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INVESTIGATION OF THE PHOTOCHEMICAL METHOD FOR URANIUM ISOTOPE SEPARATION

By
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INVESTIGATION OF THE PHOTOCHEMICAL METHOD FOR URANIUM ISOTOPE SEPARATION

By H. C. Urey

This report was prepared and the work performed by the Chemical Division of the Columbia Group under the direction of H. C. Urey assited by H. T. Beans, R. H. Crist, A. B. F. Duncan, Simon Freed, L. I. Gilbertson, C. E. Herrick, Joseph Joffe, and M. Goeppert Mayer. Research Assistants: Robert Cranston, Wallace Davis, Charles Judson, Lawrence Liberatore, Donald McClure, and Thomas Sweet.

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The chemical and isotopic analytical work involved in the photochemical investigation was performed by Dr. Hull's group in Division I. The fluorocarbon compounds were supplied by Dr. Libby's group in Division I. In this connection the project has had the invaluable advice of Dr. Miller.

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PART I. STATEMENT OF PROBLEM AND PROGRESS

INTRODUCTION

To find a process for successful photochemical separation of isotopes several conditions have to be fulfilled. First, the different isotopes have to show some differences in the spectrum. Secondly, and equally important, this difference must be capable of being exploited in a photochemical process. Parts A and B outline the physical and chemical conditions, and the extent to which one might expect to find them fulfilled. Part C deals with the applicability of the process.

A. PHYSICAL ASPECTS

The isotopes 235 and 238 differ in two properties which influence their spectra, in mass and in nuclear spin.

Such differences will be apparent only in substances which have reasonably sharp absorption spectra. Gases at low pressures might be suitable materials for experimentation. The hexafluoride seemed especially suited since the symmetrical surroundings of the center atom may be expected to offer little disturbing competition to the unsymmetrical influence of the spin. Unfortunately, only the very weak absorption band system of UF_6 in the ultraviolet near 3800 A shows vibrational structure, which under the most favorable conditions, at pressures of 36 mm. in a 1 meter tube appears rather diffuse (see Part IIA and Figures Ab1).

On the other hand, the uranyl salts have the very outstanding peculiarity of showing, at least at low temperatures, very sharp absorption and fluorescence spectra. This sharpness can only be compared to that of the rare earths, and it is conceivable that the reason for it is the same in both cases. The long lifetime of the fluorescent state (10^{-4} secs even in solutions) indicates a shielding of electronic orbits. Calculations have shown that the 5f electronic levels should become populated at about element 92 in the periodic system, and that these orbits are embedded deeply in the electronic cloud. The meager data on the atomic spectrum of uranium point in the same direction. Besides, the uranyl salts provide standard examples of photochemical reactions.

The theoretical discussions therefore are concerned mainly with UF_6 and the uranyl salts. The absorption spectra of some urano compounds are sharp also, and some of them were investigated. (IIA).

a. Mass Effect

The mass difference amounts to 1.2% only. Its influence on the vibration frequencies is therefore certainly small.

In uranium hexafluoride only two of the six vibration frequencies depend on the mass of the center atom at all. They are the two infra red active frequencies, which will presumably not form long progressions in an electronic transition. The values of these frequencies are 623 cm^{-1} and probably about 180 cm^{-1}. The shift of these frequencies for U^{235} will not exceed 0.2%, or 1.2 cm^{-1} and 0.3 cm^{-1} respectively.

The evidence in the literature for the shape of the uranyl group is controversial. It is discussed in Part IIA. We are inclined to believe that the group is linear. In that case, the totally symmetric vibration does not depend on the mass of the center atom at all. This vibration (= 860 cm^{-1}) is responsible for the regular repetition of the groups of lines in fluorescence (see Figures Ad1 to Ad3). The other two vibrations of the uranyl group (~210 cm^{-1} and 930 cm^{-1}) will show a mass effect of 0.08%, which amounts to a shift of about 0.7 cm^{-1} for the infra red active frequency 930 cm^{-1}. There is some evidence for the occurrence of this frequency in the absorption and fluorescence spectra, but none for the occurrence of higher harmonics.

The width of the absorption lines of $UO_2(NO_3)_2 + 6\ H_2O$ has been measured by Joos and Duhm[1] and was found to be 20 cm^{-1} at liquid air temperature and 4 cm^{-1} at liquid hydrogen. Under such conditions, the small mass effect can presumably not be exploited. It should be mentioned, however, that the spectra of some other salts are considerably sharper.

Altogether, we do not have much hope in the exploitation of the mass effect and prefer the investigation of the effect of nuclear spin, which is commonly called the "P" effect in this laboratory.

b. Spin Effects

The nucleus of U^{235} consists of an odd number of elementary particles, and must therefore have a half integral nuclear spin and a nonvanishing nuclear magnetic moment. U^{238} consists of an even number of protons and neutrons. Without exception, all even-even nuclei have been found to be without spin. It is therefore safe to assume that U^{235} has a nuclear magnetic moment, whereas U^{238} has none.

This nuclear spin makes itself felt in hyperfine structure, which in all probability cannot be resolved. A second influence of the nuclear spin was brought to our attention by Pringsheim. This "P" effect consists in a breaking down of selection rules for forbidden transitions. The clearest example is furnished by the atomic spectrum of mercury. The lowest levels in mercury are (0) $^1S_0$, (1) $^3P_0$, (2) $^3P_1$, and (3) $^3P_2$. The transition $^1S_0 \rightarrow {}^3P_0$ is strongly forbidden. For an isotope of odd spin, however, the total angular quantum numbers of both states involved are no longer 0, and the transition is allowed.

One may regard the spin as a perturbation, V. This perturbation mixes into the state 1 some of the properties of the state 2, to an extent which depends on the interaction V_{12} between states 1 and 2, and inversely on their difference in energy. The transition probability depends on the square of the eigen function, and we obtain for the transition probability from state 1 to 0, (in units of electron numbers for instance)

$$f_D = \left| \frac{V_{12}}{E_2 - E_1} \right|^2 f_{20} \tag{1}$$

The magnitude of such a "P" effect in the spectra of uranium compounds may be estimated with the help of formula (1).

The effect will be noticeable only if the transition $0 \rightarrow 1$ is forbidden, $0 \rightarrow 2$ allowed, and $V_{12} \neq 0$. In a symmetrical molecule, this can occur only for states of definite symmetry character.

If $V_{12} \neq 0$, its magnitude may be estimated from hyperfine structure to be about $0.5\ \text{cm}^{-1}$.

In the uranyl spectra, the lifetime of the fluorescent state is 10^{-4} sec, which corresponds to an electron number of about 3.8×10^{-5} for the sum of the intensities of all lines leading to the first electronic level. A strong line in the band will have an intensity of about 4×10^{-6}.

Stronger absorption occurs in the ultraviolet, about $2000\ \text{cm}^{-1}$ away from the point where the reversal of fluorescence lines occurs, and a sharp band system starts about $6500\ \text{cm}^{-1}$ from this place (Part II, Figure Ad2, 4).

The line which shows the "P" effect may steal its intensity from a strong companion in the same band system. If this companion were 10 wave numbers away, the enhancement due to unclear spin would be at best $f = 10^{-8}$. If the line derives its intensity from a transition with electron number $f = 1$ which is 5000 cm^{-1} away, its enhancement would also be $f = 10^{-8}$.

Of course, this "P" effect line would occur also in 238, due to the influence of all possible random perturbations. It would have been desirable to calculate these in order to compare their magnitude with the effect of the nuclear spin. Unfortunately, no method was found to estimate them. A favorable situation is that the electrons responsible are obviously well shielded in the uranyl ions against outside perturbations and, being well within the ion, are relatively close to the nuclear moment. On the other hand, the perturbing potential of a nuclear moment is usually small compared to practically all other factors.

There are no intensity data on the band system of UF_6. A strong absorption begins only at about 35,000 cm^{-1}.

There is another process in which the spin may conceivably make itself felt. This process is a spin induced predissociation. Turner[2] found that the fluorescence of iodine vapor is quenched about 50% by the application of a magnetic field of 12,500 gauss. This effect is interpreted as predissociation. The magnetic field mixes a stable and unstable molecular state. The symmetry character of the states in iodine allows a clear theoretical explanation.

A nuclear magnetic moment could here play the part of the applied magnetic field. It is possible that such spin induced predissociation might occur in some uranium compound. Such an effect might be found by photochemical experimentation in magnetic fields and by theoretical interpretation of the spectra.

c. The Search for the Favorable Line

The task of the spectroscopic section is then the location of a line showing a "P" effect in the band spectrum of any uranium compound.

Low temperatures bring about a sharpening of all lines. The most favorable conditions for the detection of any enhancement are therefore obtained at the temperature of liquid hydrogen. If an effect is found, it should be easy to follow it to higher temperatures, where it can be used in a photochemical reaction.

Two methods present themselves for the attack of the problem of finding a "P" effect, and both will be used in this laboratory.

1. Enriched materials. The first method consists of the use of materials enriched in the desired isotope. It presents, however, considerable difficulties. The material which we have available contains 14% of U^{235}. If a line were 10% stronger in pure U^{235}, it would appear only $0.14 \times 10\% = 1.4\%$ enhanced in the 14% material. Such differences would be hardly noticeable. If a line were obviously strengthened in the 14% mixture, say 10%, it would correspond to an intensification of 70% in pure U^{235}, which would be a very favorable condition. In short, only large effects can be found with this method of attack. An additional experimental complication arises from the fact that impurities, and even slightly different contents of water of crystallization, cause new weak lines to appear in the fluorescence and absorption spectra of the uranyl salts. This effect has led to erroneous conclusions in the past.

So far, the enriched material has been used in the form of the hexafluoride only. No large differences either in positions or intensities of bands appeared in the absorption spectrum. Since the structure was very diffuse this is not surprising. Hope has not yet been abandoned to find more favorable conditions for obtaining sharper spectra of this material.

2. Magnetic fields. The second method for tracing favorable absorption lines consists of the use of external magnetic fields. The symmetry of such a field is the same as that created by the nuclear magnetic dipole. The same lines will be enhanced by both effects. But the magnetic field acts on the bulk of the material. Referring back to the equation for the enhancement of an absorption line, formula (1), it follows that the matrix element V_{12} for perturbation by the nuclear magnetic dipole vanishes if and only if the corresponding matrix element for the perturbation by an applied magnetic field vanishes also. The magnitude of the perturbation by a magnetic field is larger. A field of 20,000 gauss causes a Zeeman splitting of 1 cm^{-1}, compared to the hyperfine structure splitting of about 0.5 cm^{-1}. The enhancement in the magnetic field should then be about 4 times that due to the spin. A line which is 10% enhanced in pure U^{235} would appear 40% enhanced in a magnetic field of 20,000 gauss. With some care, this ought to be observable.

Since the same crystal or liquid may be studied with and without magnetic fields, impurities do not play as large a part as in comparing samples of enriched and unenriched materials.

The absorption of the hexafluoride from the visible to the far ultraviolet was studied with and without magnetic field. No difference was found anywhere. The experimental conditions were very unfavorable, since a tube only 10 cm long could be introduced into the magnetic field. Under such conditions, the structure of the near ultraviolet band system is barely perceptible.

No absorption spectra of the uranyl salts have to date been studied in the magnetic field. The fluorescence of $RbUO_2(NO_3)_3$ and $NaUO_2(Ac)_3$ was photographed with and without magnetic field. The very large enhancement of fluorescence lines reported by Weissman and Lipkin in California was not verified. These authors have since informed us that their effect in $RbUO_2(NO_3)_2$ was due to different degrees of hydration of this salt.

3. Analysis of spectra. Since the "P" effect follows definite and sharp selection rules, a theoretical understanding of the electronic transitions would be of great value. Such understanding might for instance result in definite predictions that a "P" effect will not occur in certain compounds.

The hexafluoride is presumably octahedral. The evidence pro and contra this model will be dealt with in section Aa of the technical report, Part II. The symmetry properties of such a model are well understood. All 6 vibration frequencies are known at least approximately from infra red, Raman, and thermal data (IIAa). Attempts at interpretation of the ultraviolet absorption spectrum have been made, but the diffuseness of the structure makes such considerations somewhat ambiguous.

The sharp line fluorescence spectra of the uranyl salts are very complex. The structure of the individual groups of lines reflect presumably the symmetry of the field surrounding the UO_2^{++} group. The progress made in the understanding of this field is reported in Part II. We have, however, not yet used a powerful tool for obtaining additional information. In uniaxial crystals the fluorescence is different along different crystal axes. A careful investigation with a polarization equipment would permit us to determine whether the emitted light is dipole, quadrupole or magnetic dipole radiation. If a line is dipole radiation, the direction of this dipole with respect to the axis of the UO_2 group can be determined. If this is done, it should be possible to determine the symmetry of the electronic level involved, and make more definite predictions about the "P" effect.

B. PHOTOCHEMICAL INVESTIGATIONS

The need for spectra of reasonable sharpness restricts the available systems to gases or low temperature systems of crystals or solid semisolid solutions. In order to accomplish separation of the isotopes; (1) there must be extreme sharpness in the vibrational bands and (2) the molecules must decompose under the influence of light. These conditions can be fulfilled only if the associated state has a long lifetime. This considerably enhances the possibility of energy transfer. The "forbidden" nature of magnetically catalyzed radiation also may lead to a long-lived state.

a. Gaseous Systems

In a gas phase experiment chain reactions are particularly to be avoided.

Usually one would expect to be most successful by working in systems at low total pressure, attenuated in uranium and with a large surface area. Under these conditions it is difficult experimentally to cause the absorption of a reasonable portion of the incident light. Since in many cases it is not unlikely that the product itself is light sensitive, at least to the extent that material exchange might occur under the influence of radiation, rapid removal of the product from the illuminated portion of the vessel is indicated. Here, as in solid systems, a solid reaction product is desirable in order to minimize exchange. The vapor phase reaction between UF_6 and fluorocarbons yields a solid reaction product, but it is a chain decomposition.

Efforts with this reaction have been directed toward acquiring enough knowledge of the reaction mechanism to allow an intelligently planned separation experiment to be carried out. The experimental results so far show a strong dependency on the fluorocarbon pressure; quantum yields as large as ten have been obtained. The reaction product from the perfluorotoluene decomposition appears to be CF_3-UF_3. If C_6F_{11} is the chain carrier, the pressure dependency of the quantum yield is not surprising.

Currently with this more fundamental investigation several experiments aimed at exploiting any large spectral differences were carried out. Due to the fact that the isotope whose separation is desired is present in much smaller amounts than the other, it is possible to remove nearly completely the radiation absorbed by both of the isotopes by using a filter of the material undergoing reaction. This circumstance arises, of course, from the exponential dependence of absorption on concentration; the filtered light, at relatively small cost in intensity, will consist, in theory, nearly completely of light which can be absorbed only by the lighter isotope. This fact has been exploited in an experiment using UF_6 and perfluoroisobutane at low pressures. Analytical results of the isotope abundance are not yet available.

The UF_6 bands, at least at the pressures experimentally useful at present, are much too diffuse to be used in a vibrational separation. However, presuming that a large magnetic enhancement might occur, experiments were performed in which different portions of the banded absorption region were illuminated. These experiments were carried out at the lowest possible pressure. Abundance measurements are not yet complete.

b. Solid Systems

Glassy solutions and crystals at low temperature

Glassy solutions and crystals at low temperature present a favorable case from the point of view of spectral sharpness. The use of glasses is necessary since a microcrystalline mixture of uranium compounds and solvent leads to extensive scattering of the incident light. The net result due to scattering is that the light confined to a thin layer and effectively the absorption coefficient is increased, which causes an excessive amount of reaction in the scattering layer.

The properties of a good glassy solvent are as follows:

1. It must glass under the slow cooling necessary for the prevention of strains in the glass and the achievement of some degree of order.
2. Optical transparency in absorption region of uranium compounds.
3. Photochemical reactivity in some cases.
4. Sharp absorption spectrum of the solute.
5. Any thermal reaction must be small. This sometimes can be accomplished by mixing at low temperatures.
6. Sufficient solubility at low temperature.

A thorough knowledge of the glassy state is necessary to this investigation and a study was made of the theoretical material available on the subject.

The search for a rigid or semi-rigid solvent for UF_6 of suitable characteristics is still not complete. Certain of the Freon compounds are satisfactory except for the fact that the interaction between solvents and UF_6 is sufficiently strong to wipe out the banded structure observed in less polar glasses. It is not unlikely that in the case of UF_6 such close interaction is essential to photochemical reactivity and that this compound is not suitable for low temperature experiments. The uranyl compounds appear to have such well shielded orbits that they retain their crystalline spectral characteristics in glassy solvents at low temperature. Reaction both with a glassy solvent and reduction within the molecule of uranyl organic compounds dissolved in glassy solvents have been reported. Until recently there was some uncertainty as to the oxygen-uranium angle in the UO_2 compounds. It now appears fairly certain that the oxygens are in a straight line and no blanketing of the nuclear spin should occur. It is probably true in all cases that the spectral conditions are less favorable in glasses than in crystals.

The use of crystals: Internal oxidation or reduction

Crystals appear to meet the necessary conditions better than rigid solutions. The major advantage of rigid solutions is that comparatively large distances separate the uranyl atoms and thus the possibility of energy exchange is negligible. However, in the case of crystals of the uranyl compounds, energy exchange may not be possible since absorption takes place in a shielded level, and reduction probably occurs through the loss of an electron from the UO_2 group resulting in the immediate loss of oxygen. In fact, it has already been demonstrated by Lipkin and Weissman (Appendix to Part IIC) by means of radioactive tracers that uranous uranium does not interchange with uranyl uranium in solution. Internal reduction in a crystal of potassium uranyl ferrocyanide at $-190°$ has been reported and, undoubtedly, other compounds of this type which possess the requisite spectral and chemical properties can be found. Certain compounds of the uranous type give moderately sharp spectra at low temperature. Compounds such as $U(IO_4)_4$ thermally oxidize to $UO_2(IO_4)_2$ and the reaction would probably occur photochemically at low temperatures.

C. APPLICATION

If a difference in the intensity of an absorption line for U^{235} and U^{238}

is found, and if light of this frequency can be used to effect a photochemical process, a method is developed to separate the isotopes.

In order to obtain a clearer understanding of the magnitude of an effect which may be used in large scale production, some of the expenditure in power and money has been calculated.

Let us assume that a photochemical process has been found, with a quantum yield of >, for which the ratio of A_5, the absorption coefficient of 235, to A_8, the absorption coefficient of A_8 is

$$\frac{A_5}{A_8} = \alpha > 1 \qquad (1)$$

At any instant in the process, the ratio of the concentration of 235 to that of 238 in the reacting material is larger by the factor α than the same ratio in the bulk of the remaining material.

We visualize the process as one where light is created in an arc or spark which contains the desired line. Filters prevent non differentiating light from entering into the reaction vessel.

It was pointed out by Dr. Kistiakowsky that it may be difficult to keep all "false" light away from the reacting material. His statement, given in conversation, was that it may not be possible to cut the "false" light to less than the amount of desired light. In that case, $\alpha = 2$ would be an upper limit for the possible increase in concentration of U^{235}: The fact that the "false" light may be absorbed more readily than the "correct" light, which corresponds to a weak absorption, does not alter this fact. The set up must be, in any case, such that practically all the desired light is absorbed.

To estimate the amount of light required, a cascade of reaction steps has to be built, in which the reaction products of each step are sent on to the next higher, while the remaining material is fed back to the next lower step. In each step, a little less than ½ of the material is advanced.

The calculations for such a cascade are identical with those for a diffusion process, and the results can be obtained directly by using the formulae developed previously.* The quantity α, as defined by Eq. 1,

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*Karl Cohen, A96, Total Areas, Pumping Speeds and Stages for Diffusion Apparatus.

corresponds to the simple process factor α used by Cohen. The most efficient cascade is obtained, if the two streams entering each stage, the one from above and the one from below, have the same isotopic composition. Cohen's formulae held for $\alpha = 1 < 1$ only. For $\alpha = 1.5$ and $\alpha = 2$ the energies obtained with these formulae are slightly too low (about 10% for $\alpha = 1.5$ and possibly ½ at $\alpha = 2$).

The number of stages to obtain material containing 90% U^{235} is given by

$$N = \frac{7.14}{(\alpha - 1)\ \ln 2} = \frac{10.3}{\alpha - 1} \qquad (2)$$

These values are listed in column 2 of Table I.

The number of mols of light quanta necessary to obtain 1 kg. of 90% U^{235} is

$$\frac{1000}{235}\ \frac{130}{((\alpha - 1)\ \ln 2)^2} = \frac{1151}{(\alpha - 1)^2} \qquad (3)$$

These values are listed in column 3.

It was further assumed than an arc or spark may be found which converts one thousandth of its energy input into a line of the desired frequency. This figure may be somewhat optimistic. But if it were possible to use a resonnance line, one could do a great deal better. The line needed was assumed to have a frequency of about 20,000 cm^{-1}. One mol of quanta corresponds to 57.2 kiloclaories or .067 kilowatt hours; 67 kilowatt hours are needed in the arc to produce this amount of useful light. The energy required to obtain 1 kg of the desired material is then

$$\text{Energy} = \text{No. of mol quanta} \times 67 \text{ kilowatt hours} \qquad (4)$$

These numbers are listed in column 4.

The cheapest electric rates are about 2 cents per kilowatt hour. On this basis, the figures in column 5 are obtained.

The power needed in a plant which produces 1 kg a day is given in column 6.

The price of electrical equipment alone to construct such a plant is, according to a private communication to Karl Cohen by Rhea of

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G. E., $75 per kilowatt. The price of this part of the installation is contained in column 7.

If the plant is to reach equilibrium in 100 days, the time which the material may spend in each step is

$$t = \frac{100\,((\alpha - 1)\ \ln 2)^2}{10.3}\ \text{days} = 4 \times 10^5\,(\alpha - 1)^2\ \text{seconds} \tag{5}$$

These times are listed in column 8.

The ninth column contains the amount of liquid nitrogen needed; the tenth its price at 10 cents a liter.

These figures are estimates on the pessimistic side. It is assumed that all the light energy absorbed by the molecules has to be removed by liquid nitrogen. If the chemical reaction is endothermic, this would not be the case.

The figures in column 9 and 10 are computed on the basis that the heat of vaporization of 1 liter of liquid N_2 is 47.6 kilocalories. Column 3 gives the number of mol quanta absorbed in the cascade; each mol of quanta corresponds to 57.2 kilocalories.

If the separation of the reaction products from the bulk of the material can be done at high temperatures only, more liquid nitrogen is needed to cool the material for each step. This amount, however, is small compared to the heating due to light.

If liquid hydrogen would have to be used, matters would become rather unfavorable. Due to its low density, the heat of vaporization of one liter of liquid hydrogen is only 7.50 kilocalories. The amounts needed are given in the last column.

Table I

I	II	III	IV	V	VI	VII	VIII	IX*	X	XI*
		The production of 1 kg of 90% U_{235} requires			The plant to produce 1 kg of 90% U_{235} per day			The total cooling for the production of 1 kg of 90% U_{235} requires either		or possibly
$\alpha - 1$	No. of stages to obtain 90% U_{235}	Mol quanta	Killowatt hours	Costs $	Requires a power of kilowatt	Costs in electrical equipment million $	Transit time for 100 days equilibrium sec	Liter of liquid N_2	Price of liquid N_2 $	Liters of liquid H_2
1	11	1150	7.71×10^4	154	3.21×10^3	.241	4.4×10^5	1382	138	8.7×10^3
.5	18	4.6×10^3	3.08×10^5	616	1.28×10^4	.96	10^5	5.53×10^3	553	3.48×10^4
.2	57	2.88×10^4	1.93×10^6	3860	8.04×10^4	6.03	1.6×10^4	3.46×10^4	3.46×10^3	2.18×10^5
.1	110	1.15×10^5	7.71×10^6	1.54×10^4	3.21×10^5	24.1	4.03×10^3	1.38×10^5	1.38×10^4	8.7×10^5
.05	210	4.6×10^5	3.08×10^7	6.16×10^4	1.28×10^6	96	1000	5.53×10^5	5.53×10^4	3.48×10^6
.02	520	2.88×10^6	1.93×10^8	3.86×10^5	8.04×10^6	6.03×10^2	160	3.46×10^6	3.46×10^5	2.18×10^7
.01	1000	1.15×10^7	7.71×10^8	1.54×10^6	3.21×10^7	2.41×10^3	40	1.38×10^7	1.38×10^6	8.7×10^7

*If the photochemical reaction is endothermic, these magnitudes would be reduced.

PART II. TECHNICAL REPORT

A. SPECTROSCOPIC INVESTIGATION

a. Shape and Thermal Data on UF_6

For the record it seems desirable to bring together all available information of UF_6 at this point, although some of it is not pertinent to the present investigation.

It is usually assumed that UF_6 has the form of a regular octahedron. Actually, the only information contained in the literature is against this assumption. Braune and Pinnou[3] found three slightly different U-F distances by means of electron diffraction.

A model of slightly asymmetric octahedron does not seem reasonable. Decomposition products might account for the observed values. The evidence obtained from Raman, infra-red and specific heat data collected here, presents a strong argument for the regular octahedral structure. The following discussions assume an octahedral model, and arguments for this structure will be summarized at the end of this section.

The symmetry properties of the vibrations of a regular octahedron are well known. Six different frequencies occur. The nomenclature follows that of Eucken.[4] The symmetry characters used are those of Mullinken.[5]

The Raman spectrum of a regular octahedron should show three lines. A. B. F. Duncan found in the liquid, two only, at 603 cm^{-1} and 230 cm^{-1} respectively. The third line may not appear, either due to intrinsic weakness, due to closeness to strong one at 603 cm^{-1}, or because it is covered by the halo of the overexposed exciting line.

In the gaseous state, these lines may be expected to be of slightly higher frequency. To obtain better agreement with the infra-red spectrum, the Raman lines for the gaseous molecules were assumed to be $V_3 = 230$ cm^{-1} and $V_1 = 625$ cm^{-1} respectively. This does not noticeably influence entropy calculations, but has a small influence on the specific heats. Only two vibrations, V_5 and V_6, are infra-red active. V_5 is so far in the infra-red as to be practically unobservable. Turkevitch measured the infrared spectrum of UF_6 and formed only one fundamental, at $V_6 = 623$ cm^{-1}.

The observed overtones with their respective strength are given in Table Aa2. An interpretation was made. It lead to the frequencies contained in Table Aa1.

Table Aa1

Name	Degeneracy	Value in cm^{-1}	Symmetry character	Observation
ν_1	1	625	A_{1g}	603 Raman effect of liquid
ν_2	2	557	E_g	
ν_3	3	230	T_{2g}	230 Raman effect of liquid
ν_4	3	113	T_{2u}	
ν_5	3	174	T_{1u}	
ν_6	3	635	T_{1u}	623 Infra-red

These frequencies lead to the following active overtones.

Table Aa2

		Calculated		Observed		
		cm^{-1}	λ	cm^{-1}	λ	Strength
1	ν_5	174	57.47			
2	$\nu_4 + \nu_3$	343	29.11			
3	$\nu_5 + \nu_3$	404	24.75			
4	ν_6	625	16.00	623	16.05	1000

Table Aa2 (Continued)

		Calculated		Observed		
		cm^{-1}	λ	cm^{-1}	λ	Strength
5	$\nu_4 + \nu_2$	670	14.93	675	14.82	10
6	$\nu_5 + \nu_2$	731	13.68	713-719	14.03-13.91	½
7	$\nu_5 + \nu_1$	799	12.53	825	12.12	2
8	$\nu_6 + \nu_3$	865	11.56	850	11.68	¼
9	$\nu_6 + \nu_2$	1192	8.39	1163	8.60	4
10	$\nu_6 + \nu_1$	1260	7.94	1295	7.72	3
				2053	4.87	½

All active double combinations are contained in this list, and all of Turkevich's data are used.

Frequencies could be found to fit the infra-red data better. But they do not agree with the Raman Data and are not reasonable. Discrepancies may be blamed on the fact that the experimental data are taken at room temperature, where the bending frequencies are fully excited. Anharmonicity might explain, for instance, that the difference between V_1 and V_2, as observed from lines 6 and 7 as well as 9 and 10 is greater than that for the assumed frequencies of the non-vibrating molecule.

Heat capacities and entropies are calculated from these frequencies, and from the U-F distances given by Braune and Pinnou. The symmetry number 24 was used in the entropy.

Table Aa3 — Heat Capacities and Entropies per Mol

		C_p (cal)			S (cal. deg^{-1})	
			Observed			
T°K	T°C	Calculated	British	Booth	Calculated	Experimental
273.18	0	30.039			88.266	87.00
298.18	25	30.865	33.5 ± 1	29 ± 1		
323.18	50	31.614			93.12	93.33 (92.7 ± .4)
348.18	75	32.265	34.5 ± 1			

Table Aa3—(Continued)

			Observed		S (cal. deg^{-1})	
T°K	T°C	Calculated	British	Booth	Calculated	Experimental
373.18	100	32.815	9		98.052	99.20
398.18	125	33.314	35.5 ± 1			
423.18	150	33.737				
473.18	200	34.424				

The large value of C_p of the British report cannot be reconciled with any reasonable frequency picture. Only anharmonicity of the vibrations or non-ideality of the gas could be made to account for it.

The experimental data of the entropy are derived from Brickwedde's measurement on the solid phase with the use of Crist's data of vapor pressure and heat of evaporation. Libby estimated that the entropy of the Bertholot gas at 50°C is

$$S = 92.7 \pm .4 \text{ cal. deg}^{-1}$$

It is seen that the Raman and infra-red data conforms to the octahedral model. For a less symmetrical structure, more Raman lines and more infra-red absorption bands should appear. The entropy and heat capacities also are in satisfactory agreement with experiment.

The term in the entropy arising from the symmetry number amounts to $-R \ln 24 = -6.3$ cal/degree. That the entropy calculated with this symmetry number agrees with the measured one should of course not be used as an argument in favor of the octahedral model.

b. Absorption Spectrum of UF_6

UF_6 vapor, at a pressure of 36 mm and in a one meter path length, shows a number of diffuse absorption bands near wave number 27,000 cm^{-1}. The ultra-violet edges appear slightly sharper and their positions in cm^{-1} are reported in Table Ab1. An enlarged photograph of this spectrum appears in Figure Ab1 and a microphotometer trace in Figure Ab2. There is probably also a continuum underlying these bands.

The most prominent feature of this spectrum is a short progress ion of about five members showing a frequency difference starting with 610 cm^{-1} and decreasing to 590 cm^{-1}. There are groups of weaker bands toward lower frequencies (not seen on the microphotometer trace) separated by about 100 cm^{-1}. There are also bands separated by 100 cm^{-1} and 240 cm^{-1} between members of the principle 600 cm^{-1} progression. These bands do not become appreciable sharper in a tube 2.8 meters long and at correspondingly lower pressures, but we hope to find sharpening in much longer columns, 20 meters or more in length.

The frequency 600 cm^{-1} agrees with the value of the totally symmetric (Raman active) frequency ν, which has a value of about 625 cm^{-1} in the ground state. It is expected from theory that this frequency should appear. The 240 cm^{-1} and 100 cm^{-1} frequencies agree with the most probable values of ν_3 and ν_4 (230 and 113 respectively).

The absorption spectrum of UF_6 in Indies Oil (a branched chain fluorinated hydrocarbon) at 77°K shows the same structure as the spectrum of the gas. A microphotometer trace is shown in Figure Ab2. There is a uniform shift of all bands to lower frequencies by about 450 cm^{-1}. The spectrum also breaks off much earlier on the red side which is apparent on the original plates but not on the microphotometer trace. This is to be expected because of the lower temperature.

The absorption of thin films of solid UF_6 have shown no structure. The film thickness, however, is very difficult to control and the most favorable thickness may not have been used. Work on this is continuing.

The absorption in this region is weaker by a factor of about 10^{-3} than absorption around 42,000 cm^{-1}. The latter absorption is continuous and extends with gradually diminishing intensity to about 31,000 cm^{-1}.

A sample of UF_6 vapor in which about 14% of the uranium was U^{235} was investigated in a one meter tube at a pressure of 36 mm. There was no apparent difference in intensity or position of any bands in comparison with ordinary UF_6.

A sample of UF_6 vapor in a quartz tube 10 cm long in a magnetic field of 19,000 gauss was also investigated. The entire spectral region from 50,000 to 12,000 cm^{-1} was covered with low dispersion. No additional bands appeared with the field and there was no apparent change in intensity at any wave length. The complicated structure near 27,000 cm^{-1} was not resolved under these conditions.

c. Fluorescence of UF_6

Solid UF_6 at 77° K, excited by Hg 3660 (27,800 cm^{-1}) shows a bright violet fluorescence. This disappears as the temperature is raised and is apparently absent at room temperature. No fluorescence could be observed in the vapor with very long exposures. The fluorescence spectrum consists of a number of diffuse bands separated by about 220 cm^{-1}. The wave numbers are listed in Table Ac1 and a photograph shown in Ac2. The maximum of intensity is at about 23,700 cm^{-1} and the intensity decreases uniformly on both sides to 22,000 cm^{-1} and 24,700 cm^{-1} respectively. The intensities and positions of the bands are not changed by a magnetic field of 25,000 gauss and no new bands appear.

d. Spectra of Uranyl Salts.

The study of uranyl salts was begun with the aim of trying the effect of magnetic fields on the spectra of these compounds. As has already been pointed out, changes in spectra produced by the field should be similar to those changes caused by altering the U^{235}: U^{238} ratio. Because of this the two salts were selected for which Weissman and Lipkin (Report December 17, 1942) found intensification of some fluorescence lines in samples enriched in U^{235}. These salts were $Rb(UO_2)(NO_3)_3$ and $NaUO_2(C_2H_3O_2)_3$.

At first the fluorescence spectra of these salts at 77°K was studied which was then the lowest temperature available here, with and without a magnetic field. No large effect was found, but the lines were 3-5 cm^{-1} wide at this temperature. It became clear that two improvements were necessary: (1) lower temperatures in order to make the lines more narrow, and (2) an interpretation of the spectra in order to explain at least the most prominent lines as a guide for future experiments. The measurements of Nichols and Howe[6] were not satisfactory for our purposes. We also needed the measurement of absorption spectra of these compounds for correlation with the fluorescence spectra.

The absorption and fluorescence lines of sodium uranyl acetate were photographed at 77°K. These are given in Tables Ad1 and Ad2. An enlargement of the fluorescence spectra at 173°K, 77°K, and 20°K is reproduced in Figure Ad1. A microphotometer tracing of the absorption spectrum is shown in Figure Ad2.

$UO_2(NO_3)_2 \cdot 6H_2O$ has a somewhat simpler spectrum and data on absorption and fluorescence at 77°K are given in Tables Ad3 and Ad4. An enlarged reproduction of the fluorescence spectrum is shown in Figure Ad3 and a microphotometer trace is shown in Figure Ad4.

We have less complete data on the following uranyl salts: $NH_4UO_2(C_2H_3O_2)_3$, $RbUO_2(C_2H_3O_2)_3$, and $RbUO_2(NO_3)_3$. Fluorescence frequencies for these compounds are given in Tables Ad5, Ad6, Ad7, and enlarged reproductions of their spectra are shown in Figure Ad5. It is intended to complete these data by absorption and fluorescence measurements at 20°K and to study the effect of a magnetic field at this temperature.

Some progress is made on the theoretical understanding of the uranyl spectra. The evidence in the literature on the shape of the UO_2 group is contradictory.

Fankuchen[7] made x-ray investigations of several double uranyl acetates and formed the UO_2 group to be linear. Conn and Wu[8] concluded from the infra-red and Raman data that the group is bent. Closer inspection shows that their arguments are not very strong. In the Raman spectrum, they obtained two lines, corresponding to 210 cm^{-1} and 850 cm^{-1}. 210 cm^{-1} must be assymmetrical bending vibration, which should not appear in a linear gaseous molecule. The corresponding Raman line is, however, weak. Moreover, some later investigators[9] formed this line to be double. This can be understood if the group is linear, since this vibration is doubly degenerate, and the crystalline field may split it and make it weakly Raman active. In the infra-red spectrum, they found on strong frequency at 930 cm^{-1}. Their apparatus did not allow them to detect the frequency at 210 cm^{-1}, which should occur. Besides, however, they found very weakly an absorption at 850 cm^{-1}. This frequency should not be infra-red active. The crystalline field, however, may be responsible for a breakdown of the selection rules.

Altogether, the evidence for a linear model seems stronger. The regular repetition of the groups in fluorescence has long ago been attributed to the fact that the totally symmetric frequency of 850 cm^{-1} adds on to the electronic transition. The structure of the individual groups is still in doubt. A somewhat speculative interpretation will be outlined.

The coordination number of hexavalent uranium is 8. According to Fankuchen, the uranium atom in $NaUO_2(Ac)_3$ is surrounded by 8 oxygen atoms, which are located about at the corners of a cube which is "squashed" along the space diagonal. The O-atoms of the UO_2 groups are nearer to the center than those of the acetates. Two oxygens come from each acetate group. It is tempting to assume that the environment of the uranium atom in $U(NO_3)_3 \cdot 6H_2O$ is analagous, namely that the six oxygens from the water molecules with the two oxygens of the uranyl group form the "squashed" cube. Since now each oxygen comes from a different molecular aggregate, the symmetry can be higher. It is seen that the fluorescence and absorption of $U(NO_3)_2 \cdot 6H_2O$ is much simpler than that of $NaUO_2(Ac)_3$. The fluorescence spectrum of $RbUO_2(NO_3)_2$ resembles that of $NaUO_2(Ac)_3$, and may have about the same local symmetry.

It is striking that in all spectra of compounds where the UO_2 group may be surrounded by 6 oxygen atoms the second strong line in the first fluorescence group is missing. The distance of this line in the 2nd group from the 1st strong line in the first group is about 920 cm^{-1}. One would like to attribute this line to the occurrence of the infra-red active frequency of 930 cm^{-1}. A similar effect occurs, at least in $NO_2(NO_3)_2 \cdot 6H_2O$, in the absorption around 27,000.

All these regularities disappear in compounds like $UO_2\ Cl_2 \cdot 2KCl \cdot 2H_2O$, where 6 equal atoms cannot surround the UO_2 group.

The absorption spectra of $U(NO_3)_2 \cdot 6H_2O$ and of $Na\ UO_2(Ac)_3$ show clearly that a second bandsystem sets in about 6500 cm^{-1} to the violet of the beginning of the first. If the excited state contains an inner f level, this orbit should be strongly coupled to the spin. Calculation showed that the difference between an $\underline{f}\ 7/2$ and an $\underline{f}\ 5/2$ state should be about 1 electron volt or 8000 cm^{-1}. It is tempting to interpret the second electronic level in this manner.

e. Spectra of Other Uranium Compounds

Although our main interests have been directed to the study of UF_6 and the uranyl compounds, a few other spectral studies may be related briefly. UCl_6 might be expected to show spectra similar to UF_6 in spite of its very different physical properties. Since the vapor pressure is very low, UCl_6 vapor must be examined in a tube completely surrounded by vapor baths. Experimental difficulties (lack of substances boiling at suitable temperatures) did not permit variation of the pressure, and films deposited on the windows which could not be removed. A weak continuous band with center at about 20,000 cm^{-1} appeared. Much stronger absorption also appeared around 27,000 cm^{-1} corresponding to that in UF_6. The ultra-violet region below 30,000 has not been investigated.

Thin films of UCl_6 at about 77°K show more definite structure. In the 20,800 cm^{-1} region there is diffuse diffractional structure. At lower frequencies about 17,000 cm there is much weaker but sharper absorption. Some structure in this latter region is also shown in glasses at the same low temperature. These studies are still in progress and will be extended to even lower frequencies when we have available infra-red sensitive plates.

We have also examined, although incompletely, four uranium salts of different types. Some time ago we studied the absorption of $U(BH_4)_4$ vapor in the visible and ultraviolet down to 33,000 cm^{-1}. This compound is known to decompose photochemically. It also decomposes thermally at fairly low pressures so that only the absorption at very low pressures can be obtained. We found a continuous band at about 21,000 cm^{-1} in a cell 50 cm long at a pressure of about 4 millimeters.

The solid compound $K_4U(C_2O_4)_4 \cdot 5H_2O$ at 77°K shows considerable structure. The bands are somewhat diffuse and lie at about 19,500, 18,000, and 15,000 cm^{-1}. There is evidence that bands exist further in the infra-red which will be photographed later.

Hydroxylamine urynate, $(NH_3OH)_2UO_4$, shows relatively sharp bands in the region 23,000-25,000 cm^{-1}. These have been photographed (but not measured) with low dispersion. They will be photographed with high dispersion if clear crystals can be obtained.

A compound of quite unusual type $U(OC_2H_5)_5$ has been photographed in thin solid at 77°K. Probably this compound has the actual formula $(U(OC_2H_5))_2$. Films a few tenths of a millimeter thick showed a strong continuous absorption in the green and shorter wave length and other bands further in the red and infra red. Studies of this compound are also being continued.

Table Ab1—Absorption Spectrum of UF_6 (in cm^{-1}) Gas

24364	Bands measured only at 144.5 mm pressure. Very weak. Whole group in question 27°C. (?)	
24440		
24504		
24794		
24860		Bands measured in pressure range 44.7–61.7 mm 12–18°C.
24972		
25108		
25211	somewhat sharper	
25344		
25478		
25538		
25720		
26031		
26175		
26277		
26379		
26573		
26644		
26756		
26935	doubtful	
27015	violet edge of moderately strong absorption	
27135		
27184		
27234	violet edge of strongest absorption	
27343		
27420		
27490		
27568		
27655		
27820	violet edge of strong absorption	
27907		
28080		
28415	center	

Table Ac1 — Fluorescence Bands in UF_6 (in cm^{-1})

22230
22450
22662
22883
23098
23319
23537
23739
23994
24166

Table Ad1 — Fluorescence of $NaUO_2(C_2H_3O_2)_3$ (in cm^{-1})

Temp. 77°K

	16378	
	16427	very faint
(2)	16820	
(1)	16865	
	17240	
	17305	
	17348	
(6)	17457	
(5)	17490	
(4)	17567	
(3)	17593	
(2)	17670	
(1)	17730	head
	17818	
	17965	sharp, narrow
	18080	
	18135	
	18185	
(6)	18293	
(5)	18332	
(4)	18410	
(3)	18434	
(2)	18503	
(1)	18568	head
	18607	very faint
	18619	
	18650	
	18693	
	18732	
	18818	strong, narrow
	18922	
	19040	?
(6)	19143	
(5)	19183	
(4)	19255	
(3)	19285	
	19344	
(1)	19419	head
	19465	
	19540	
	19578	
	19598	
	19662	strong, narrow
	19787	very diffuse center
(6)	19995	
(5)	20037	
(4)	20107	
(3)	20143	
(2)	20201	
(1)	20278	head
	20397	
	20432	
	20459	
	20520	
(6)	20860	
(5)	20885	
(4)	20950	
(3)	20996	
	21037	
	21101	line or red edge
(1)	21130	head
	21250	

Table Ad2—Absorption Spectrum of $NaUO_2(C_2H_3O_2)_3$ at 77°K. (in cm^{-1})

21128	
21253	
21288	
21325	weak
21358	
21394	
21690	
21741	
21823	
21840	
21854	broad band
21962	
22042	
22115	
22152	
22187	
22306	
22401	
22455	
22525	
22560	broad band
22695	
22725	
22768	very strong
22850	
22884	
22914	
23019	
23077	
23116	
23204	
23270	broad band
23404	
23444	
23480	very diffuse
23535	broad band
23637	
23682	
23766	
23814	broad band
23881	
23935	broad band
24124	
24161	
24240	
24239	very strong
24350	
24395	
24473	broad band
24618	
24689	peaks in strong band
24807	
24870	
24957	
25010	strong
25064	
25110	
25183	strong band
25330	
25443	strong
25481	
25582	
25696	
25753	
25916	broad band
26035	
26671	center of diffuse region
27141	first band of 2d spectrum
27737	
27870	
27915	
27981	
28029	
28438	

Table Ad2 — (Continued)

28510	
28565	
28619	
28657	edges of wide line
28685	
28779	
29200	
29257	
29310	edges of wide line
29326	
29368	edges of wide line
29396	

Table Ad3—Absorption Spectrum of $UO_2(NO_3)_2 \cdot 6H_2O$ (in cm^{-1}) at 77°K

20582	
20621	
21253	
21292	
21316	
21354	
21405	
21648	very weak
21973	
22013	
22048	
22088	
22195	
22214	
22360	
22787	
22881	
22906	
23241	
23383	edges of broad band
23423	
23495	
23607	
23943	
24105	edges of broad band
24134	
24302	
24520	edges of broad band
24563	
24806	edges of broad band
24877	
24987	
25327	edges of broad band
25338	
25520	edges of broad band
25567	
26238	edges of broad band
26295	
27249	second spectrum
27397	edges of broad band
27410	
27976	
28027	
28652	
28692	
29395	very diffuse edges
29490	

Table Ad4 — Fluorescence $UO_2(NO_3)_2 \cdot 6H_2O$ (in cm^{-1})

16227	19072 s
16295	19142
16680	19191
17100 s	19247
17173 s	19287
17256	19
17525	19480 s
17773	19512
17859	19559
17940 s	19648 s
18018 s	19727 s
18040 s	19770 s
18115	19820
18212	19850
18237	19882
18276	19939
18383	20348
18418	20386
18624	20435
18685	20471
18654	20514
18793 s	20547
18871 s	20573
18896 s	20601
18977	20635 s
19007	20606 s

s indicates an especially strong line.

Table Ad5— Fluorescence of $NH_4UO_2(C_2H_3O_2)_3$ (in cm^{-1})

19642
19956
20033
20118
20205
20226
20274
20392
20496
20756
20793
20831
20863
20906
20957
21136
21405
21485
21512
21552
21615
21801
22065
22144
22175
22212
22271
22463
22727
22802
22826
22843
22930

Table Ad6 — Fluorescence of $RbUO_2(NO_3)_3$ (in cm^{-1})

16720
16780 head
(17252 probably missed)
17407
17449
17518
17601
17669 head
17728
17793
17902
18145
18273
18317
18375
18472
18539 head
18598
18673
18785
19025
19150
19198
(1 missed)
19351
19420 head
19480 weak
19500 weak
19555 weak
19609 weak
19673 weak
19910
20034
20087
(1 missed)
20235
20310 head
20387
20450
20499
20919
20970
21035
21194 head

Table Ad7—Fluorescence of $RbUO_2(C_2H_3O_2)_3$ (in cm^{-1})

19623	21600	
19938	21686	
20010	21730	
20105	21783	
20257	22050	
20308	22127	
20478	22145	edges of band
20652	22175	
20735	22200	
20778	22260	
20812	22339	edges of band
20848	22352	
20889	22388	
21004	22444	
21063	22708	
21118	22790	
21388	22806	edges of band
21471	22839	
21506	22917	
21542		

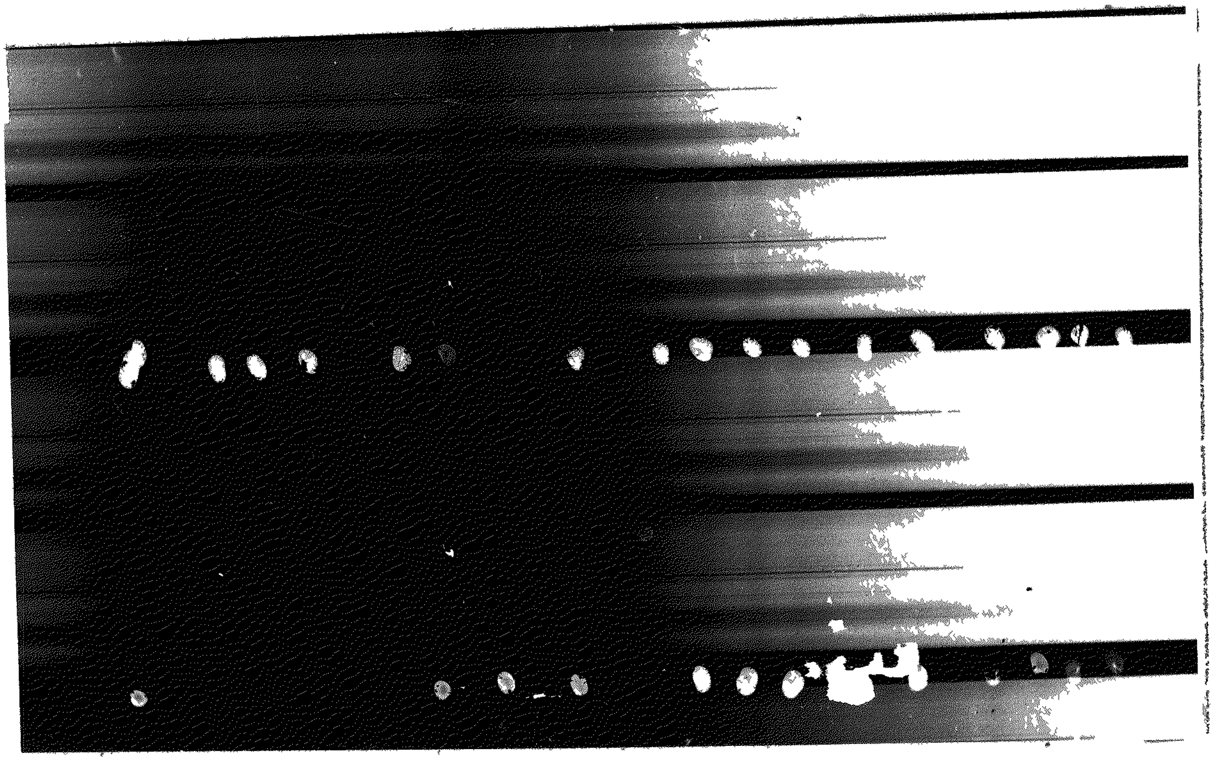


Fig. Ab_1—Absorption of UF_6 (region 24364 cm^{-1} to 28415 cm^{-1}).

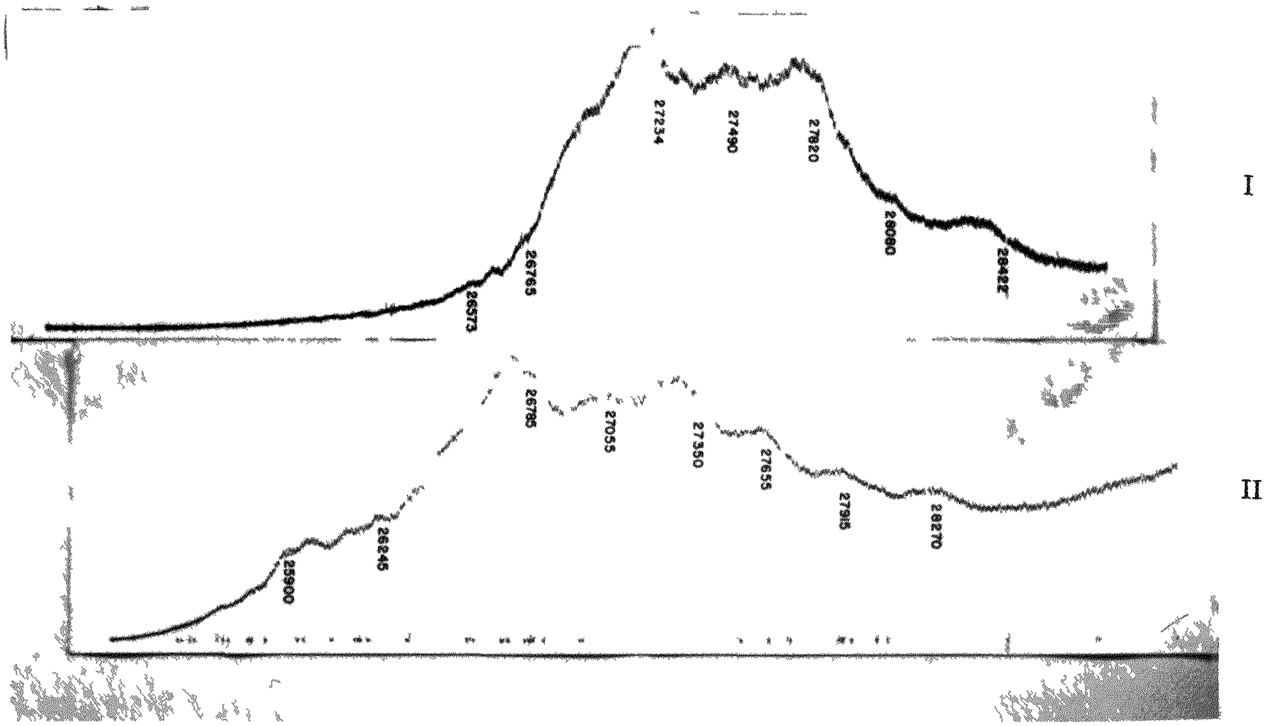


Fig. Ab_2—I, UF_6 vapor. II, UF_6 in Indies Oil, 77°K.

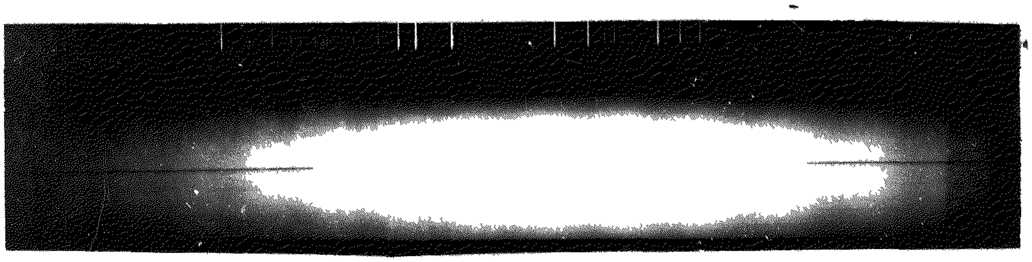


Fig. Ac_1—Fluorescence of Solid UF_6 at 77°K excited by Hg 3660 Å.

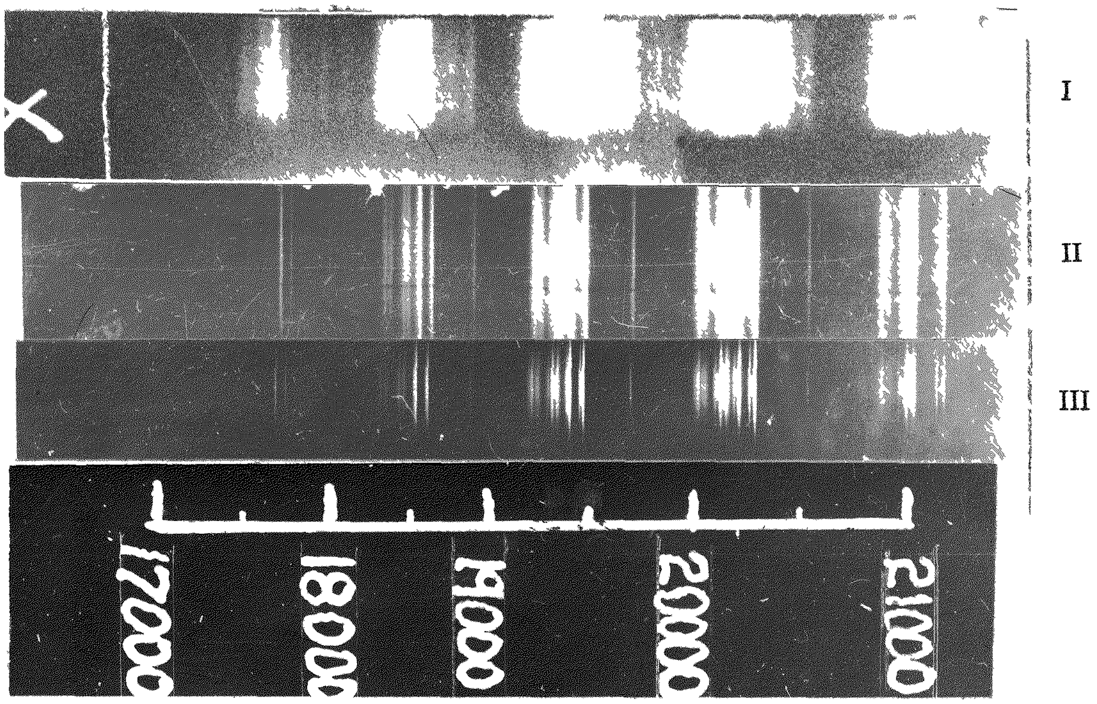
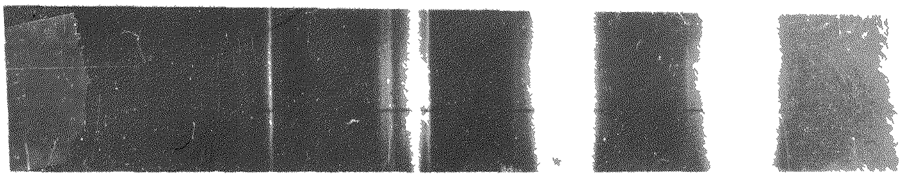


Fig. Ad_1—Fluorescence of $NaUO_2\,(C_2H_3O_2)_3$ I at 172°K; II at 77°K; III at 20°K. Scale cm^{-1}.

Fig. Ad_2—Absorption of $NaUO_2(C_2H_3O_2)_3$ at 77°K.



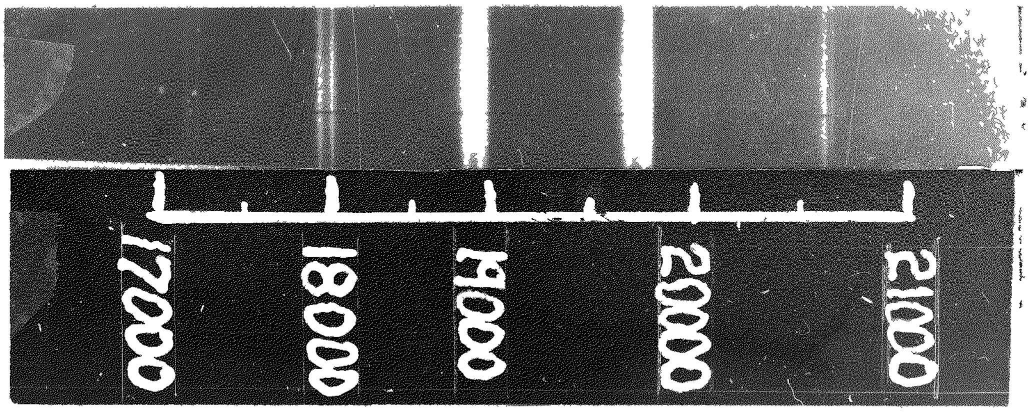


Fig. Ad_3—Fluorescence of $UO_2(NO_3)_2 \cdot 6H_2O$ at 77°K. Only the strongest lines appear.

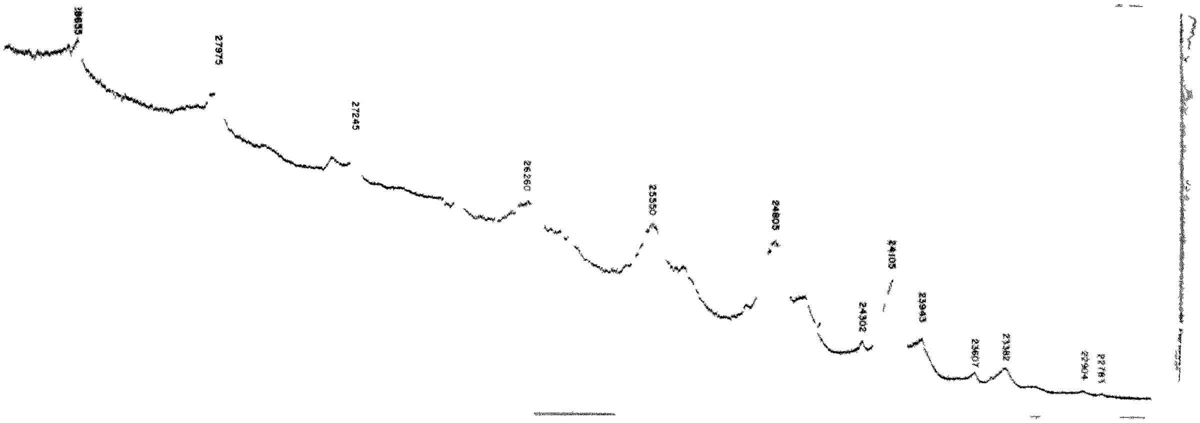


Fig. Ad_4—Absorption of $UO_2(NO_3)_2 \cdot 6H_2O$ at 77°K.

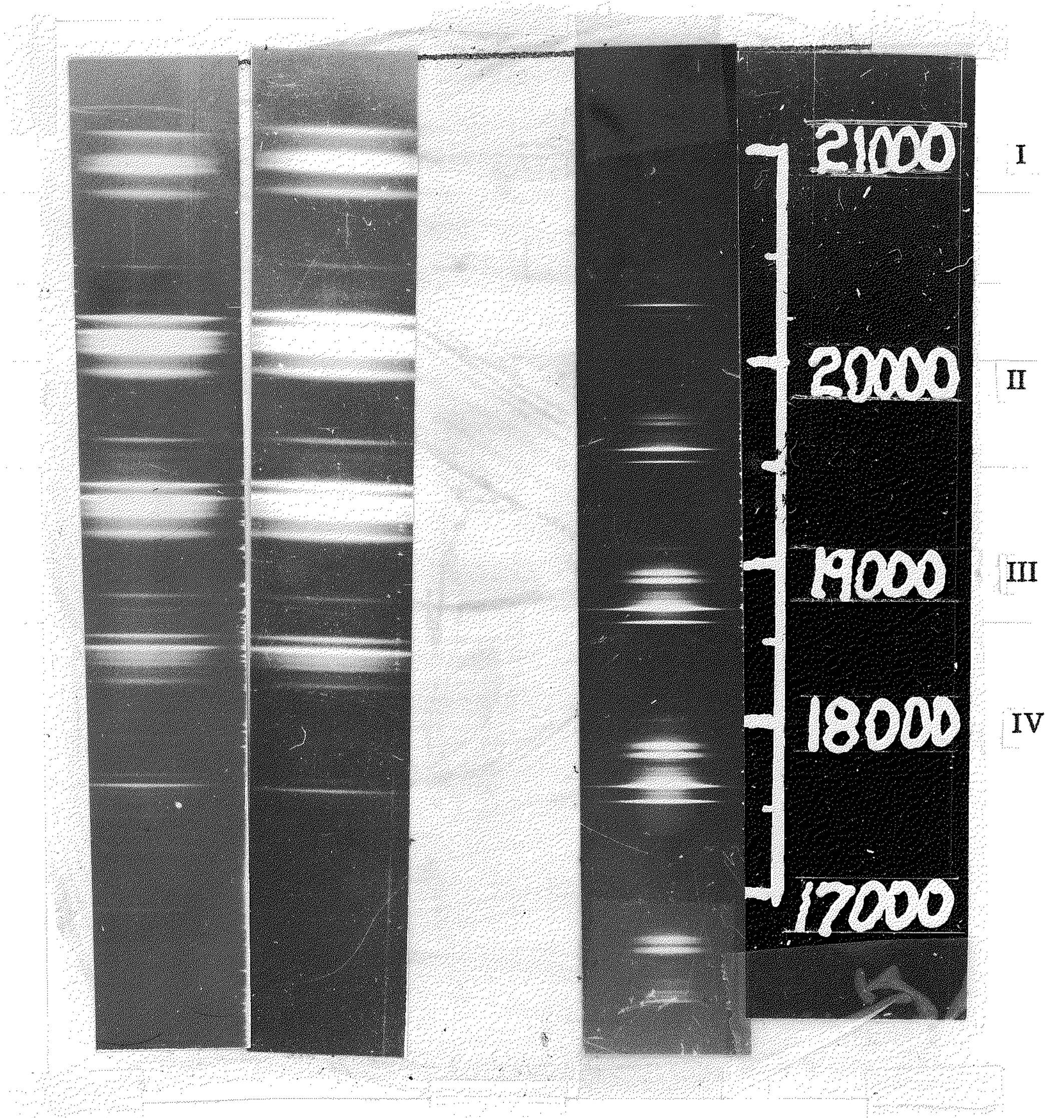


Fig. Ad$_5$—Fluorescence of uranyl salts. I—NH_4 UO_2 $(C_2H_3O_2)_3$ at 77°K. II—Rb UO_2 $(C_2H_3O_2)_3$ at 77°K. III—Rb UO_2 $(NO_3)_3$ at 77°K. IV—Rb UO_2 $(NO_3)_3$ at 20°K.

B. PHOTOCHEMISTRY

a. Gas Phase

1. UF_6 and Perfluorotoluene. The perfluorotoluene available was contaminated by water and unfluorinated material. Unfluorinated material was removed by treatment with UF_6 in a cyclic refluxing apparatus. This procedure is described in the section on Solid Phase reactions. Excess UF_6 and HF were removed from the perfluorotoluene by extraction with water. This product was dried over $CaCl_2$ and then transferred to a vacuum system, where it was allowed to stand over anhydrous KF for several hours. This removed most of the residual water and HF. Traces of water were removed by distilling the toluene on to sodium. The purified material was stored in glass over anhydrous KF and pumped free of gas. Pure uranium hexafluoride was obtained from Priest.

In the early studies, the laboratory was not as well equipped as it is at present. A spark using aluminum, zinc or iron electrodes was employed in some of the work. A 2 K.V.A. transformer was the largest available. An H-3 mercury arc with the glass envelope cut away was also used. For the earliest work, a phototube was used to compare intensities. Later, intensity measurements were made with a thermopile and galvanometer system calibrated against a Bureau of Standards carbon lamp.

A Bauech & Lomb monochromator, f. 4.5 was used to isolate the mercury lines in a few experiments. Later an f 1.9 monochromator became available. Corning filters gave suitable monochromation in some cases.

The first photochemical experiment was done with the aluminum spark. A Corning # 556 blue filter passed a wavelength region extending from 3300 Å to about 6000 Å. This light was collimated through a cell 70 cm long in which the UF_6 and the perfluorotoluene at 25°C, the saturation pressures of the two components being 111 mm for UF_6 and 40 mm for perfluorotoluene.

The first indication of a gas phase reaction was the appearance of the beam passing through the cell. Particles of a reaction product made the beam distinctly visible. A deposit of some white material covered the bottom of the cell after two hours of irradiation. The perfluorotoluene in this experiment apparently was not dry, as some decomposed

UF_6 was present in a side arm on the cell. The excess UF_6, perfluorotoluene and other gases were removed by pumping and water was put into the cell. The reaction product dissolved immediately yielding what appeared to be a solution of U^{IV}.

Two additional experiments with somewhat improved techniques were carried out.

A more systematic study of the reaction, including measurements of the quantum yield at various wavelengths was then undertaken. The galvanometer, thermopile, and standard lamp provided the means by which absolute intensity measurements could be made. To made sure that the absorbing molecule was actually UF_6, absorption measurements were made on the perfluorotoluene at various wavelengths.

At wavelength 3660 Å, perfluorotoluene does not absorb. The light source used was an H-4 mercury arc, filtered by Corning #3860 and #738 filters, which effectively isolate the 3660 Å line.

In the first run, a 20 cm quartz cell was filled by metering in 60 cc of the perfluorotoluene vapor at −10°C and 150 cc of UF_6 vapor at −8°C. The absorption of the mixture at room temperature for the 3660 Å line was about 30% to 32%. The exposure lasted 20 hours, and it was calculated that 1.243×10^{18} quanta were absorbed. 1.95 mg of U as U_3O_8 was present in the reaction product. This gave a quantum yield of 3.40.

A second run at 3660 Å was made in the same quartz cell with 110 mm UF_6 and 0.5 gm perfluorotoluene in the cell. About 70% of the incident light was absorbed. The exposure time was 22 hours. After 16 hours exposure, the absorption rose to 91%. Because of small galvanometer deflections, the measurements were not very accurate. The rate of absorption was about 4.7×10^{13} quanta/sec and 3.7×10^{18} quanta were absorbed during the 23-hour exposure. The analysis gave 4.99 mg U as U_3O_8. The quantum yield was 2.92 from this data.

An f-1.9 monochromater was used to isolate the Hg 3120 line and a Corning #3060 filter removed stray visible light. The 3340 Å and 3660 Å lines were too weak to be photographed.

In the first run, using a 20 cm quartz cell with both UF_6 and perfluorotoluene at 25°C, there was complete absorption. The exposure lasted 16 hours and 40 minutes, 1.47×10^{13} quanta per second being absorbed and giving a total of $.99 \times 10^{18}$ quanta. 1.13 mg of U_3O_8 was found in the tube, giving a quantum yield of 2.45.

The second run was made in a 10 cm quartz cell with both reactants at 25°C. There was complete absorption at 25°C; at −20° the absorption was 36%. This showed that absorption was not due to HF or F_2 inasmuch as these gases are not condensed at the lower temperature. During the 21-hour exposure, 1.75×10^{18} quanta were absorbed and 2.06 mg of U_3O_8 was deposited. The quantum yield was 2.52.

At 2500 Å it was found that perfluorotoluene in a 20 cm cell at its vapor pressure at 25°C absorbs 52% of the incident light. The light source was the spark with the f-1.9 monochromater. This experiment was not completed.

Table I

	I-(U Produced)	P of UF_6	P of perfluorotoluene
3660	3.40	20 mm	30–50 mm.(i.e.) vapor pressure
	2.92	130 mm	30–50 mm at 28°C
3120	2.45	130 mm	30–50 mm
	2.52	130 mm	30–50 mm
2500			

In later experiments, fairly large quantities of the reaction product were collected for analysis. The material was weighed in the absence of air, and the uranium content was determined by the counting method. Three samples were prepared in the following manner: A 200 cc bulb, fitted with a breakseal tube and a seal off side tube suitable for holding the sample during the weighing, was filled with UF_6 and perfluorotoluene at 111 mm UF_6 pressure and 40 mm perfluorotoluene pressure. After about 24 hours at 3660 Å irradiation, each bulb had a thick deposit of reaction product. A small glass bead in each bulb served to roll the compound into balls which could be easily dropped into the sampling tube.

The tubes were weighed, sealed off, cracked open and the reaction product was removed, after which the empty tube was weighed again. Buoyancy corrections were made. Results calculated from a counting method of analysis indicated 72.4%, 85.0%, and 75.1% U_3O_8 in the three samples. This corresponds to 66 ± 5% uranium in the photochemical product.

Both Dr. Hurd and Dr. Hull agree that the uranium in the compound is in the tetravalent state, judging from the color of the solution in water. S. Keihl, in one of the earliest experiments, came to the same conclusion. The only compound of carbon fluorine and tetravalent uranium having 66% uranium appears to be $UF_3 \cdot CF_3$.

Photochemical experiments were conducted using UF_6 as a filter. In these experiments, the photochemical reaction between UF_6 and perfluorotoluene is induced by light filtered through another cell in which this same reaction is proceeding. In the first cell, the light absorbed will be largely that causing $U^{238}F_6$ molecules to react, since these molecules predominate over the $U^{235}F_6$ molecules 120 to 1. If the light is half absorbed, therefore, the ratio of radiation causing the two types of molecules to react is changed by a factor of about 800. Thus, the ratio in the second cell of $U^{235}F_6$ molecules to $U^{238}F_6$ molecules reacting will be much higher than in the first cell.

For this experiment an H-6 1000 watt capillary mercury arc was used. Both of the cells had 55 mm windows; the first cell being 64 cm in length, the second cell, 100 cm. With three lenses a strong beam could be collimated along a 2 meter path through the cells.

The transmission of the pyrex windows was 90%. From this and known absorption data on UF_6, it was calculated that the first cell should absorb 2.5 times as much light as the second cell. The reactants were kept at their saturation pressures at 0°C. The exposure lasted about 50 hours. The time was kept as short as possible in order to reduce the amount of exchange. 13.49 mg of U, as U_3O_8, formed in the first tube and 5.377 mg in the second tube. Counting is still in progress on these experiments.

2. Uranium Hexafluoride and Perfluoroisobutane. In view of the chain reaction found with UF_6 perfluorotoluene mixture, a more detailed study of this vapor phase photolysis seemed necessary. Perfluorotoluene was replaced by perfluoroisobutane since a much wider range of pressures could be studied.

UF_6 was metered in a magnetic stopcock metering system of 416 cc volume. The vapor pressure was varied between 17 and 110 mm. Because of slight leakage of the magnetic stopcocks of the metering system, the exact amount of UF_6 in a given sample was subject to as much as 10% error, but it is expected that chemical analysis of unreacted UF_6 will yield exact values of the pressures used in individual experiments.

The perfluoroisobutane samples were metered in a system of 425 cc volume. Pressure measurements were made on a capillary manometer. Using this system, with pressures of from 17 mm to 850 mm, samples of 425 cc volume were accurately taken. The error was very small.

The UF_6 used in these experiments was obtained from Priest and had been purified by a 60 plate distillation.

The perfluoroisobutane was purified by standing over anhydrous KF is a well evacuated and flamed system, and by subsequent distillation on to a sodium mirror.

The cells used in these experiments were of pyrex and were 20 cm long with windows of about 5 cm diameter, with a total volume of about 400 cc. Blank cells, similar to the reaction cells were used.

An H-4 G. E. mercury arc was used as a light source. This had a variable resistor in the secondary of the arc transformer to vary the intensity of the arc. All runs were made at constant absorbed intensity. Corning filters #738 and #3860 were employed. Photographic plates showed that these filters transmit less than 1% of light other than 3660 Å.

The light intensities were measured with a thermopile whose receiving plate was 1.5 cm long and 0.2 cm wide. The thermopile was mounted on a travelling device, allowing for the measurement of light intensities of beams that were more than 0.2 cm wide. The thermopile was checked quite frequently against a standard lamp, usually before and after each experiment.

The galvanometer used in conjunction with the thermopile has a sensitivity of 0.36 μV/mm when the scale is a distance of 1 meter.

In these experiments, which were all conducted at room temperature, previously prepared samples of UF_6 and perfluoroisobutane were mixed and then distilled into well flamed reaction cells. This procedure left behind any decomposed U formed when the reactants were mixed. After exposure, the unreacted UF_6 and perfluoroisobutane were frozen into a side tube by liquid air. This tube was subsequently sealed off from the cell.

The reaction product, a white powder which coated the lower sides of the cells, was analyzed for uranium as U_3O_8. This product has been found to be extremely pure and to be very readily dissolved by HNO_3.

Although final conclusions cannot be drawn from the experimental data at hand, a few tentative statements concerning the mechanism of the reaction may be made. First, the quantum yields certainly indicate a chain reaction. Second, the length of the chain depends upon the pressure of the perfluoroisobutane.

The fact that the quantum yield continues to increase with large increases in the pressure of perfluoroisobutane may indicate that organic radicals formed are recombining largely at the walls. This would indicate that these radicals have an exceedingly long lifetime and would have to undergo three body collisions which are relatively inefficient. A necessary conclusion would be that the chain-carrying steps are inefficient collision processes. This would account both for the pressure sensitivity of the quantum yield at such high pressures and the associated long lifetime of the intermediates. Thus the chain-carrying radicals must be stable fragments, probably of high molecular weight with considerable possibility of being stabilized by resonance. Such a chain carrier in the perfluorotoluene reaction might be C_6F_{11}.

Present indications are that the quantum yield does not depend strongly upon the pressure of UF_6. One is led to assume either that the initial collision of excited UF_6 and perfluoroisobutane is highly efficient or that the chain is long.

It is evident that very low pressures and possibly lower temperatures are necessary in order that the gas reaction be successful. The use of packed vessels may be of great aid in reducing chain lengths, which must be done to avoid exchange of isotopes.

It is possible that some of the UF_6 bands in the 3660 Å region might arise from, or be enhanced by, the nuclear magnetic moment of the U^{235}. To test this point, a series of experiments have been undertaken in the region 3500 Å to 4000 Å. Using an iron spark activated by a 10 K. V. A. transformer, an intensity of approximately 5×10^{13} q/sec could be obtained with an f 1.9 monochromator. The spectral width of the exit beam was about 75 Å. Since exceedingly long exposures were required, a thermostating arrangement about the cell was used to reduce the thermal reaction.

Unfortunately, rather high pressures of reactants are necessary because of the extremely weak absorption of UF_6. Two experiments have been made, but isotopic analyses are not yet complete.

b. Liquid Phase Study

Although liquid phase reactions were not of interest as far as isotopic fractionation is concerned, they were useful as reference points in evaluating the photoactivity of the fluorocarbons at low temperature.

Table II—Summary of Data on UF_6–Perfluoroisobutane Photochemical Reaction at 3660 Å 20 cm Cells

Run No.	Approx. P_{UF_6}* mm	P_{PFisoB} mm	Ia/sec (quanta/sec) ×10^{13}	Hours exposure	Ia (quanta) ×10^{13}	% absorp. by UF_6	U_3O_8 (mg) analysis of product (Hull)	UF_6 decomposed (corrected for blank) g	Mols UF_6 decomposed (corrected for blank) ×10^{-5}	Molecules UF_6 decomposed (corrected for blank) ×10^{13}	Quantum yield Φ	% UF_6 photo chem decomp	Total % UF_6 decomp
1	15	860	7.04	6.0	15.2	15	16.28	0.0089	2.52	15.2	10	7.9	20
01		860					9.2						
2	106	860	6.75	10.93	26.8	68	11.36	0.01195	3.4	20.4	7.6	1.5	1.8
02		815					1.82						
3	106	97	6.7	16.17	3.9	68	4.72	0.00523	1.487	8.95	2.3	0.85	0.74
03		99					0.55						
4	12	17	5.1 ± 0.5	15.0	2.76 ± .26	12	2.59	0.00264	0.749	4.5	1.65 ± .15	2.9	3.6
04		16.4					0.49						
5	27	101	8.37	8.37	2.52	25	3.32	0.00323	0.93	5.6	2.2	1.6	2.1
05		99					0.71						
6	43	16.7	7.15	16.27	4.19	39	4.72	0.0053	1.5	9.05	2.2	1.5	1.7
06		15.7					0.5 + ca						
7	34	17.4	6.06	15.45	3.37	59							
07		17.5					1.21						
8	32	375				29 at start							
9	27	102	7.4	2.72	7.23	26							
09		102											

*Values of P_{UF_6} determined by the % absorption in a 20 cm cell and the absorption coefficients, $\alpha = 5.35 \times 10^{-4}$/cm/mm pressure. This reduces to $P_{UF_6} = (-1aT/\alpha 1) = -93.5$ la T, T = fraction of light transmitted, 1 = length of cell (20 cm).

Values of UF_6 pressures calculated from use of absorption P_{UF_6} = pressure of UF_6 data agree quite well with expected values of P_{UF_6}. However, chemical analysis of unreacted UF_6 will give more checks.

+Blank lost in handling: the value 0.5 mg for the blank taken from considerations of blanks *03 and 04.

Note: the 0 before a number indicates blank.

Three liquid phase photochemical reactions between fluorocarbons and UF_6 have been completed. The fluorocarbons were purified and treated with UF_6 according to the methods given in the solid phase discussion. The solutions were divided into two equal parts. One was poured into the reaction cell; the other served as a blank. All work was done under vacuum.

Light was obtained from a G. E. H-4 mercury arc and was monochromated at 3660 Å with Corning glass filters #5860 and #738. A linear thermopile having a surface area of approximately 30 sq. mm. was used. This thermopile was calibrated and used according to the Bureau of Standards specifications. The cells were of Pyrex, cylindrical, 25 cm in diameter and 2.5 cm long.

During the irradiation, a solid reaction product was formed in all cases. With perfluoroheptane, the solvent and UF_6 were rapidly distilled off, leaving the end-product. In the case of perfluoro Indies Oil, as much UF_6 as possible was pumped away; the solid and product was centrifuged and the liquid poured off.

The results are given in the following table:

Exp. No.	Solvent	Temp. min	Time	Total quanta absorbed	Total molecules formed	
C 3 L	Perfluoro Indies Oil	26°C	969	2.0×10^{19}	1.5×10^{19}	0.75
C 9 L	Perfluoro-heptane	26°C	868	2.08×10^{19}	1.4×10^{19}	0.703
C 12 L	Perfluoro-heptane	26°C	148	3.4×10^{18}		approx. 1

For some reason the blank in C 12 L was very high. The product was certainly not present before the evaporation. However, the direct uncorrected quantum yield computed from the amount of end-product in the reaction cell was 2.2. Since the previous runs showed the thermal reaction to be about equal to the photochemical reaction, quantum yield of 1 may be very reasonable.

c. Solid Phase Study

1. Uranium Hexafluoride and Perfluorocarbons. Several fluorocarbons were obtained from the Libby group. These were perfluorotoluene, perfluoroheptane, and several perfluoro Indies Oils. Indies Oils are high molecular weight branched carbon compounds with low volatility. Since glassing compounds were desirable for low temperature work, the Indies Oils were the only usable fluorocarbons. They have glasses with some shattering. Perfluorotoluene and perfluoroheptane could not be made to glass.

Treatment of these fluorocarbons with UF_6 showed they were either insufficiently fluorinated or contained traces of water. The latter difficulty was removed by drying with sodium; the former required that the fluorocarbons be given some preliminary treatment with UF_6.

The low boiling fluorocarbons such as perfluorotoluene and perfluoroheptane were further fluorinated by cyclic refluxing with UF_6 (see Figure 1). The resulting mixture was treated with water; the fluorocarbon was separated and dried over KF. The partially dried fluorocarbon was distilled under vacuum into a tube containing a sodium mirror. A further distillation from this tube into the reaction cell completed the purification process. The high boiling fluorocarbons were treated with UF_6 using a low boiling fluorocarbon as a refluxing carrier. The method is best described by reference to Figure 2. The high boiling and low boiling fluorocarbons were poured into A through B. Uranium hexafluoride was frozen in under vacuum at A and then B was sealed off leaving a small tube to catch residue from the reaction. The mixture was refluxed using in the boiler a liquid whose boiling temperature caused rapid reflux. In most cases cellosolve acetate boiling at 156.8°C was used in the boiler. The low boiling fluorocarbon condensed and dripped on the cold finger D dissolving UF_6 which had collected on it. This solution ran back into the tube A and mixed with the high-boiling solvent, resulting in reaction. The solution obtained by this operation was treated with water; the fluorocarbons were separated and partially dried with KF. The fluorocarbon mixture was then pumped to remove the low-boiling fluorocarbon. The high boiling fluorocarbon was slowly distilled on to sodium to remove the last traces of water and finally poured, under vacuum, into the reaction cell.

The absorption spectra of the purified perfluorocarbons were photographed. The results are given in the following table:

Compound	State	Temp.	Type of cell	Absorption
Perfluorotoluene	Liquid	25°C	Quartz	None to 2500°A; limit of plate
Perfluoroheptane	Liquid	25°C	Pyrex	None to 3000°A; pyrex limit
Perfluoro Indies Oil (G. D. 727A)	Liquid	25°C	Pyrex	None to 3300°A; weak to 2900°A
Perfluoro Indies Oil (G. D. 727A)	Solid	−180°C	Pyrex	None to 3300°A; weak to 2900°A

An absorption photograph of a glass composed of UF_6 in perfluoro Indies Oil G. D. 727A was taken. Banded absorption in the region of 3660°A was found. A hydrogen discharge tube and the Hilger quartz spectrograph 484 were used throughout. The glass was quite shattered; however it transmitted enough light for the photograph.

The solubilities of UF_6 in the perfluorocarbons were determined by the use of a metering system involving ground glass magnetic valves. The metering system is shown in Figure 3. The pressure of the UF_6 in the metering system was maintained by thermostating the UF_6 reservoir. The temperature, system volume, and the vapor pressure of UF_6 being known, the weight could be calculated from the gas law. The accuracy was better than 10%. Solutions were prepared for photochemical study in a clear Dewar cell with plane pyrex windows (see Figure 4). The distance between the windows in the cell was 1 cm. Low concentration of UF_6 in the Indies Oil were necessary to prevent complete shattering of the glass. About 0.3 g UF_6 in 5 cc Indies Oil gave a glass which shattered only to a small extent.

Radiation from a G. E. H-4 mercury arc was used; monochromation was accomplished with Corning glass filters #3860 and #738. No attempt was made to determine the amount of absorption since scattering through the shattered glass was very great. The solid solution was irradiated for 12 hours with about 5×10^{14} quanta per sec.

The solid solution fluoresces strongly. A photograph of the fluorescence taken with the Hilger quartz spectrograph 484 showed bands between 4100°A and 4300°A. There was no photochemical reaction discernible, the solution being perfectly clear when brought to room temperature.

2. Search for Rigid Solvents. The requirements for a glassy rigid solvent have been given in Part B. Experiments having shown that solutions of the fluorocarbon and UF_6 were inert at −180° towards light, a systematic study of the vitreous state was made. The results of this survey are given below in some detail.

The Vitrification of Organic Compounds

The most extensively measured thermodynamic property of glasses is the specific heat. Most of the $C_p - T$ curves of glasses which have been obtained to date have the same general characteristics, regardless of the type of molecule. (See Fig. 1). Starting from very low temperatures, the $C_p - T$ curve for the glass is slightly higher than the curve for the corresponding crystal. At some distance below the softening region of the glass, there is a rapid increase in C_p in a range of 10–20°. The curve then rises continuously to join that for the supercooled liquid. In some glasses, crystallization takes place during, or after, the transition so that the C_p curve returns to the low value characteristic of crystals. These general features of $C_p - T$ curves have been verified for the simple monohydric alcohol glasses and polyhydric alcohol glasses by Parks and Huffman, J. Phys. Chem., 31, 1842 (1927), 32, 1366 and Kelley, J. Am. Chem. Soc. 51, 781 (1929), for all the noncrystallizing octanols by Cline and Andrews, J. Am. Chem. Soc. 53, 3668 (1931), for hydrocarbons by Huffman, Parks, and Thomas, J. Am. Chem. Soc. 52, 3241 (1930), for mixtures of alcohols by Parks, Thomas, and Gilkey, J. Phys. Chem. 34, 2028 (1930) and for several other compounds by Parks, Thomas, and Light, J. Chem. Phys., 4, 64 (1936) and Ferry and Parks, Thomas, and Light, J. Chem. Phys. 4, 64 (1936) and Ferry and Parks, ibid. 70.

Mixtures of two glass forming substances form a glass having a C_p transition about midway between the transitions of the components and occurring over a temperature range about twice as great as for the pure substances. In a ternary mixture of polyhydric alcohols this same general behavior was found, but considerable hysteresis occurred at the transition point.

Contributing to the uncertainty in C_p measurements on glasses is the low thermal conductivity in certain temperature ranges and the variable character of the aggregate depending on its thermal history. As regards the first, Parks and Thomas, J. Am. Chem. Soc. 56, 1423, (1934) obtained a $C_p - T$ curve for alpha-d-glucose which had a sharp hump at the top of the transition rise, and the transition occurred 25° higher than should have been expected from previous work. They attribute most of this difference to the fact that measurements were made much more rapidly in their experiments so that thermal equilibrium may not have been reached. Parks and Huffman, J. Phys. Chem. 31, 1842 (1927) found that propylene glycol glass which had been formed rapidly had a specific heat about one percent higher than the glass formed by slow cooling. However, with uniformity in thermal treatment, all $C_p - T$ curves for glasses which have been studied have the same general characteristics regardless of the polarity or shape of the molecule.

The thermal conductivity as a function of temperature has been estimated from the time required for a calorimeter to reach equilibrium in the C_p measurements, (Parks and Huffman, J. Phys. Chem. 31, 1842, (1937)). In the transition region the equilibrium time in a typical experiment on propylene glycol rose from 4 min. to 30 min. and shortly thereafter fell to 7 min. Except in this range, the conductivity is about the same as for the crystal. This sudden rise in the time necessary to reach equilibrium might well explain the humps on top of the C_p transitions which are sometimes observed.

Several investigators have made dilatometric measurements of the coefficient of thermal expansion. All agree that with increasing temperature a sharp rise (200 to 300% in a few degrees) occurs in the vicinity of the C_p transition. Parks and Huffman, J. Phys. Chem., 31, 1842, (1927) working with propylene glycol, glycerine, and glucose, find the rise a few degrees above the C_p transition and from 3 to 30° below the beginning of the softening range.

The viscosity of a liquid increases as the temperature falls. In a case of a vitrifying liquid, there is a region of rapidly increasing viscosity usually occurring 10° to 20° above the C_p transition region.

A viscous liquid does not necessarily form a glass. For example, cetyl alcohol, which is quite viscous just above its melting point, does not glass, but always crystallizes. On the other hand, 3-methyl-hexane, which is quite fluid at ordinary temperatures, always forms a glass. These facts and a consideration of the thermo- dynamic properties of glasses brings us to consider the mechanism of glass formation.

In a glass, the molecules are oriented almost entirely at random, as shown by X-ray work. (Miller, Phys. Rev. 47, 813, (1935), and Warren, J. Appl. Phys. 8, 645 (1937)). X-ray studies of liquids reveal local order of a type characteristic of the forces between molecules and of the shape of the molecules. In the transition to the solid phase, a certain amount of reorientation will ordinarily take place, depending upon how different the liquid structure is from the crystal structure.

The local ordering of some substances in the liquid state resembles closely the arrangement in the crystal lattice; the molecules of these compounds will suffer a minimum amount of reorientation on crystallizing. The entropy change for the transition to the crystalline state is not unfavorable and glass formation is unlikely. The molecules in this class are the spherical, or nearly spherical, and the rodlike or straight chain molecules. In the case of an asymmetric molecule, where efficient packing in the liquid state does not correspond to the arrangement in the crystal lattice, the entropy decrease is greater and a glass is more likely to form. Let us now consider the importance of viscosity. As a measure of internal friction, one would expect that it would hinder the reorientation of asymmetric molecules and promote glassing. But in the case of cetyl alcohol where reorientation does not have to take place, the viscosity is of no importance. The ability of a liquid to supercool is an important factor in glassing as it increases the viscosity. According to Ferry and Parks, J. Chem. Phys. 4, 70 (1936), the temperature of the transition in the thermal properties of a wide variety of substances which will glass, is generally that temperature at which the visocsity is about 10^{13} poises; hence if a liquid can be supercooled to reach this viscosity a glass will almost certainly form.

The rather sudden transition in the thermal properties of substances which glass indicates fundamental molecular changes. Translational motion decreases as is shown first by the increased viscosity, then by the drop in the coefficient of cubical expansion; rotational motion gradually becomes frozen during the C_p transition which occurs several degrees lower. Much more information on these points is given by the dielectric constant and dispersion measurements.

The dielectric constant-temperature curves (e-T curves) resemble the $C_p - T$ curves in some respects. The curve for the glass at low temperatures changes slowly with temperature, as it is dependent on atomic and electronic polarizations only. The values are of the order of 3 or 4 units. At about the temperature of the C_p transition, the e value increases several hundred percent and joins continuously into the curve for the super-cooled liquid. Anomalous dispersion in the transition region is high, but above and below, there is no anomalous dispersion at least up to 50 kc. The absorptive part of the dielectric constant is derived from the data in the transition region. Sometimes the glass crystallized during the transition when the temperature is rising. This is indicated by a more or less sharp drop to the low value characteristic of crystals. When the melting point is reached, a sharp rise to the high value for liquids occurs. These general features of e-T curves have been verified for halogenated hydrocarbons by Turkevich and Smyth, J. Am. Chem. Sec. 62, 2468: 64, 737; Baker and Smyth, J. Am. Chem. Soc. 60, 1229, 61, 2063, 2068, for camphanes and other complex organic molecules by White and Bishop, J. Am. Chem. Soc. 62, 8, for glucose by Thomas, J. Phys, Chem. 35, 2103.

The dielectric constant measurements of Turkevich and Smyth, J. Am. Chem. Soc., 62, 2468, on the methyl chloromethanes, which do not glass, show why many molecules crystallize rather than glass. These compounds are methanes with either Cl or methyl substituted for the four hydrogens. No anomalous dispersion was found for any of these compounds. They crystallize sharply, or with a few degrees of supercooling, to isotropic crystal (as shown by the polarizing microscope). The e value for the liquid rises linearly with falling T until the F. P. is reached. There is no sharp drop at the freezing point, however, but only a decrease in the slope of the curve. Some distance below the freezing point there is a sharp drop to the low value usually found for crystals, and no dispersion up to 50 kc is found here. The polarizing microscope shows that the low temperature crystal is anisotropic. Whereas, the heat of fusion is low, the heat of the second transition is of the same order as the heat of fusion for many other molecules. These results are interpreted as follows: The nearly spherical molecules rotate freely in the liquid state. On freezing, the molecules still rotate in the cubical lattice as shown by the fact that the heat of fusion is very low, and the molecules still follow a 50 kc field. The lower transition is the point where rotation ceases. The molecules acquire a definite orientation as shown by the change from an isotropic to an anisotropic lattice. Thus a molecule which can rotate in the crystal will never form a glass, but if the molecule is altered in some way such as by adding a methyl group to tertiary butyl chloride to form tertiary amyl chloride, the rotation is hindered sufficiently so that a glass can be formed. Further support to the interpretation is given by the fact that the variation in the temperature of the lower transition points with the changing structure of the methyl chloromethanes resembles the variation in melting points with similar structural changes in molecules which do not rotate in the crystal lattice. The melting points of the methyl chloromethanes do not have any such variation with structure.

The dielectric constant curves for glasses interpreted on this basis indicate that there is a gradual immobilization of the dipoles of the substance in the glassy state rather than a sudden cessation of rotation. The dispersion curves show that at the higher temperatures in the transition, the molecule cannot follow a 50 kc field, but can follow a 5 kc field. As the temperature drops, the relaxation time increases and dispersion occurs for even a .5 kc field, after which there is apparently complete rotational freezing.

To summarize—very symmetrical molecules which form cubic lattices, and especially those which exhibit rotational freedom in the crystal comparable to that in the liquid, go into the crystal lattice with a minimum of reorientation and hence do not tend to supercool or glass. Rod-like molecules, although they often form viscous liquids, are probably locally arrayed parallel to each other in the liquid state, as any other orientation would require a larger volume and hence be energetically unfavorable. Therefore, the molecules of these substances do not have to be reoriented to form the crystal. X-ray data on n-heptane confirms these conclusions. The efficient but random packing of moderately asymmetrical, pear-shaped molecules permits them to remain in the liquid arrangement below the melting point and hence to supercool and glass.

Baker and Smyth, J. Chem. Phys., 7, 574 (1939), have given a simple theory of the mechanism of orientation in isobutyl bromide and isoamyl bromide glasses. From dispersion data (Baker and Smyth, J. Am. Chem. Soc., 61, 2068) they calculated the mean relaxation time γ at the temperature of maximum dispersion. Using the reciprocal of this as the rate constant for a unimolecular reaction, they relate $1/\gamma$ to the activation energy of reorientation of the molecule by means of the simple Arrhenius equation: $1/\gamma = k' = Ce^{-A}/RT$ A/R values result when log γ is plotted against $1/T$. To evaluate the steric factor C in the Arrhenius equation, the equation derived by Eyring for a unimolecular process is introduced:

$$k = \frac{KkT}{h} = -\Delta F/RT = \frac{KkT}{h} e - \Delta S/Re - \Delta H/RT$$

The quantity ΔH is taken as the activation energy A, of the process and by comparison is related to the entropy of activation.

The entropy of activation calculated from this equation is quite large, being 167.1 eu per mole for isobutyl bromide and 106.1 eu per mole for isoamyl bromide. In the liquid, this entropy of orientation is small. This is interpreted to mean that in a glass many molecules must cooperate in permitting the reorientation of one. The activation energies in the glassy state, however, are probably not much different from those in the liquid state. At first sight it would appear that the heat of activation for isobutyl bromide (23,000 cal./mole) should be lower than that for isoamyl bromide (18,000 cal./mole). However, the elongated pear shape of the isoamyl bromide may tend to make it rotate preferentially along its long axis. This is supported by the magnitude of the activation energy of viscous flow for the compounds. According to the concepts of Eyring, since viscous flow occurs with the least amount of extra volume, the energy of vaporization, which requires the volume of a whole molecule, will be greater than the activation energy of viscous flow. For rod-like molecules, this ratio is around 4 and for more nearly spherical ones, it is around 3. For isoamyl bromide, it is found to be 4.3 and for isobutyl bromide, 3.5. This result agrees with what we would expect from the molecular structure.

The relative importance of the various factors in glassing can be determined qualitatively by a review of the compounds which form glasses. From this one ought to be able to predict the glassing properties of other compounds with some accuracy. The properties of the molecules of a substance which give it a tendency to vitrify are (1) the presence of asymmetric carbon atom and the possibility of heating a slightly differing steric forms of the same molecule: (2) a moderately asymmetric shape, such as a pear shape; and (3) hydrogen bonding extending over several molecular diameters. Long chains strongly oppose these factors. The type of group causing the asymmetry is also important, and a group may be more important for glassing in one compound than it is in another. It is difficult to account for the glassing or crystallizing tendency of some compounds with the reasons given above. Hence, there may be other factors, or a more quantitative study of the molecule may be necessary. In our qualitative estimation of the glassing tendency, we must remember that the entropy and activation energy of reorientation in the theory of Baker & Smyth are the quantities which ultimately determine this tendency.

The accompanying Table gives data on the glassing of many compounds. The ones which cannot be crystallized at all usually have an asymmetric carbon atom, but 2-methyl pentane, 3-methyl pentane and 4-methyl heptanol-4 are exceptions.

The octanols 1 through 4 are easily crystallized, showing that the effect of the OH group in causing asymmetry and hydrogen bonding is masked by the effect of the long chain. The lower alcohols, ethyl and n-propyl, glass more easily.

The chloro-methyl methanes compared with the chloro-methyl compounds having the shape of t-amyl chloride, illustrate the fact that the same groups may have a different effect in a different molecule. The first group of compounds is formed by replacing the Cl in CCl_4 with methyl groups. All these from CCl_4 to neopentane are crystalline and show rotational freedom in the crystal. Hence their symmetry is very high, and it appears that the Cl group has about the same size as the CH_3 group. If we add another CH_3 to neopentane, 2,2, dimethyl butane is formed. This also shows rotational freedom in the crystal. Replacing CH_3 with Cl, as in the other group of compounds, we would expect to find rotational freedom in all the members. However, t-amyl chloride does not have the characteristic low temperature transition of rotating molecules, and 1,2 dichlor isobutane, the next member, invariably glasses.

There are other similar cases. 2-methyl butane crystallizes, but if the end CH_3 group is replaced by Cl or Br, the resulting isobutyl halide glasses easily. In contrast to 2-methyl butane, 2-methyl pentane invariably glasses. Isoamyl chloride, formed by replacing the end CH_3 with Cl, is very difficult to glass. However, isoamyl bromide glasses quite readily. Evidently, a very small change in force fields or the size of a group is sufficient in some cases to cause a large change in the glassing properties.

It is interesting to note that 2-methyl hexane crystallizes while 2-methyl heptane glasses. Thus, we have four members of the homologous series of 2-methyl paraffins. The ones with an even number of carbons cannot be crystallized, while the ones with an odd number of carbons cannot be glassed. This bears out further the statement made at the end of the last paragraph.

Polyhydroxy compounds such as glycerine, propylene glycol and glucose glass easily. Hydrogen bonding is probably responsible for most of the glassing tendency. dl-lactic acid can be vitrified easily. It contains an asymmetric carbon atom and, in addition, there must be extensive hydrogen bonding in the liquid. The fatty acids cannot be glassed although there is strong hydrogen bonding in the liquid. However, it is probable that there is a strong dimerizing tendency so that the hydrogen bonding does not extend beyond a molecular diameter.

Ethyl cyclobutane, which glasses very easily, shows the effect of the side chain. The molecules of cyclobutane itself probably rotate freely in the crystal, but the ethyl side chain prevents a rotation. Many other hydrocarbons of this type show a strong tendency to supercool. Data on whether or not the glass is lacking. Some of them mentioned by Smittenburg, Hoog & Henkes, J. Amer. Ch. Soc. 60 17 (1938) are isopropyl benzene, methyl cyclopentane, methyl cyclohexane, toluene, and isopropyl cyclohexane. The unsubstituted rings all appear to have rotational freedom in the crystal.

There are many compounds which strongly supercool but do not glass. Some are 2-methyl hexane, 2,2 dimethyl pentane, 2,4 dimethyl pentane, 2,5 dimethyl hexane. Isoamyl chloride can be made to glass by plunging into liquid air, but will ordinarily crystallize after 26° of the supercooling. Although some of these compounds are more symmetrical than those which glass, it is obvious that superficial symmetry considerations do not enable one to predict the glassing properties with accuracy. More highly symmetrical compounds, such as 2,2 dimethyl butane, 2,3 dimethyl butane, 2,2,3 trimethyl butane, 2,2,3,3 tetra methyl butane, neopentane, t-butyl ethylene, carbon tetrachloride and 2,2 dichlor propane go over to the crystal with very little or no supercooling and low heat of fusion. These retain rotational freedom in the crystal lattice.

The compounds discussed here are limited to the hydrocarbons, halides and alcohols. These are the only classes of compounds whose glassing properties have been studied very extensively, with the exception of a few studies on camphanes, piperine, etc. Practically none of the olefins, aliphatic amines, aromatic amines, nitro compounds, naphthalenes and other condensed ring systems, aldehydes, ketones, acids and other compounds with several of these groups have been studied. It is to be expected that aromatic amines and nitro compounds will crystallize much more readily than glass, because of the strong orienting effect of the NH_2 and NO_2 groups. For instance, nitrobenzene would be much more difficult to glass than toluene. The potential energy of the molecule would be but slightly affected by the orientation of a methyl group, while the presence of a nitro group would make some orientations energetically much more favorable than others.

The same conclusion can be drawn regarding most of the other types of compounds listed.

3. Reaction of Uranium Hexafluoride with Freon Type Compounds. Solutions of uranium hexafluoride in several Freon type compounds have been prepared. Generally these solutions are thermally unreactive in the liquid phase at the melting point. The solid solution has been found to be photochemically reactive at liquid nitrogen temperature in all but one case.

Before carrying out these experiments it was necessary to investigate the physical properties of these Freon type compounds. The glassing temperature and freezing point were investigated first. For some of these compounds the melting and boiling points were supplied by Miller. A cryostat was constructed and used to investigate the glassing properties and glassing temperatures. The data in Table 3 under the heading m.p. and b.p. is that supplied by Miller. The data on glassing properties is from our observations.

The cryostat consisted of a copper block suspended in a Dewar flask. Liquid nitrogen was pumped through a glass tube passing through the block. A small coil of wire covered with sodium silicate and alundum cement served as a heater to evaporate the nitrogen. The block fitted inside of the Dewar snugly and the evaporated nitrogen passed out through a series of baffles in the copper block, thus cooling the block efficiently. By varying the voltage applied to the heater, the rate of evaporation was regulated. Changing the rate of evaporation and the height of the liquid nitrogen in the Dewar flask, made it possible to control the temperature of the copper block. A copper-constantan thermocouple used in conjunction with a potentiometer served to measure temperature. A twenty mm tube containing the pure compound was placed within the copper block and the solidification observed through a pair of windows as the block was slowly cooled from room temperature to liquid nitrogen temperature. The possibility of obtaining a glass on slow cooling and the temperature at which solidification occurred were observed. A diagram of the copper block is shown in Fig. 5.

If the uranium hexafluoride is to be activated photochemically in the Freon solution, it is desirable that the Freon itself should not absorb light in the neighborhood of 3660 Å. The absorption spectra of those Freons which can be made to glass and which are therefore suitable for photochemical tests were photographed at room temperature. A tungsten light source and a Hilger 484 small quartz spectrograph were used.

Table

Compound	M. P. °C	B. P. °C	Transition region °K	Temp. of mech. rigidity °K	References
ethyl alcohol	−117.3	78.5	90−95 crystallizes at 95		3, 4
n-propyl alcohol	−127	97.1	92−105	107	3, 4
n-butyl alcohol	−89.2	117.7			
sec-butyl alcohol	−89	99.5	100−120		5
isobutyl chloride	−131.2°	68.85	93−113		1
isobutyl bromide	−118.5	91.9	108−123	153	2
isoamyl chloride	−104.4	99.15	?		1
isoamyl bromide	−111.9	120.65	118−138	158	2
t-amyl chloride	−73	d.	?		1
equimolal ethyl & propyl alcohol			92−105		3
propylene glycol		189	150−165	185	4
glycerol	?	290	180−190	221	4
glucose	146		275−290		4
dl-lactic acid	18	$115^{(3mm)}$	198−210		5
1,2 dichlorisobutane		107.9	113−128	107	1
3-methyl hexane		91	80−95	100	5, 6
2 methyl pentane		60.3			8
3 methyl pentane		63.3			8
2,3 dimethyl pentane		89.8		100	8, 6
3 methyl heptane		119.1			8
2,3 dimethyl hexane		115.8			8
3,4 dimethyl hexane		117.9			8
2,2,3 trimethyl pentane		110.1			8
ethyl cyclobutane	−143.2	70.7	glasses strongly		8
6 methyl heptanol-3	−89		Do. Do.		7
2 methyl heptanol-2	−72		Do. Do.		7
4 methyl heptanol-2			150−165		7
4-methyl heptanol-3			120−145		7
5-methyl heptanol-1			135−145		7
4-methyl heptanol-4			160−180		7
5-methyl heptanol-2			135−145		7
3-methyl heptanol-2			135−140		7
2-methyl heptanol-4			160−180		7
2-methyl heptanol-1			160−180		7
6-methyl heptanol-2			150−165		

Table References

1. Turkevitch & Smyth, J. Amer. Ch. Soc. 64 737 (1942)
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3. Gibson, Parks, Latimer, J. Amer. Ch. Soc. 42 1547 (1920)
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6. Huffman, Parks, Thomas, J. Amer. Ch. Soc. 52 3241 (1930)
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8. Smittenberg, Hoof, Henkes, J. Amer. Ch. Soc. 60 17 (1938)

The results are shown in Table . The upper limit of transmission from 2500 A to 3300 A.

The low temperature absorption of uranium hexafluoride dissolved in three of these compounds was photographed in a pyrex cell sealed into a Dewar flask. See Fig. 4. Complete absorption was obtained in each case below 4000 Å, but no evidence of structure could be observed. This suggests that some sort of interaction occurs between the uranium hexafluoride and the Freon in solution which causes the disappearance of structure in the uranium hexafluoride absorption band at these temperatures. It appears that the absorption coefficient is considerably increased. The compounds photographed are listed in Table III.

The thermal activity of these compounds was next considered. The compounds as received were dried by distillation through a tube of phosphorous pentoxide, distilling in a vacuum from room temperature to liquid nitrogen or dry ice temperature. The dry compound was then treated with a known weight of uranium hexafluoride measured with the metering system described in an earlier part of this report. In many cases there was a considerable amount of reaction when this mixture was warmed up to the melting point of the Freon. The solution was permitted to stay at this temperature for some time until no further reaction was apparent, and then was distilled into another tube. After this preliminary treatment the solutions were generally found to be unreactive at temperatures slightly above the melting point and frequently were unreactive at room temperature. This indicated that the reaction which took place in the first tube must have been due to the presence of impurities in the Freon used. However, one compound which was tried, diperfluoromethyl benzene, showed such a rapid reaction on preliminary treatment that no conditioning was attempted. Several compounds, on treatment with uranium hexafluoride, exhibited a yellow color which could not be removed by distillation. The cause of this is not known. Photographs of the absorption spectra showed very intense absorption extending into the violet. One compound, 1, 2 dichloro-perfluoro-cyclobutane, was discarded as impossible to glass before any experiments with uranium hexafluoride were carried out. Conditioned solutions of uranium hexafluoride in the remaining available compounds were prepared. In Table the reactivity before and after conditioning is tabulated for each of these compounds. In no case, except as noted above, is the thermal reactivity great enough to interfere with the carrying out of photochemical tests. The source of radiation used was H-6 G. E. mercury arc filtered with a Corning #5860 glass filter which was used to isolate the 3660 Å line in the mercury spectrum. A Dewar flask with two plane windows in the bottom made it possible to shine light through the bottom of the flask in a vertical direction. A cell with a plane bottom contained the solution to be irradiated. The cell was placed near the bottom of the Dewar and cooled slowly by pumping liquid nitrogen into the flask. Condensation of water was avoided by having the cell at room temperature before inserting it in the Dewar, which was covered with a metal cap, and by filtering the liquid nitrogen through glass wool. When the solution had been cooled to liquid nitrogen temperature, the Dewar was filled with liquid nitrogen and the cell was exposed to light. In some cases a narrow beam was used exposing only a small area of the material while in others the beam covered nearly all of the cell window. For preliminary tests the former method offers the advantage that the reaction is observed more quickly, but if the amount of material formed is to be measured, the latter method would be preferable. A diagram of the apparatus used for photochemical tests is shown in Fig. 6.

After the preliminary conditioning the solutions were distilled in vacuum into a tube with a break seal using liquid nitrogen or dry ice on the receiving tube. Using this break seal, the solution was distilled twice more, first into a trap, and then into the final receiving vessel. This vessel consists of a tube which is to be used as a blank, attached to the cell to be used for photochemical tests. These two cells were sealed off, and the solution was brought to just above its melting point. The solution was then divided into equal portions by pouring into each of the two cells and sealing off. The cell containing the blank solution was given the same thermal treatment as the reaction cell, and gave a definite indication of any thermal reaction under the conditions used. Unless otherwise noted in Table IV the results were obtained by comparison with a blank.

The product observed has been a green precipitate, insoluble in the Freon, and which appeared to be white in very small quantities. This was presumed to be uranium tetrafluoride or a complex containing this molecule. By incorporating a sintered glass filter into the reaction cell as shown in Fig. 7 this insoluble product was removed by filtration. After the reaction was completed the break sea on the cell was attached to a phosphorous pentoxide tube by a ground glass joint.

Table III — Physical Properties of Freon Type Compounds

Compound	M. P.	B. P.	Glassing properties	Color	Absorption spectra Alone	Absorption spectra With UF_6
$CFCl_2CFCl_2$	25°	92.7°	does not glass	water white	not meas. no glass	not meas.
CF_2ClCF_2Cl	−94°	3.8°	does not glass	water white	not meas. no glass	not meas.
$CFCl{=}CFCl$	−130.5°	21°	best glass obtained	water white	not meas. no photochemical reaction	not meas.
$CFCl_2CF_2Cl$	−35°	47°	good glass	water white	trans. to 2500 Å	expt. in progress
CHF_2CF_2Cl	below-80°	−12°	glass cracks very badly	water white	not meas. not tested photochem.	not meas.
$CHFClCFCl_2$		72.5°	glasses about −135°	water white yell. with UF_6	trans. to 2500 Å	trans. to 4000 Å at 196°C
CF_2BrCF_2Br	−112°	46.4°	does not glass but crystals translucent	water white yell. with UF_6	trans. to 3000 Å	trans. to 4000 Å at −80°C
$CF_2ClCF_2CF_2CF_2Cl$		63°	glasses at −120°	water white	trans. to 2500 Å	not meas.
$CF_2ClCFClCFClCF_2Cl$		132°	glasses at −110°	water white	trans. to 3300 Å	trans. to 4000 Å at −196°

Table III—(Continued)

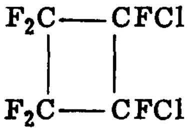
Compound	M. P.	B. P.	Glassing properties	Color	Absorption spectra	
					Alone	With UF_6
$(CF_3)_2C_6H_4$			does not glass, cryst. −40°	water white	not meas.	not meas.
			does not glass	water white	not meas.	not meas.

Table IV—Reactivity of Freon Type Compounds with UF_6

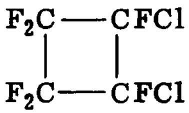
Compound	Reactivity before conditioning	Reactivity after conditioning	Photochemical reactivity −196°
$CFCl_2CFCl_2$	yellow color low temp. ppt. room temp.	very little reaction if any at room temp.	no glass not suitable
CF_2ClCF_2Cl	considerable reaction at 0°, green color	after long condit. unreactive at b.p., 0°	no glass not suitable
$CFCl{=}CFCl$	slight reaction −80° no reaction short time at room temp., green prod.	same as before	no reaction obs. UF_6 may have precipitated
$CFCl_2CF_2Cl$	none obs. −35°, slow reaction at room temp. white ppt.	same as before	reacts, green product
CHF_2CF_2Cl	slight reaction at b.p. negligible	same as before	slight reaction only
$CHFClCFCl_2$	considerable reaction at room temp., green prod.	unreact. at room temp.	largest amount found, green & white ppts.
CF_2BrCF_2Br	slow react. 15°, no reaction low temp.	same as before	green line appears in 10 min., but prod. sol. −80°
CF_2ClCF_2	reacts at −80°, pink	unreactive at	reaction obs.
CF_2ClCF_2	color	room temp.	white ppt. no blank
$CF_2ClCFCl$	slow react. −80°,	unreactive −80°	considerable
$CF_2ClCFCl$	yellow col.	reacts slowly 25° white ppt.	reaction, dark green line
$(CF_3)_2C_6H_4$	rapid reaction −40°	conditioning not attempted	not meas.
	reactivity not studied		

Table V

Compound	Formula	Drying method	Solubility	Reactivity	Remarks
Freon 113	CF_2CFCl_2	P_2O_5	Very soluble	Slight at room temperature on standing	Solution yellowish brown at room temp. green at −190°C
Freon 114	$CF_2Cl\text{-}CF_2Cl$	P_2O_5	Soluble	Reacts rapidly below 0°C but not at −190°C	Brown to green color change on cooling. Gelatinour ppt. on react
Chloroform	$CHCl_3$	P_2O_5	?	Reacts rapidly, slightly above −190°C	Reaction so quick it is difficult to tell if soluble
Carbon Tetrachloride	CCl_4	P_2O_5	Very soluble	No apparent reaction at any T from 25°C to −190°C	Solution very dark due to high conc. of UCl_6. Difficult to distinguish any color change on cooling
Perfluoro heptane	C_7F_{16}	UF_6, Na, and P_2O_5	Slightly soluble	No visible reaction	Conc. of UCl_6 very low.
3me, -hexane	C_7H_{16}	P_2O_5	Slightly soluble	No visible reaction	Conc. of UCl_6 very low
Indies Oil BP/147-157°C 10mm	Fluorinated paraffinic HC's	Na	Soluble	Reacts at room temp.	Deep green glass at −190°C
Isobutyl bromide	$H_3C\text{-}C\text{-}CH_3$ Br	Na_2SO_4	Orange sol. in dilute conc.	Reacts below 0°C	Reacts rapidly on warming from −190°C

Dry air was admitted to the cell, the cell was then inverted and the opposite side of the filter was pumped. The filter was sealed off and the material on the filter was ready for chemical analysis.

The results of the photochemical tests are tabulated in Table IV which summarizes all of the results of the experiments with Freon type compounds as solvents for uranium hexafluoride reactions. Of the seven compounds which were found suitable for photochemical tests, only one showed no indication of photochemical reaction at liquid nitrogen temperature. These fluorocarbons containing reactive hydrogen, chlorine, or bromine atoms are therefore suitable for use in the reaction with uranium hexafluoride at liquid nitrogen temperature. It is difficult to conclude which of the various types of Freons are most reactive until quantitative experiments are carried out.

4. Solvents for UCl_6. A number of organic compounds which previously were found to glass at low temperatures were treated with UCl_6 for the purpose of determining, (1) whether they would dissolve UCl_6 at their glassing point and, (2) whether the solutions were stable, and if so, in what temperature range.

The procedure used in pretreating the compounds is outlined below. Exceptions are indicated and reasons are given.

Drying. It is essential that each of the compounds be absolutely dry as UCl_6 hydrolyzes very rapidly. With one exception, all of the compounds were dried in the following manner: The drying system, Figure 8, was pumped and flamed until completely outgassed. Stopcocks 1 and 2 were closed and the reservoir, A, removed and then rapidly replaced after introduction of the material which was to be dried. Stopcock 1 was then opened and the pressure allowed to equalize between A and B. Tube B contained P_2O_5 and glass beads, completely mixed and tightly packed to prevent channeling.

A Dewar flask containing liquid air or dry ice—trichloroethylene mixture was then placed around trap C. Stopcock 2 was then slowly opened and pumping continued until all of the solvent had been collected in C. Stopcocks 1, 2, and 3 were then closed and the Dewar removed from C and placed around a storage tube D. When all of the solvent had distilled the storage tube containing the dry solvent was sealed off and removed from the drying system.

Compounds treated in this manner were

1. $CF_2Cl-CFCl_2$ (Freon 113)
2. CF_2Cl-CF_2Cl (Feron 114)

3. Chloroform
4. Carbon tetrachloride
5. Perfluoroheptane (also dried with UF_6 and Na)
6. 3-methyl hexane

A fractionation product of Perfluoro Indies Oil was dried by distilling into a tube containing a sodium mirror. This was done because the boiling point of the Indies Oil was very high making distillation through the P_2O_5 system impractical. The drying apparatus, Figure 9, was evacuated and outgassed. The fluorocarbon was then allowed to drain into the still A through breakseal I, and the pumping continued. This operation was designed to remove most of the water. Constriction 2 was sealed off and pumping was continued through the sodium-mirrored trap B. Water was poured into the jacket of A through the condenser and was brought to a boil. When distillation into B was complete, constrictions 3 and 4 were sealed off and the oil was allowed to stand over sodium until ready for use. It was then attached to the UCl_6 system through the breakseal on B. Isobutyl bromide was dried in the same manner as the other compounds, with the exception of one step in the procedure. In this case anhydrous Na_2SO_4 was used in place of P_2O_5 to insure against reaction with the drying agent.

Conditioning and Solubility Determination. In order to insure against the presence of water or any other reactive impurity in the final solution, each of the solvents was conditioned by allowing it to come in contact with UCl_6 before the final solution was made. The conditioning was carried out by distilling the solvent through four successive bulbs, each of which contained a comparatively large amount of UCl_6, Figure 10.

Before putting the UCl_6 in the bulbs (B) and solubility tube (C) the system was first evacuated and outgassed. The bulbs (B) and solubility tube C (1) were then opened and UCl_6 introduced through the open side tubes. The side tubes were quickly sealed off and pumping started again. This operation was carried out as rapidly as possible to prevent the hydrolysis of any more UCl_6. The UCl_6 in C (1) was then distilled by means of a water bath from C (1) to C (2) and the lower bulb sealed off and removed.

The conditioning bulbs B were attached to the vacuum line through S shaped tubes. This was done to prevent bumping of the solvent from carrying over any decomposed UCl_6 during the distillations. The solvent, after conditioning, was distilled into bulb C (2) where it was allowed to dissolve or to react with the UCl_6. If the thermal reaction was small, C was removed from the system and a small amount of solution poured from C (2) to C (3). C (2) was then sealed off from C (3) and, as in the case of Freon 113 $-UCl_6$ solutions, the absorption spectrum was photographed at −190°C. In each case the solutions were kept at −190°C and the temperature raised only if no evidence of solution or reaction was noticeable.

The UCl_6-Freon 113 photograph showed several absorption bands in the red and near-red with one strong band at 5620 Å. The experimental results are given in the accompanying table, Table V.

d. Related Studies

1. Evaporation Method. Attempts to form solutions of UF_6 in substituted hydrocarbons resulted in rapid thermal reaction. It was thought that the use of alternate layers of UF_6 and solvent deposited at very low temperatures would give a psuedo-solution, possibly without thermal reaction. It is possible that very reactive solvents may be used in this method. Such alternate layers should be very thin, of the order of 1 to 10 molecules thick. Thus very low pressures of UF_6 and solvent should be used, necessitating the use of low temperatures for these depositions.

Several experiments have been tried. In one group of experiments, the solvent and UF_6 were evaporated simultaneously from separate reservoirs maintained at −80°C upon a glass plate maintained at −180°C. Contact of the two gases could have occurred about one cm before striking the glass plate, altho from mean free path considerations, this was not probable. Methyl alcohol, ethyl alcohol, and 3 methyl hexane were the solvents tried. In all cases thermal reaction was rapid.

In succeeding experiments, UF_6 and n-octane at −80°C were evaporated alternately upon the surface maintained at −180°C giving each layer time to assume this low temperature before the next layer was put on. No thermal reaction was observed. However such alternate deposition of layers was extremely slow with the apparatus used. A new evaporation apparatus is being built which will greatly increase the speed of deposition of these layers. After radiation, it is planned to pump off the reactants very rapidly at low pressure so that the thermal reactions will be negligible.

2. Colorimetric Analysis. In analyzing the products obtained from a photochemical reaction it is desirable to have a rapid method for the

estimation of small quantities of uranium. It appears that the colorimetric method of Priest and Priest (SAM Laboratories June 30, 1943) for the determination of uranyl ion with sodium cresotate is applicable. These authors report a precision of 2% with concentrations as low as 0.02 mg per ml. According to their report it will be possible to dissolve the precipitated products in nitric acid, neutralize, and add the color intensifying agent. The reagent has been purified and the method is being developed.

3. Investigation of Alcoholates of Uranyl Nitrates. An investigation of the spectra of the alcoholates of uranyl nitrate in the crystal state will be made because it has been shown that the alcoholates of the rare earth salts exhibit simpler spectra than the hydrates. It is hoped that photochemical reactions can be produced in the crystals. The literature lists no alcoholate of uranyl nitrate; attempts are being made to produce these alcoholates, the first being methyl alcoholate.

The method is best described from the Figure 11. Uranyl nitrate hexahydrate which has been pumped for 2 days was ground with an equal part of ground glass chips. The mixture containing about 4 g of the salt was placed in the dryer, C, and the drying tube was evacuated through C. The dryer was maintained at steam temperature for 12 hours. MeOH was refluxed in A with I_2 and Mg to produce the absolute alcohol. Following the drying, the breakseal was broken and about 60cc of the alcohol was distilled into C. The uranyl nitrate solution formed was refluxed for 2 hrs under atmospheric pressure. Breakseal K was then opened and the solution was collected in J through the filter stick in C. Evaporation of the resulting solution in a stream of dry nitrogen gave crystals which will be studied.

4. Uranous Salts. Many of the uranous compounds are relatively unstable and might be expected to be photochemically reactive.

A list has been made of the simple uranous salts reported in the literature, and their methods of preparation have been studied. A few salts such as the fluoride, sulphate, arsenate, and the phosphates are insoluble in water and may be prepared in this way. The halides and sulphide are decomposed in water, but may be made by direct combination from the metal or the oxide. A number of compounds including the carbonate, nitrate, perchlorate and others have not been prepared in the solid state according to Mellor. These are the more unstable compounds which might be suitable for photochemical work.

A search of the original literature on uranous perchlorate, periodate, chlorate, and iodate has been made. Uranous iodate and periodate are precipitated in aqueous medium. Uranous periodate decomposed by intra-molecular oxidation-reduction into uranyl iodate. Uranous iodate is also unstable with respect to uranyl iodate, free iodine being formed. The perchlorate and chlorate have not been prepared in the solid state. They are more unstable than the corresponding iodine derivatives. The decomposition of their solutions presumably follows the same course as that of the periodate and iodate. The possibility that these reactions might take place photochemically at low temperatures is suggested.

Samples of uranous chloride and bromide are available in this laboratory. The properties of these compounds have been investigated in the literature with a view to initiating experiments with these compounds.

5. The Conversion of Very Small Amounts of Uranium to Uranium Hexafluoride. The useful photochemical reactions, carried out under the conditions previously described, can be expected to yield from two to ten milligrams of reaction product. The present method of determining the isotopic abundance ratio in such small samples is by counting. Experiments are in progress for converting these to UF_6 for analysis on the mass-spectrometer, whereby the abundance can be determined much more accurately and quickly. Large amounts of uranium compounds can be converted to UF_6 in the requisite purity and in high yields, but little has been done on the semi-micro scale.

Three conversion methods have been tried and the best one from the point of view of convenience has been selected. The methods are: 1. treatment of UO_2F_2 with fluorine at 290°, 2. treatment of U_3O_8 with fluorine at 360°, and 3. treatment of UO_2F_2 with CoF_3. The third method does not take place with appreciable speed even at 420°. The first method is satisfactory except that the preparation of UO_2F_2 from samples is difficult. The second method seems to be the best. It appears to give the purest product although this cannot be decided until actual mass spectrometer tests have been made.

The present procedure for conversion to UF_6 is as follows: The tube containing the photochemical reaction product is washed with 10-15cc hot nitric acid. This is poured into a 50cc beaker and the tube is washed with distilled water several times. The liquid is evaporated to dryness on the steam bath. The salt is dissolved in the minimum amount of water and transferred to a 5cc beaker. This and the washings from the 50cc beaker are evaporated to a small volume and then transferred with a microburette to the small glass tube subsequently to be used as reaction vessel in the fluorination. The uranyl nitrate solution is carefully evaporated and then ignited to UO_3. The tube is then sealed to the vacuum system, evacuated, flamed out to remove water, and treated with fluorine at 100–200° to remove impurities. After thorough evacuation, the fluorination at 360° is begun.

The glass fluorination apparatus used at present must be rebuilt each time. A more convenient apparatus would be desirable, and to obtain this another method may be used. This consists in the conversion of UO_2F_2 into UF_4 followed by conversion of UF_4 to UF_6 by means of CoF_3.

75

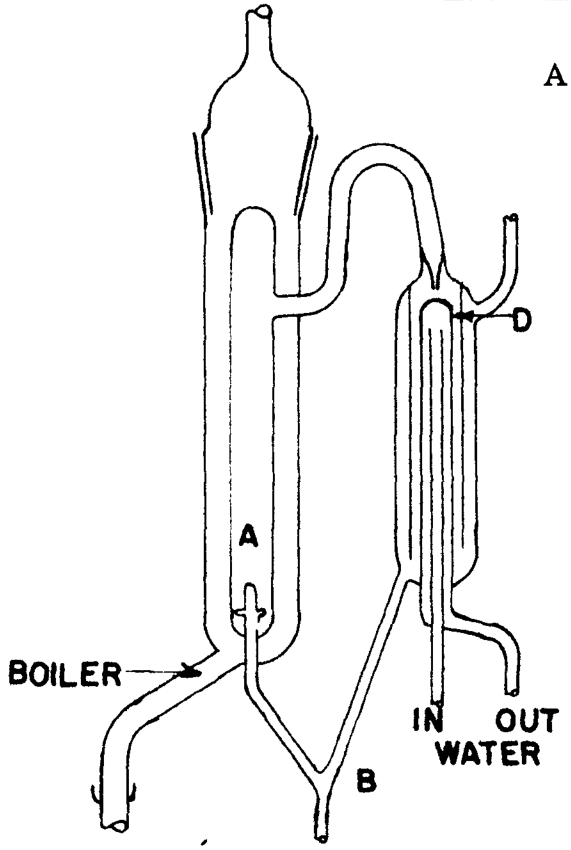
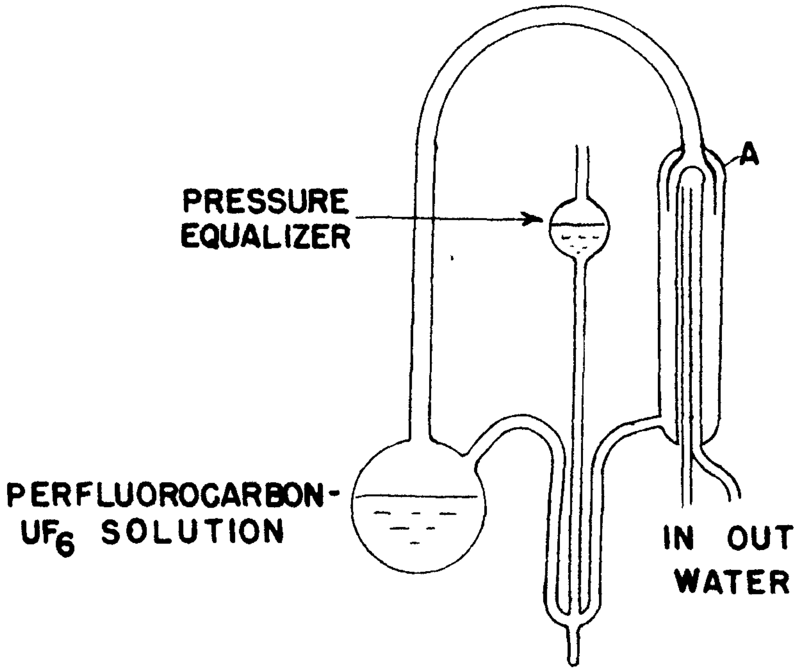


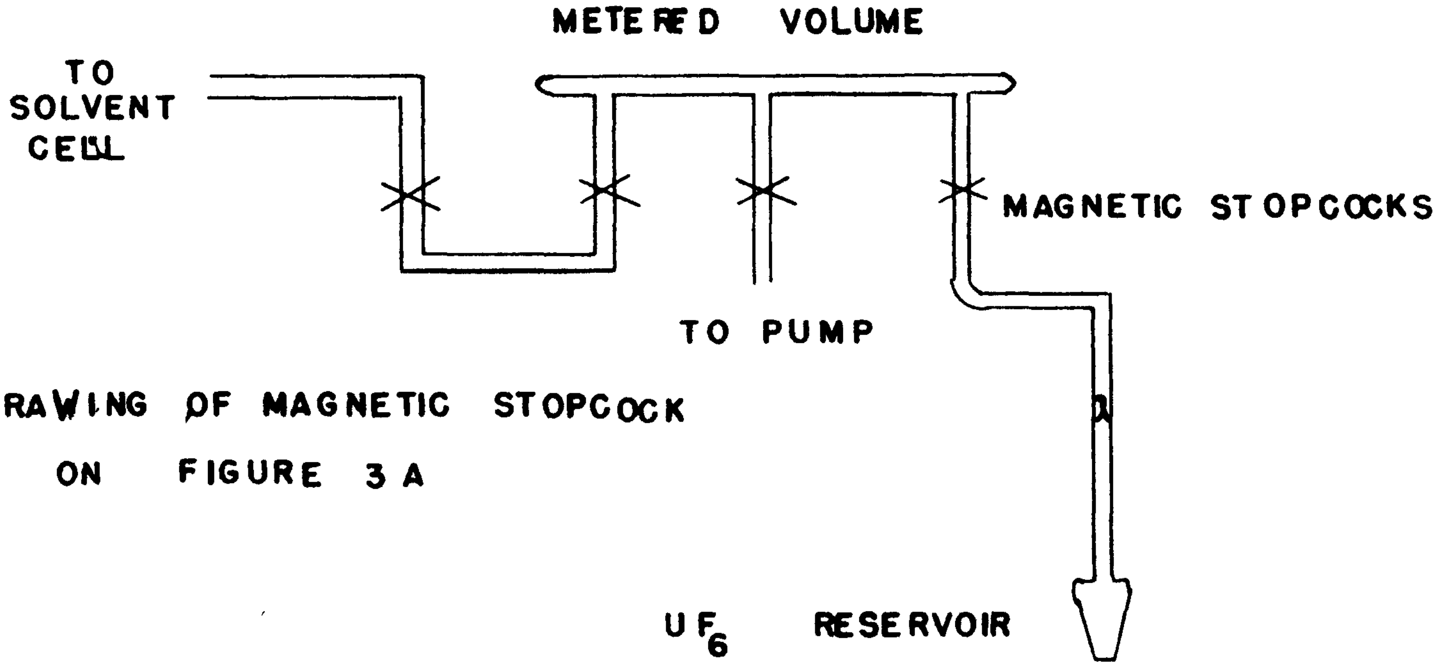
FIGURE 1



SOLUTION DISTILLS TO COLD FINGER A, RUNS BACK INTO DISTILLING FLASK AND BOILS AGAIN.

FIGURE 2

76



DRAWING OF MAGNETIC STOPCOCK ON FIGURE 3A

FIGURE 3

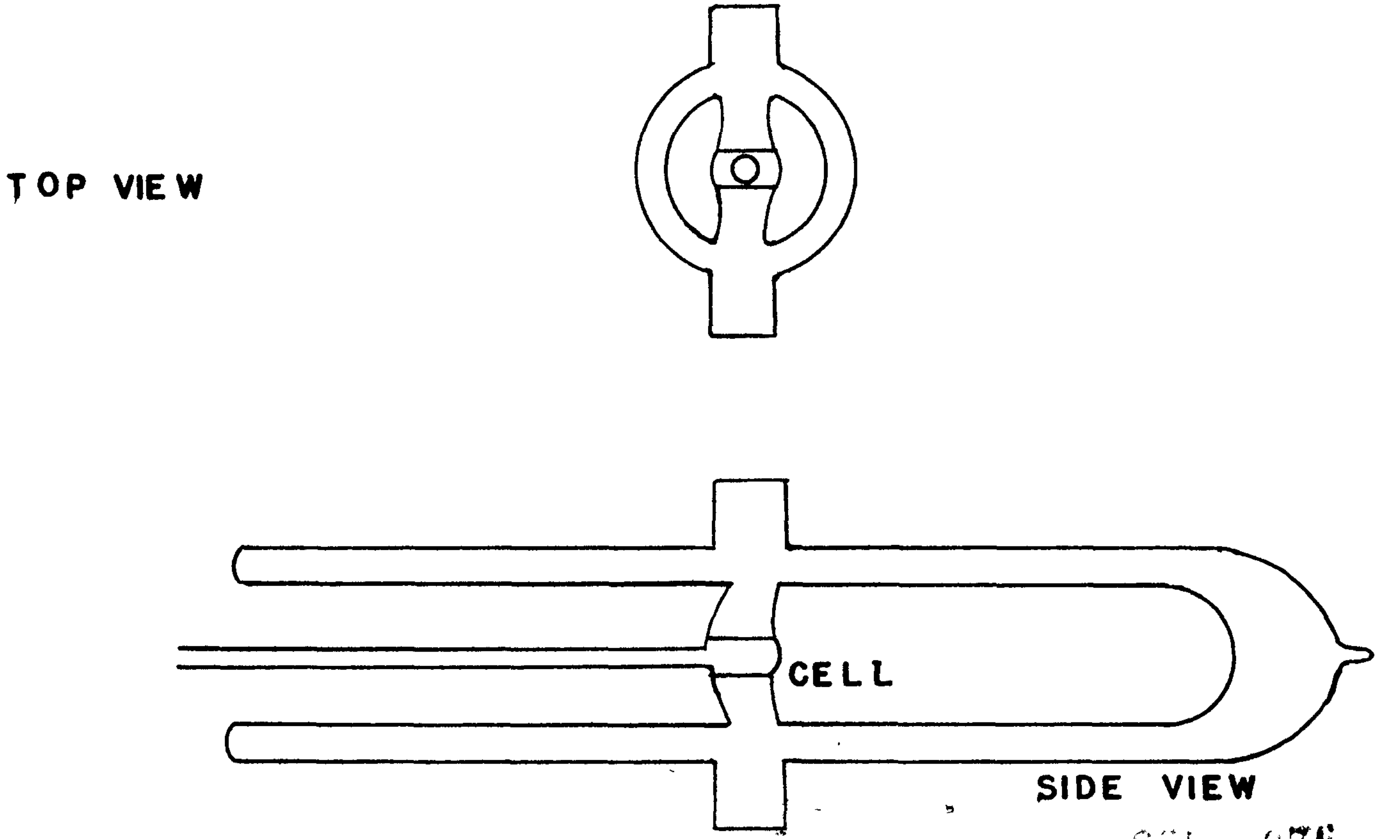


FIGURE 4

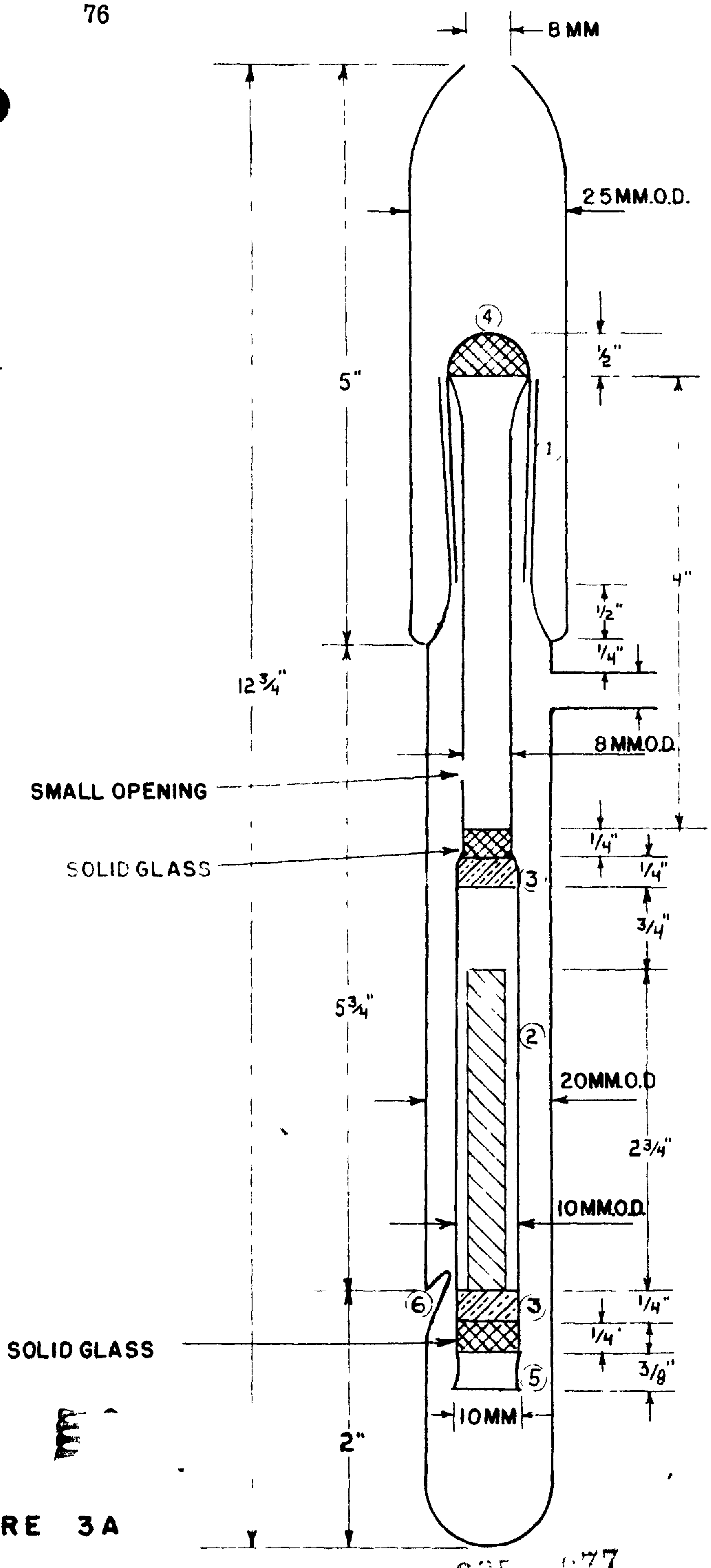


FIGURE 3A

NOTES

1 JOINT IS 14/35 $ AND MUST BE GROUND TO FIT WITHOUT RACKING OR EXCESSIVE STICKING EVERYTHING MUST BE LINED UP AS WELL AS POSSIBLE IN ORDER TO ELIMINATE DISTORTION

2 IRON ROD 1/4" DIAMETER SHOULD BE FREE TO MOVE 3/4" IN TUBE

3 TIGHTLY PACKED ASBESTOS

4 SEALED OFF AND STRENGTHENED

5. FLARED OPENING THAT IS STRENGTHENED BY THICKENING IT SHOULD BE SUCH THAT ON RAISING THE INSIDE PLUG, IT CAN BE MADE TO REST ON PROJECTION.

6 PROJECTION SHOULD BE OF THICK GLASS AND STRONG YET IT SHOULD NOT TOUCH INSIDE PLUG WHEN DOWN. IT MAY BE BULBED OUT 3MM. IN ORDER TO MA

THE PROJECTION LONGER.

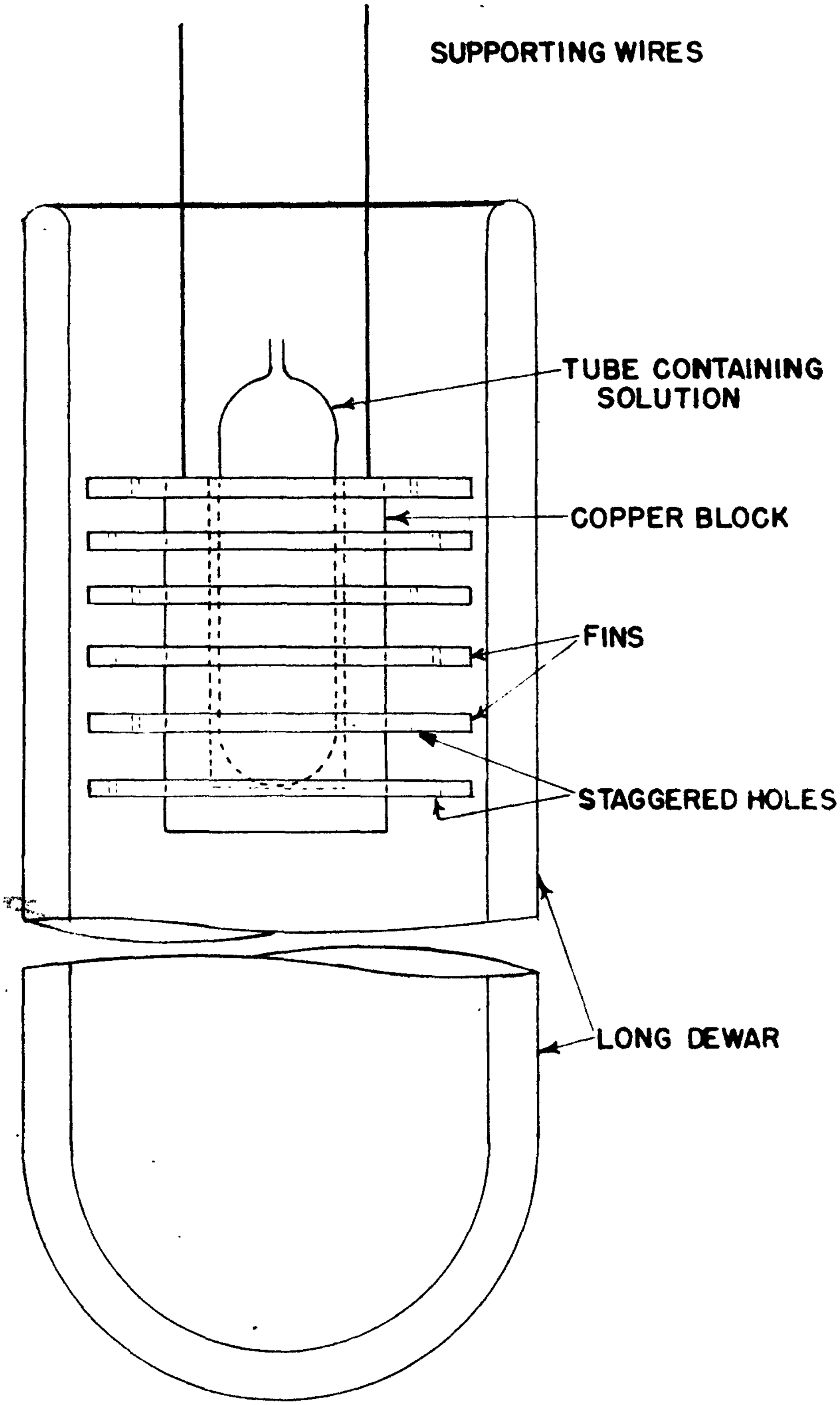


FIGURE 5
CRYOSTAT

REACTION CELL

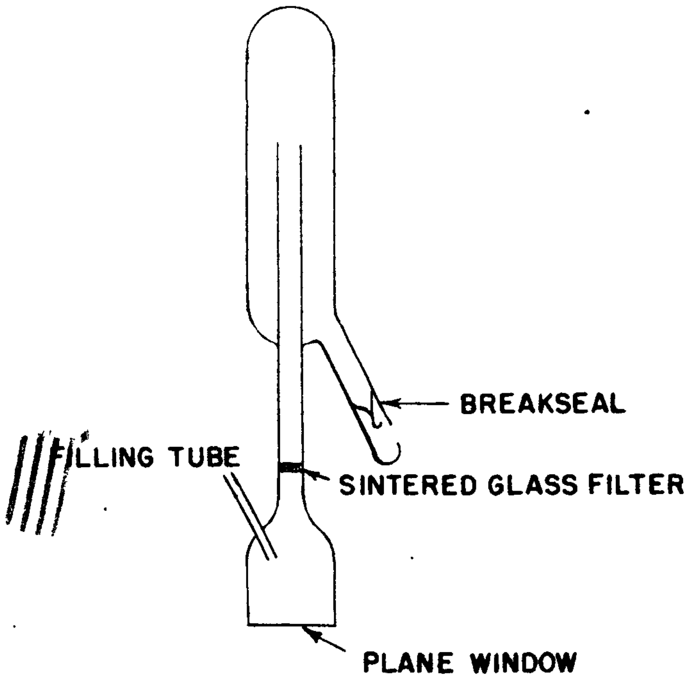


FIGURE 7

DEWAR FOR FREON WORK

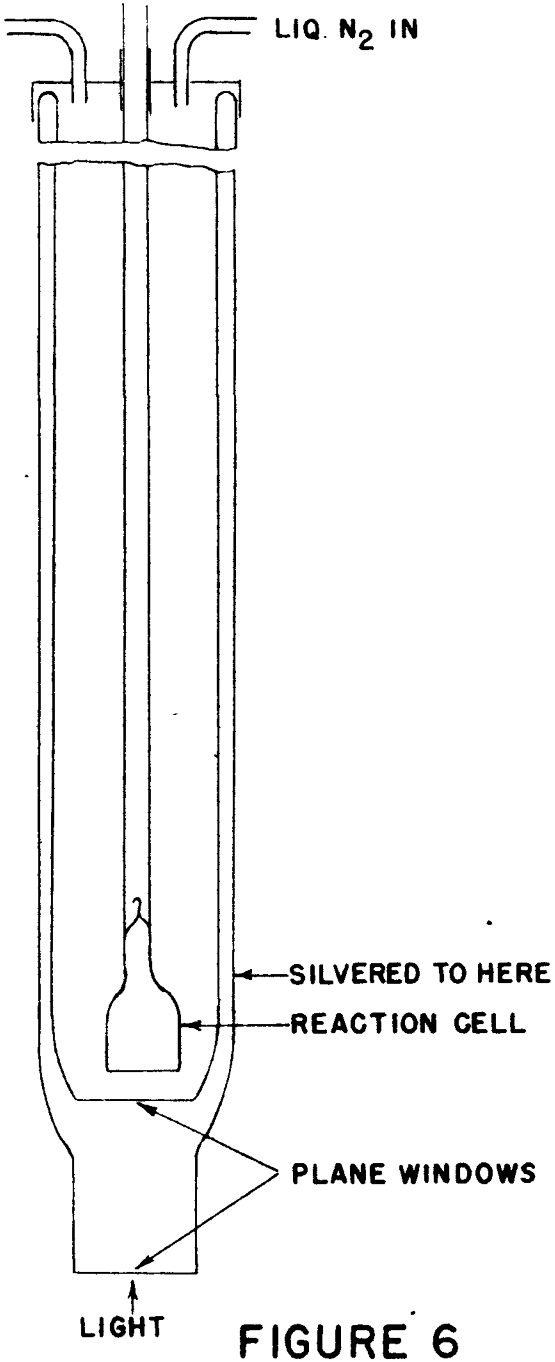


FIGURE 6

DRYING SYSTEMS

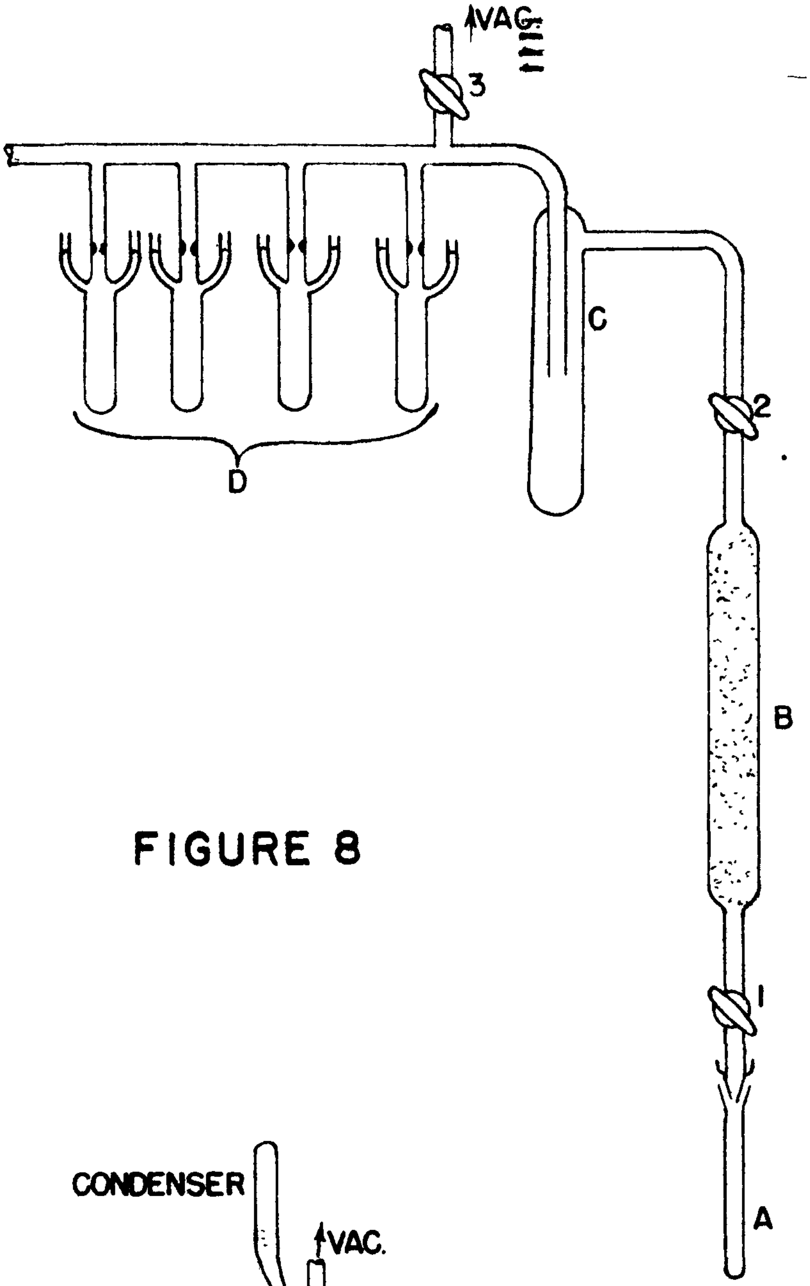


FIGURE 8

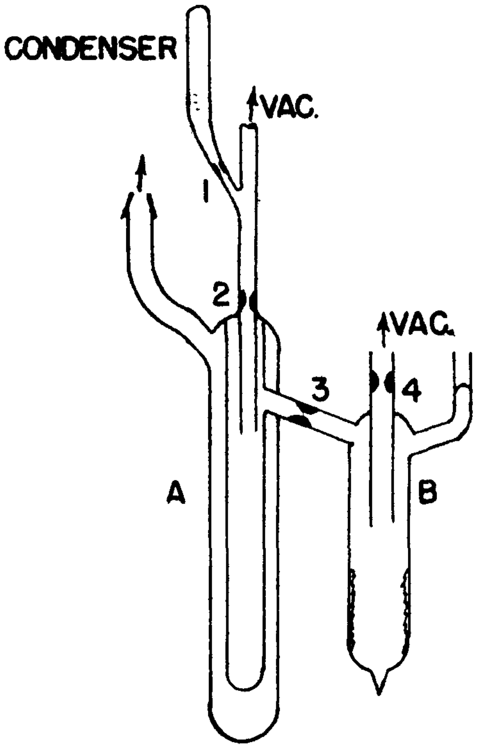
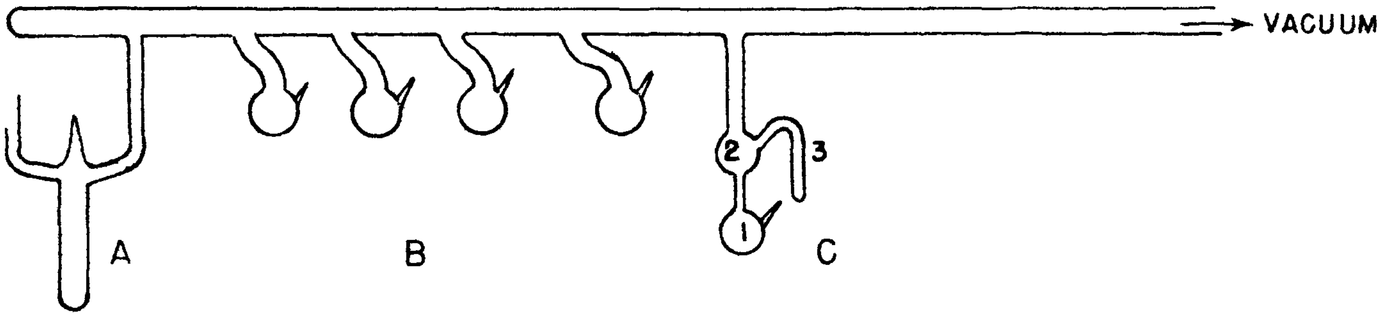


FIGURE 9

CONDITIONING APPARATUS



A	SOLVENT STORAGE
B	CONDITIONING BULBS
C	U CL$_6$ DISTILLATION & SOLUBILITY TUBE

FIGURE 10

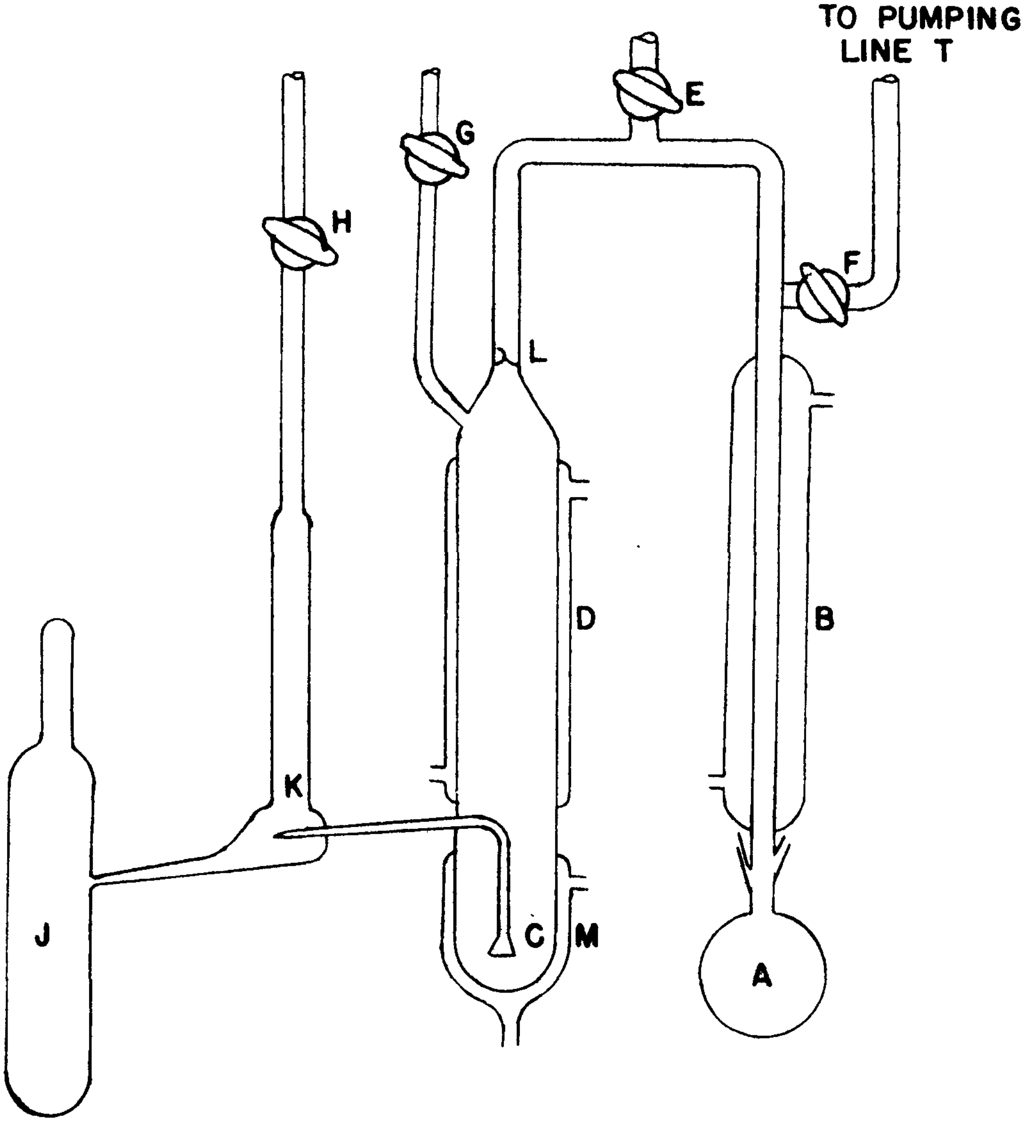


FIGURE II

APPARATUS FOR PRODUCTION OF $UO_2(NO_3)_2 \cdot 6MeOH$

C. SOME PREVIOUS WORK ON THE SPECTRA AND PHOTOCHEMISTRY OF URANYL COMPOUNDS

The fluorescence and absorption spectra of many uranyl compounds have been taken both from crystals and solutions.

Nichols and Howes—The Fluorescence of Uranyl Salts. Carnegie Institution of Washington, 1919.

Jones and Strong—A Study of Absorption Spectra. Carnegie Institution of Washington, 1910.

H. & J. Becquerel and H. Kammerlingh Onnes—Ann. de Chim. et de Phys. 20, 45 (1910).

Lipkin and Weissman—Report of December 17, 1942, Columbia Serial No. 100XR-79, File Index No. 2.11.

The absorption spectra of crystals and solutions of quadrivalent uranium are also exceptionally sharp compared with most colored ions. Also sharp are the spectra of trivalent uranium. (Ephrain and Mesener, Helv. Chim. Acta 16, 1260 (1933)). All these spectra sharpen as the temperature is lowered but it has not yet been shown that the extent of the sharpening equals that from uranyl ion. These spectroscopic results have been of great assistance in indicating which kind of substances have relatively simple spectra and which complex. Such selections are required in our program to understand the spectra so as to isolate the lines due primarily to the odd isotope. In the light of more recent knowledge, they have been of further value in suggesting what crystallographic and chemical properties compounds should have to arrive at still greater refinement and simplification in the spectra. In this way we shall be led, it is expected, to those substances which possess a greater contrast in the spectra chiefly due to the odd isotope relative to the remainder of the spectra.

The further requirement which must be met by our compounds is a capacity to react photochemically, either (1) with their own negative ions as occurs within the crystal uranyl potassium ferrocyanide: (2)

with molecules of selvation as with uranyl chloride ethyl alcohol of selvation; or (3) with the solvent. The latter should be selected in such a manner as to compose a system with the uranium salt which gives sharp spectra. The sharp spectra which occur at low temperatures afford the opportunity for irradiating with a sharp line which may discriminate sharply between the line due chiefly to the desired isotope and other lines. Any blurred structure in the spectrum acts so as to decrease the effectiveness of any photochemical separation.

In addition to the difference in spin, which distinguishes the isotopes, is the difference in the masses. This difference would be expected to introduce a difference of 1 cm^{-1} in one of the vibrational frequencies in the uranyl compounds (and also about the same in the hexafluoride). This rests on accepting that the UO_2^{++} group is linear—a model borne out by X ray data, infra-red data.

However, several writers have interpreted their data as consistent with a bent model for UO_2^{++}. If that were true the totally symmetrical vibration frequency which appears in the absorption spectrum as an interval of about 750 cm^{-1} would be different for the two isotopes.

Accordingly, Lipkin and Weissman carried out a number of photochemical reactions at the temperature of dry ice 193°K to effect such a separation. None were successful. No success was to be expected if the ion were linear in the first approximation, now the accepted model.

However, a positive contribution of these experiments, as well as others carried out with other possibilities in mind, was the discovery of a good many solutions where uranium reacts photochemically at low temperature. In this connection it is worth noting again that they discovered a photochemical reaction within a crystal of uranyl potassium ferrocyanide at low temperature.

Prior to the photochemical experiments, the absorption spectra of the solutions had been taken so as to determine at what frequencies irradiation may induce the reaction. These are given in Table I to Table XII, with the frequencies listed.

The photochemistry was usually carried out by means of a carbon arc with filters. In one instance, a high intensity mercury arc (General Electric, 1000 watt, high pressure arc) was employed with filters.

The present program, it may be worth pointing out, would limit the irradiating source to a sharp line corresponding to some particular line in the absorption spectrum which was identified as preferentialy due to the odd isotope.

Here are appended descriptions of photochemical experiments which Lipkin and Weissman have carried out—the sources, filters, concentrations and yields, and a summarizing list, Table XII. Following is a direct quotation from the Lipkin and Weissman report.

The absorption and fluorescence spectra of uranyl acetate dihydrate dissolved in a mixture of 3 parts absolute ethanol, 1 part ether and 1 part isopentane were examined visually at liquid air temperature by means of a Bausch and Lomb spectrometer. The results are summarized in Table I. In addition, these spectra were also examined photographically. The absorption bands thus observed are tabulated in Table II, but the fluorescence picture was not analyzed in detail.

Uranyl chloride obtained by the evaporation of an ethanol solution of this compound (microanalysis showed the recovered solid to be $UO_2Cl_2C_2H_5OH$) was dissolved in 5 parts ether, 5 parts isopentane and 2 parts absolute ethanol and the absorption spectrum at 95°K was photographed. The data on this spectrum is summarized in Table III. The fluorescence spectrum of this same solution was also photographed, but no quantitative measurements were made on the plate.

Uranyl chloride (hydrated) was dissolved in concentrated hydrochloric acid and the absorption spectrum at room temperature measured by means of the Beckman spectrophotometer (see Fig. 1). Furthermore, this same chloride was dissolved in 95% ethanol and the fluorescence of the solution was examined visually at liquid air temperature (see Table IV). It should be mentioned in passing that $UO_2Cl_2 \cdot C_2H_5OH$ in an alcohol-containing solvent undergoes photochemical reduction at liquid air temperature much more rapidly than the hydrated chloride.

Visual observations of the absorption and fluorescence spectra of uranyl phosphate in viscous phosphoric acid were made at room temperature. The results are summarized in Table V. It should be noted that the absorption band at 5160 Å diminishes in intensity as the temperature is lowered from room temperature to −80°C and therefore, corresponds to the transition from the first vibrational level of the ground electronic state to the zero vibrational level of the first excited electronic state. This conclusion is also amply supported by other evidence. Photographs of the absorption and fluorescence spectra at −80°C of uranyl phosphate in 85% orthophosphoric acid plus 10% ethanol were also obtained, but were not quantitatively analyzed.

Oxalic, citric, tartaric, lactic, and pyruvic acids form complex ions with uranyl ion. The absorption spectrum of an ethanol solution of uranyl chloride containing a five-fold excess of citric acid was examined visually at room temperature. In addition, the fluorescence spectrum of this same solution was examined visually at liquid air temperature. These data are summarized in Table VI.

The fluorescence bands of an ethanol solution of uranyl chloride containing a three-fold excess of tartaric acid were observed visually at liquid air temperature. A summary of the data is given in Table VII.

The absorption spectrum of uranyl chloride dissolved in 85% lactic acid was examined visually at room temperature, while the fluorescence spectrum of this same solution was examined at liquid air temperature. The results are summarized in Table VIII.

Oxalic acid in ethanol solution was added to an ethanol solution of uranyl chloride and then enough concentrated HCl was added to dissolve the precipitate first formed. The absorption spectrum of this solution was observed visually at room temperature, while the fluorescence spectrum was observed at liquid air temperature (see Table IX).

The absorption spectrum of crystalline anhydrous uranous tetrachloride was observed visually at room temperature. The data are summarized in Table X. In addition, the absorption spectrum of uranous phosphate in phosphoric acid was examined visually at room temperature with the results given in Table XI.

Qualitative Observations on the Photochemical Reduction of Uranyl Ion

A number of qualitative observations were made on the photochemical behavior of systems containing uranyl ion. Various reducing agents were tried in a variety of solvents and at different temperatures. These results are summarized in Table XII.

Attempts were made to find uranyl compounds which underwent photochemical reaction in the crystalline state. The only compound which was found to behave in this way was uranyl potassium ferrocyanide. The other crystalline compounds which were examined, but did not undergo reaction, were: hydrated uranyl sulfite, anhydrous uranyl sulfite, uranyl phosphite, hexamethylene tetramine uranyl sulfate, uranyl metarsenite, uranyl hypophosphite, hydroxylamine uranyl acetate, hydroxylamine uranyl propionate, hydroxylamine uranate, uranyl ethyl mercaptide, uranyl oxalate, uranyl thiosulfate and uranyl acetylacetonate.

Attempted Photochemical Separation of the Uranium Isotopes

The following experiments on the partial photochemical reduction of uranyl to uranous were carried out with the hope that some isotopic separation would be observed. The experiments were carried out with varying temperatures, conditions of illumination, solvents and reducing agents.

Twenty cubic centimeters of a saturated solution of uranyl acetate dihydrate in a mixture of 3 parts absolute alcohol, 1 ether, 1 isopentane was illuminated for one hour at liquid air temperature with the blue and near ultraviolet light from a 50 amp. high-intensity carbon arc. This spectral region was isolated by passing the radiation from the arc through aqueous $CuSO_4$ solution and a Corning No. 585 filter. The illumination produced both fluorescence and reduction. After the illumination the rigid solution was rapidly warmed to room temperature, treated with HF, and the precipitate of uranous fluoride immediately centrifuged off. The reduced uranium amounted to 25% of the total uranium in the solution. A solution of 1.05 gm of hydrated UO_2Cl_2 in 10 cc of the solvent was unchanged after one hour of illumination by the same spectral region as above. However, 100-minute illumination at liquid air temperature of a solution containing 1/3 this amount of hydrated chloride per 10 cc of solvent yielded several percent reduction. The uranous ion was again separated by rapid precipitation with hydrofluoric acid.

A sample of uranyl chloride containing one molecule of ethyl alcohol instead of water of crystallization (this material was prepared by crystallization of uranyl chloride from absolute alcohol and drying in vacuo at 100°C) was dissolved in the alcohol-ether-isopentane mixture and partially photoreduced. This solution yields more rapid reduction than the solution made from hydrated chloride even though the fluorescence yield remains high. Four grams of the chloride were dissolved in 65 cc of the alcohol-ether-isopentane solvent and illuminated at liquid air temperature by the blue and ultraviolet light of the carbon arc. The uranous ion was separated by precipitation as fluoride.

Thirty (30) grams of a solution of uranyl phosphate in phosphoric acid (1 mole of uranyl phosphate per 1000 gm solution) was treated with 3 gm of 50% phosphorous acid. This solution was illuminated at $-80°C$

by the blue and ultraviolet light from the carbon arc. Under these conditions the solution fluoresces brightly and undergoes photochemical reduction. After 45 minutes illumination the solution was quickly brought to room temperature and treated with hydrofluoric acid. In order to completely purify the uranous fluoride, it was treated with sulfuric and nitric acids and the excess nitric acid driven off. The sulfuric acid solution after dilution with water was treated with alcohol and the uranium completely photoreduced by illumination with the carbon arc. The uranium was then once again precipitated as the uranous fluoride. This step was used in the purification of all samples which might have been contaminated with phosphate. The purification after this step was carried through by the standard ammonia-ammonium carbonate method.

A similar experiment on a phosphoric acid solution containing hypophosphorous acid and the reducing agent (4 gm 50% hypophosphorous acid per 30 gm of the uranyl phosphate solution) yielded several percent reduction after two minutes illumination at −80°C. The reduced uranium was separated and purified in the manner already described.

To test the effect of the concentration of uranyl ions, the reduction with hypophosphorous acid in a phosphoric acid medium was carried out at a much lower concentration of uranyl phosphate. 0.0005 mole of uranyl phosphate in 800 gm of syrupy phosphoric acid containing 30 gm of hypophosphorous acid was illuminated for 30 minutes at −80°C by the blue and ultraviolet light from the carbon arc. The uranous and uranyl fractions were separated in the usual way. The uranous fraction yielded 37 mg of U_3O_8 and the uranyl fraction 7 mg of U_3O_8.

An experiment designed to take advantage of any deviations in isotopic ratio from the normal ratio in the first vibrational level of the ground electronic state of uranyl ion was performed as follows: A solution of 0.40 mole of uranyl phosphate in 300 ml of 85% orthophosphoric acid and 300 ml of 50% hypophosphorous acid was illuminated at −80°C by a band of frequencies extending from 5120–5170 Å, which is the position of the absorption band corresponding to the aforementioned transition. The reacting solution was contained in a one liter spherical flask silvered on the outside for conservation of light. Into this flask was inserted a double walled vessel (shaped like an ordinary Dewar flask) 240 mm long, 70 mm outside diameter, and 10 mm clearance between walls. The source of light for this experiment was a solution of uranyl phosphate in glassy phosphoric acid contained in the central tube and excited to fluorescence by the unfiltered radiation from a 1000 watt high-pressure quartz mercury arc. Between the walls was a filter solution prepared by dissolving 180 gms of UCl_4 and 120 gms of UO_2Cl_2 in 600 cc of 85% H_3PO_4. All visible light on the short wave length side of the 5110–5180 Å fluorescence band of the source was filtered out by the 1 cm depth of filter solution. It was found, unfortunately after the experiment had been completed, that the filter solution was somewhat transparent in the region of 3650 Å which may in part have vitiated the monochromatic character of the light source. The illumination of the reacting solution in the manner described was continued until 10% reduction had taken place.

0.10 mole of uranyl sulfate was dissolved in 66 ml of concentrated sulfuric acid and 43 ml of absolute ethanol added. This solution was placed in a pyrex glass cell and illuminated at −80°C by light consisting only of wave lengths above 4350 Å. This light was obtained by filtering the radiation from the 50 amp high-intensity carbon arc through aqueous copper sulfate solution, a Corning No. 430 filter and two Corning No. 338 filters. At the end of several hours of illumination the uranous ion formed photochemically was rapidly separated from the uranyl by precipitation with hydrofluoric acid. The precipitate weighed 0.32 g after drying at 105°C.

150 ml of an ethanol solution containing 0.17 mole of uranyl chloride monohydrate was mixed with 350 ml of a solution of 0.95 mole oxalic acid dihydrate in absolute ethanol and 115 ml concentrated hydrochloric acid. The resulting clear yellow solution was placed in a test tube 12.5 inches long and $2^{11}/_{16}$ inches in diameter which was silvered on the outside. After cooling to −80°C it was illuminated by light containing only wave lengths longer than 4900 Å (obtained by filtering the radiation from the high intensity carbon arc through aqueous copper sulfate solution, a Corning No. 428 filter, a Corning No. 368 filter, and a Corning No. 338 filter. After illuminating for some time the white uranous oxalate which formed was separated by centrifuging and washed with dilute HCl. It was then ignited to oxide and weighed (0.85 g).

An Experiment on the Exchange of Uranyl and Uranous Ions

To test whether exchange occured during the precipitation of UF_4 from a mixture of uranyl and uranous ions, the following experiment was performed. A mixture of uranyl and uranous phosphates was prepared by the addition of 0.0012 mole of phosphorous acid to 15 gm of a phosphoric acid solution containing 0.0030 moles of uranyl phosphate and long illumination of the mixture. To this solution was added 3.9 gm of a phosphoric acid solution containing artificially radioactive uranyl phsophate. The active isotope in this mixture was the seven-day U^{237}.

The mixture of uranyl and uranous phosphates was treated with NH_4F solution, centrifuged, and the UF_4 precipitate washed 3 times. The uranyl fraction was treated with sulfuric acid, heated to fuming, diluted with water and ethyl alcohol, completely photo-reduced and UF_4 precipitated with hydrofluoric acid. The two samples of uranous fluoride were dried, and the beta activities of 10 mg samples determined on an electroscope. The initial activities were uranous fraction .0382 div./sec. and uranyl fraction 0.206 div./sec. At the end of 9 days the activities were uranous fraction 0.0318 div./sec. and uranyl fraction 0.0847 div./sec. The activity in the uranyl fraction decayed with a half-life of 164 hours, while the small activity in the uranous fraction decayed with an initial half-life of about 600 hours. The former period corresponds to the half-life of U^{237} while the latter corresponds to the half-life of UX_1. The method of precipitation carries all the UX_1 present in the original uranium into the uranous fraction. We may conclude from these measurements that there is no exchange of uranium between uranyl and uranous ions in the course of the fluoride separation.

Table I—Absorption and Fluorescence Spectrum at Liquid Air Temperature of Uranyl Acetate Dihydrate in Ether-Isopentane-Ethanol Mixture

Absorption			Fluorescence		
λ Å*	ν, cm^{-1}	Δν†	λ Å*	ν, cm^{-1}	Δν†
4446	22,436				
4536	22,040				
		478			
4589	21,785	694			
4691	21,311		4758	21,011	
4720	21,181		4790	20,871	
4768	20,967		4820	20,741	
4782	20,906				
		732			785
4870	20,526		4920	20,320	
4913	20,342		4953	20,164	
4949	20,200		4973	20,103	
			5002	19,986	
			5030	9,875	
					832
			5139	19,491	
			5170	19,337	
			5196	19,240	
			5220	19,152	
			5244	19,064	
					853
			5376	18,599	
			5432	18,404	
			5490	18,210	
					726
			5653	17,678	
					645
			5805	17,222	
			5935	16,844	

*Each group of bands represents a single vibrational level.

†These values were obtained by taking the differences of the "centers of gravity" of the various vibrational levels.

Table II—Photographic Absorption Spectrum of Uranyl Acetate Dihydrate in Ether-Isopentane-Alcohol at 98°K

Absorption band interval, Å	Strength of* absorption	Remarks
3773	VW	Too weak to observe anything but center of band
3798	VW	Too weak to observe anything but center of band
3836	VW	Too weak to observe anything but center of band
3863–3875	MW	
3890–3900	VW	
3935–3957	VW	Possibly a doublet
3968–3990	MW	
4010–4030	VW	Of doubtful existence
4050–4062	W	
4075–4096	W	
4130–4138	W	Possibly a doublet
4163–4186	MS	
4200–4210	W	
4250–4266	W	
4290–4308	S	
4340–4355	W	
4388–4405	W	
4418–4450	VS	
4470	VW	Too weak to observe anything but center of band
4525–4540	W	
4562–4583	S	
4600	W	This band appears to be a shoulder on the above band
4691–4785	VW	Possibly a doublet
4820–4920	VW	

*VS = very strong; S = strong; MS = moderately strong; MW = moderately weak; W = weak; VS = very weak

Table III — Photographic Absorption Spectrum of $UO_2Cl_2 \cdot C_2H_5OH$ in Ether-Isopetane-Alcohol at Liquid Air Temperature

Absorption band interval, Å	Strength of* absorption	Remarks
5068–4989	MW	
4968	VW	Very sharp band
4882–4865	W	This band is a "shoulder" on the following band
4865–4813	MS	
4788–4735	MS	
4708–4680	VW	
4628–4600	MS	Doublet. Faint minimum at 4600 Å
4600–4558	MS	
4503–4448	MS	
4445–4403	VS	
4403–4385	MS	This band is a "shoulder" on the above band
4360–4310	MW	This band is a "shoulder" on the following band
4310–4280	VS	
4280–4260	W	This band is a "shoulder" on the above band
4189–4149	MS	
4138	W	This band is a "shoulder" on the above band
4080	VW	
4066–4035	MW	This band is a doublet with a minimum at 4050 Å
4035–3950	W	Wide "shoulder" on above band
3937–3923	VW	
3898–3833	W	Doublet with a minimum at 3870 Å
3800–3760	VW	Diffuse
3705–3670		Beginning of ultra-violet
3635		continuum

*See note in Table II for meaning of symbols.

Table IV—Fluorescence Spectrum of Uranyl Chloride in Ethanol Solution at Liquid Air Temperature

Wave Length of Absorption Maximum, Å

4890
5153
5340) Doublet
5420)
5600) Doublet
5673)
5872) Doublet
5942)
6190

Table V—Absorption and Fluorescence Spectra of Uranyl Phosphate in Glassy Phosphoric Acid at 293°K

Absorption			Fluorescence		
λ, Å	ν, cm^{-1}	Δν	λ, Å	ν, cm^{-1}	Δν
4642	21,536				
		682			
4794	20,854		4794	20,854	
		658			670
4950	20,196		4953	20,184	
		822			836
5160	19,374		5167	19,348	
					903
			5420	18,445	
					891
			5695	17,554	
					842
			5982	16,712	

Table VI—Absorption and Fluorescence Spectra of Uranyl Citrate in Ethanol Solution

Absorption (293°K)			Fluorescence (90°K)		
λ, Å	ν, cm^{-1}	$\Delta\nu$	λ, Å	ν, cm^{-1}	$\Delta\nu$
4623	21,625				
		697			
4777	20,928				
		707			
4944	20,221		4952	20,188	
		884			844
5170	19,337		5168	19,344	
					855
			5407	18,489	
					857
			5670	17,632	
					816
			5945	16,816	
					808
			6245	16,008	

Table VII — Fluorescence Spectrum of Uranyl Tartrate in Ethanol Solution at Liquid Air Temperature

λ, Å*	ν, cm^{-1}	Δν
4950	20,196	
		848
5167	19,348	
		855
5406	18,493	
		867
5672	17,626	
		824
5950	16,802	
		806
6250	15,996	

*These values represent the peaks of the fluorescence bands which are quite broad even at liquid air temperature.

Table VIII—Absorption and Fluorescence Spectra of Uranyl Chloride 85% Lactic Acid

Absorption (293°K)*			Fluorescence (90°K)		
λ, Å	ν, cm^{-1}	Δν	λ, Å	ν, cm^{-1}	Δν
4640	21,546				
		688			
4793	20,858				
		686			
4956	20,172		4940	20,237	
		820			825
5166	19,352		5150	19,412	
					857
			5388	18,555	
					870
			5653	17,685	
					840
			5935	16,845	
					798
			6230	16,047	

*These absorption bands are quite broad, but each of these broad bands seems to be composed of three narrower, diffuse bands.

Table IX—Absorption and Fluorescence Spectra of Uranyl Oxalate in Ethanol Solution

Absorption (20°C)			Fluorescence (90°K)		
λ, Å	ν, cm^{-1}	Δν	λ, Å	ν, cm^{-1}	Δν
4622	21,630				
		737			
4785	20,893				
		590			
4924	20,303		4935	20,258	
		880			865
5147	19,423		5155	19,393	
					856
			5393	18,537	
					843
			5650	17,694	
					855
			5937	16,839	
					805
			6235	16,034	

Table X—Visual Absorption Spectrum of Crystalline Anhydrous Uranous Tetrachloride at Room Temperature

Absorption band maximum, Å	Remarks
4500	Beginning of violet continuum
4773	Weak
4917	Moderately strong
5172	Strong
5604	Moderately strong
5773	Weak
6107	Moderately strong
6430	Weak
6680	Strong
6885	Strong

Table XI—Visual Absorption Spectrum of Uranous Phosphate in 85% Orthophosphoric Acid at Room Temperature

Wave length, Å	Remarks
4350	Beginning of violet continuum
4717–4900	
4900–5042	This is a "shoulder" on the above absorption band
5350–5470	
5410	There is a narrow region of transparency at this wave length
6170–6320	
6440	Very narrow band
6550–6700	

Table XII

Uranyl Compound	Reducing agent	Solvent	Temp	Fluorescence	Reduction
Sulfite	H_2SO_3	H_2SO_4	90°K	Strong*	No
Sulfite	H_2SO_3	H_2SO_4	193	Weak	Yes
Sulfite	H_2SO_3	H_2SO_4	293	None	Yes
Bromide	EtOH	EPA†	90	Yes	Yes
Salicylaldoxime	EtOH	EtOH	293	None	No
Phosphate	p-$C_6H_4(NH_2)_2$	H_3PO_4	293		Yes
Sulfate	EtOH	H_2O	293	None	Yes
Phosphate	$(CH_2OH)_2$	H_3PO_4	193	Weak	Yes
Oxalate	EtOH	Triethanolamine	293	None	No
Acetylacetonate	EtOH	EtOH	293	None	No
Acetate	Triethanolamine	Triethanolamine	293		Yes
Acetate	HCOOH	H_2O	293	None	Yes
Sulfate	Glycerol	Glycerol	293	None	No
Sulfate	H_2NNH_2	H_2SO_4	293	None	No
Bromide	$SOCl_2$	$SOCl_2$	293	None	No
Acetate	$SOCl_2$	$SOCl_2$	293	None	No
Chloride	$CH_3CH_2CO_2H$	EtOH	293	None	Yes
Chloride	EtSH	EtSH	293	None	No
Chloride	Lactic acid	H_2O	293	None	Yes
Chloride	Tartaric acid	H_2O	293	None	Yes
Chloride	Tartaric acid	$H_2O + NH_4OH$	293	None	Yes
Chloride	Citric acid	H_2O	293	None	Yes
Chloride	Citric acid	$H_2O + NH_4OH$	293	None	Yes
Chloride	Levulinic acid	H_2O	293	None	No
Chloride	Pyruvic acid	H_2O	293	None	Yes
Chloride	Pyruvic acid	$H_2O + NH_4OH$	293	None	No
Chloride	Glycollic acid	H_2O	293	None	Yes
$(NH_4)_2CO_3$ complex	H_2NNH_2	H_2O	293	None	Yes
Acetate	Lactic acid	Lactic acid	193	Yes	Yes

*Also shows strong phosphorescence.

†Mixture of ether, ethanol and isopentane.

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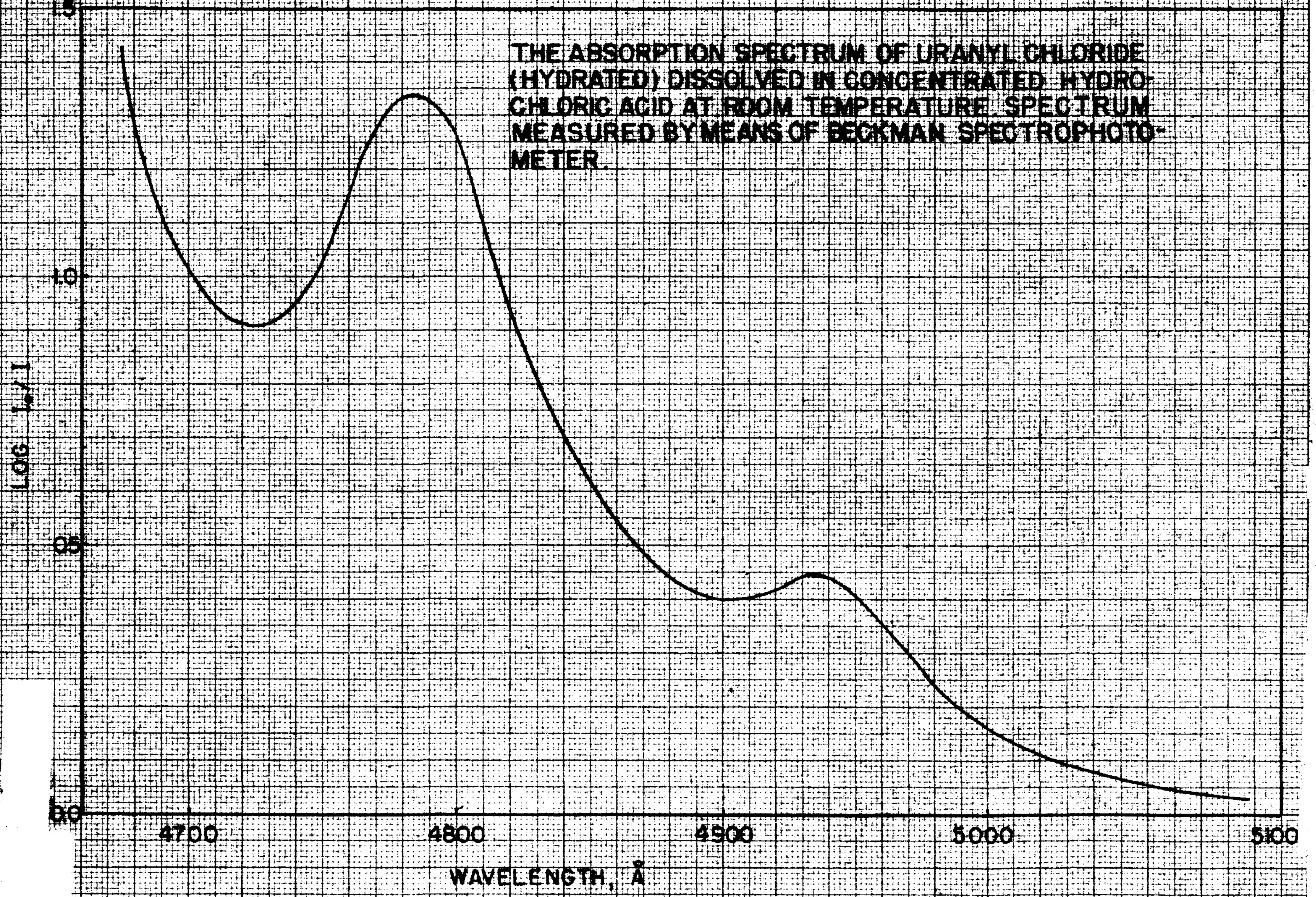
635-102

FIGURE I

A-750



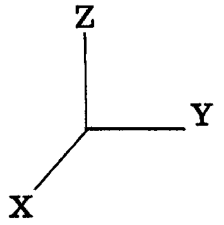
THE ABSORPTION SPECTRUM OF URANYL CHLORIDE (HYDRATED) DISSOLVED IN CONCENTRATED HYDROCHLORIC ACID AT ROOM TEMPERATURE. SPECTRUM MEASURED BY MEANS OF BECKMAN SPECTROPHOTOMETER.

D. MULTIPOLE NATURE OF THE RADIATION AND STUDIES ON UNIAXIAL CRYSTALS

We have previously indicated the fact that it is almost certain that the absorption and emission acts of uranium in its various oxidation states may not consist exclusively of electric dipole radiation permitted by the usual selection rules. Expecially does this seem probable with uranyl salts. For an analysis of the spectra and the ultimate assignment of the spectra to the various isotopes it would be very advantageous to have available information concerning the nature of the radiation from uranium compounds and the effects of the immediate environment on the nature of the radiation. It is likely that the magnetic moment of nucleus of U^{235} will make one type of radiation more probable than another and thus an immediate partial assignment of the U^{235} spectrum could be made. Such studies can be made on both solutions and crystals. Because of the sharpness of the fluorescence spectra from crystals, it is advisable to study crystals first which the method requires to be uniaxial. In addition, it is much easier to do spectroscopic work with crystals than with solutions at liquid hydrogen temperature where the bands are very sharp. Even the most mobile solvents and glasses crystallize and crack badly at 20°K.

We shall give a brief discussion of the information expected from such experiments. For simplicity we restrict ourselves to dipole processes exclusively in this discussion. Consider a crystal with its optical axis along Z.

Using the nomenclature used by Deutschbein (Ann. der Physik <u>36</u>, 183 (1939)), whose work we shall refer to presently, we shall call the radiation from such a crystal with its electric vector polarized along Z the extraordinary radiation. If one views along K with electric vector parallel to Z, we see the extraordinary radiation which can consist of both types of radiation and that along the ordinary radiation now if we look along Z we can see the electric dipole portion of the ordinary radiation, the magnetic dipole portion of the ordinary radiation, the magnetic dipole portion of the ordinary radiation which is polarized along X and the magnetic dipole portion of the extraordinary radiation.



Using this method Deutschbein found in the fluorescence of europium ethylsulfate-nonahydrate that the lines labelled m in the following diagram were magnetic dipole radiation. The lines m in the ordinary spectrum are magnetic dipole along the crystal axis.

Fluorescence of Europium ethylsulfate nonahydrate at room temperature. (a) Viewing along X; electric vector polarized in the Z direction. (b) Viewing along X; electric vector polarized in the Y direction. (c) Viewing along Z (optical axis); electric vector perpendicular to Z.

Furthermore, it was found by Freed and Weissman (Phys. Rev. <u>60</u>, 440 (1941)) by the method of wide-angle interference that when the crystals were dissolved the nature of the radiation remained practically unaltered. Thus we can expect considerable aid in the interpretation of the absorption and emission of uranium compounds by studies with polarized light on single uniaxial crystals, which may be later utilized in solutions. Similar experiments can be performed in solutions by orienting the molecules by some photochemical process in a rigid medium using polarized light (see Lewis and Bigeleison, J. Am. Chem. Sec. <u>65</u>, 520 (1943)).

The simplification of the spectra obtained by the use of polarized light on oriented molecules in crystals would simplify the problem of interpreting the nature or quantum characteristics of the excited state involved if one also considers the symmetry properties of the groups surrounding the excited uranium atom. This is analogous to the simplifications observed in Stark effects by viewing polarized light at various directions to the electric field (in our case the crystal field would be analogous to the electric field) and in Zeeman effects by viewing with polarized light in various directions to the axis of the magnetic field. Such experiments will require single, uniaxial crystals.

A study of the available crystallographic literature of uranium compounds has been made to discover the uniaxial crystals which contain uranium. They may be divided into the following classes:

1. UX_6 $X = F$
2. RUO_2X_3 $R = Cs, Rb, K, NH_4$
   $X = Ac, NO_3$
3. $R_3UO_2X_5$ $R = NH_4, K$
   $X = F$
4. $R_2UO_2X_4$ $R = (CH_3)_4N, (C_2H_5)_4N, K$
   $X = Cl$
5. $R(UO_2)_2(XO_4)_2 \cdot nH_2O$ $R = Cu, Ca$
   $X = Ac, P$
6. $Li_2U_2O_{10} \cdot 10\ H_2O$
7. UO_2HPO_4. 4 to 41/2 H_2O
8. $KZn(UO_2)_3\ (Ac)_9 \cdot 6H_2O$

There are several other types of uniaxial crystals which are known to form only fine powders. They are omitted from the above classification.

Not all combinations of R and X in the various classes have been described in the literature. However, it seems likely that all combinations could be prepared as uniaxial crystals. The following single, uniaxial crystals have been grown: $Rb(UO_2)\ (NO_3)_3$, $NH_4UO_2(Ac)_3$, $XUO_2(Ac)_3$. H_2O, $UO_2(NO_3)_2 \cdot 6H_2O$ (rhombic), $RbUO_2(Ac)_3$.

The single crystals are being grown by careful slow evaporation of the saturated solution of the salt containing carefully selected seeds. The uniaxial character is being checked with the aid of a polarizing microscope. Even considering the fact that it is much more likely that single crystals have a uniform composition than polycrystalline material, the chemical composition of each crystal will be checked.

E. THE LIQUID HYDROGEN PLANT

The plant for the liquefraction of hydrogen by a throttle expansion cycle has been in operation since April 15, 1943. It is similar to liquifiers developed at the Royal Society Mond Laboratory, Cambridge, by P. Kapitza and his associates. Use is made of a Kapitza circuit to allow use of commercial hydrogen as feed gas. The liquefier, constructed by members of the Physics Department of Columbia University in 1939, has been used to provide small amounts of product from time to time; being last previously used in the summer of 1942. Since April 15, 1943 approximately ninety liters of liquid hydrogen have been produced. Over this period, liquid nitrogen consumption for precooling has averaged 1.5 liters per liter of liquid hydrogen produced.

The plant is now capable of operating at its rated capacity of about 4½ liters of liquid hydrogen per hour. Continuous operation of the unit is impossible at the present time because of the fouling problem arising from low freezing impurities primarily oxygen, present in the feed gas. This results in a daily maximum capacity of about five liters of liquid hydrogen. With the inclusion of a catalytic purification system to remove oxygen from the feed gas, a new gas drier and a replacement of the liquid seal of the present gasholder, the production of ten liters of liquid hydrogen per eight hour day is believed practicable. These changes represent moderate expenditures.

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