY AT PURDUE AND THE OHIO STATE UNIVERSITY]

## Chlorofluoropropanes

BY E. T. McBEE, ALBERT L. HENNE, H. B. HASS AND NORMAN ELMORE<sup>1</sup>

The origin of this work was a desire to prepare  $\text{CH}_2\text{ClCF}_2\text{CF}_2\text{Cl}$ , a new compound wanted for further investigation. The sequence of reactions permitted the preparation of additional fluorinated compounds, some of which are new while the others gave improvements in previously reported data. The research also confirmed the uniquely asymmetrical course followed by the chlorination of  $\text{CH}_3\text{CF}_2\text{CH}_3$ <sup>1a</sup>; this reaction proceeds stepwise to yield  $\text{CH}_3\text{CF}_2\text{CH}_2\text{Cl}$ ,  $\text{CH}_3\text{CF}_2\text{CHCl}_2$ ,  $\text{CH}_3\text{CF}_2\text{CCl}_3$ ,  $\text{CH}_2\text{ClCF}_2\text{CCl}_3$ ,  $\text{CHCl}_2\text{CF}_2\text{CCl}_3$  and finally  $\text{CCl}_3\text{CF}_2\text{CCl}_3$ , instead of a mixture of symmetrical and unsymmetrical compounds at each stage.

The starting compound was  $\text{CH}_3\text{CCl}_2\text{CH}_3$ , obtained from chlorinated propane<sup>2</sup>; its fluorination to  $\text{CH}_3\text{CF}_2\text{CH}_3$  followed previous directions.<sup>1a</sup>

This difluoride was chlorinated at low temperature in sunlight or artificial light, and also at high temperature in the dark; asymmetrical chlorination prevailed in all cases. The resulting chlorofluorides were fluorinated with a strong fluorinating agent, as shown in the experimental part, after repeated failure of milder agents and conditions. The fluorination did not proceed further than indicated.

(1) This work was presented for the degree of Master of Sciences at Purdue University, by Mr. Elmore, whose present address is Standard Oil Development Co., Linden, New Jersey. The fluorination work was carried out in Dr. Henne's laboratory at The Ohio State University.

(1a) Henne and Renoll, *THIS JOURNAL*, **59**, 2434 (1937).

(2) Hass, McBee, Hinds and Gluesen Kamp, *Ind. Eng. Chem.*, **28**, 1178 (1936).

### Experimental Results

The table lists the properties of three compounds (1, 2, and 3) which were obtained in a better state of purity than previously reported, and four (4 to 7) which are new. The latter were analyzed for chlorine by the method reported by McNevin,<sup>3</sup> but this was done while the method was still under investigation, and the deficiency is known to be due mostly to incorrect combustion. Only the last compound (no. 7) seems still impure, as indicated by the low molecular refraction and the low atomic refraction for fluorine (0.96 instead of an expected 1.15).

### Experimental

**Preparation of  $\text{CH}_3\text{CF}_2\text{CH}_3$ .**—2,2-Dichloropropane was obtained from by-product dichlorides from the chlorination of propane.<sup>2</sup> It was converted to  $\text{CH}_3\text{CF}_2\text{CH}_3$  by the procedure already reported.<sup>1a</sup>

**Chlorination of  $\text{CH}_3\text{CF}_2\text{CH}_3$ . Liquid Phase Chlorination.**—The  $\text{CH}_3\text{CF}_2\text{CH}_3$  was liquefied in a flask maintained at  $-10^\circ$  to  $-5^\circ$  and fitted with a reflux condenser and a chlorine inlet tube. Chlorine was added to the liquid and chlorination occurred in the presence of light. The temperature was maintained below  $0^\circ$  until all the  $\text{CH}_3\text{CF}_2\text{CH}_3$  had been chlorinated and then it was allowed to increase gradually to  $102^\circ$ , the boiling point of  $\text{CH}_3\text{CF}_2\text{CCl}_3$ . This procedure yields about 10.4%  $\text{CH}_3\text{CF}_2\text{CHCl}_2$ , 61.7%  $\text{CH}_3\text{CF}_2\text{CCl}_3$ , and 28% of more highly chlorinated material consisting of  $\text{CH}_2\text{ClCF}_2\text{CCl}_3$ ,  $\text{CHCl}_2\text{CF}_2\text{CCl}_3$ , and  $\text{CCl}_3\text{CF}_2\text{CCl}_3$ .

**Vapor Phase Chlorination.**—Chlorine was added to  $\text{CH}_3\text{CF}_2\text{CH}_3$  in a large bottle, over water at room tempera-

(3) McNevin and Baxley, *Ind. Eng. Chem., Anal. Ed.*, **12**, 299 (1940).