URANYL FLUORESCENCE INTENSITY AND DECAY

by

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INFORMATION DIVISION

July 1954

This paper will be published as part of the Chemistry of Uranium, Part II, National Nuclear Energy Series, Division VIII. It is issued at this time to permit review and comment prior to publication and to make the information available to other Atomic Energy Commission Laboratories promptly.

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Contract W-31-109-eng-38
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Chapter 3

**URANYL FLUORESCENCE INTENSITY AND DECAY**

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URANYL FLUORESCENCE INTENSITY AND DECAY

by

Eugene Rabinowitch

1. PRELIMINARY REMARKS ON SLOW-DECAYING FLUORESCENCE

It seems advisable to preface the description of the experimental results in the field of the fluorescence of uranyl salts with brief remarks about intensity measurements of slowly decaying fluorescence (of which that of uranyl salts is the best-known example). When working with dye-stuffs or other organic compounds, whose fluorescence stops almost instantaneously (more exactly, within $10^{-7}$ sec) after the cessation of illumination, the intensity of fluorescence usually is measured in the steady state of illumination. In the determination of the yield, the amount of light energy (or the number of quanta) emitted per second in the steady state is compared with the amount of light energy (or the number of quanta) absorbed during the same period. In experiments on slow-decaying fluorescence or phosphorescence (for differentiation between these two phenomena, see below, p. 9), on the other hand, emission often is excited by a flash, and momentary intensity of emission is measured at various times after the flash and integrated graphically; alternatively, the total energy emitted after a single flash can be determined by an integrating instrument. In this case, the term "yield of fluorescence" often is taken to mean the ratio of the total light energy emitted after a flash to the amount of light energy absorbed in the flash. Whether the yield determined in this way is identical (or almost identical) with the yield in steady light, depends on the duration of the flash, $t_f$, compared to the (actual, not natural) lifetime of the excited state, $\tau$. If the flash is long compared to this lifetime, as in typical fluorescent dyestuffs, ($\tau_n < 10^{-7}$ sec, while the flash may last several microseconds or even milliseconds), a stationary state is reached at the end of the flash (assuming the intensity of the flash is uniform through its duration); the total integrated emission of light after the flash, which we call $L$, is then independent of the duration of the flash, and the yield calculated from this emission is inversely proportional to this duration. If, however, the flash is short compared to the natural lifetime of the excited state (as can easily occur in the case of uranyl fluorescence, where $t$ is of the order of $10^{-4}$ sec.), the number of excited molecules present at the end of the flash, and with it, the initial intensity of emission, $F_0$, (as well as the integral of the emitted energy, $L$), must increase with the duration of the flash. In the limiting case, when $t_f \ll \tau$, both $F_0$ and $L$ must become proportional to $t_f$, and the yield, derived from the measurement of $L$, is independent of the duration of the flash.
Let us assume that the number of non-excited uranyl ions in a unit volume of fluorescent material is \([\text{UO}_2^{++}]\). This number is not markedly depleted even in very strong light, because, for all practically attainable light intensities, the interval between two successive excitations of a given uranyl ion is long compared to the lifetime of excitation, so that every ion spends much more time in the non-excited, than in the excited state. The rate of formation of excited molecules, in a layer which is situated at depth \(L\) and which is optically so thin as to be practically uniformly illuminated, is, in a parallel beam of monochromatic light:

\[
+ \frac{d[\text{UO}_2^{++*}]}{dt} = \epsilon I \quad [\text{UO}_2^{++}] = \epsilon I_0 e^{-e[\text{UO}_2^{++}]L} [\text{UO}_2^{++}]
\]

where \(I_0\) is the number of einsteins of quanta impinging on unit area (1000 sq cm) per unit time (1 sec), \(\epsilon\) the molar absorption coefficient (with base e), which is inversely proportional to the natural life time of the excited state, \(\tau_0\), and \([\text{UO}_2^{++}]\) the concentration of uranyl ions in moles/liter. Since we have assumed illumination with a parallel beam of monochromatic light, the light intensity will decline with depth, \(L\), as a simple exponential function (as assumed in Eq. 1). Integration of this equation over a layer of total thickness \(L_0\) gives, as could be expected:

\[
\frac{d}{dt} \left[ \int_0^L [\text{UO}_2^{++*}] \, dz \right] = \epsilon [\text{UO}_2^{++}] \int_0^L I \, dz = I_0 \left(1 - e^{-[\text{UO}_2^{++}]L_0} \right) = I_a
\]

where \(I_a\) is the absorbed light flux (in einsteins per second per 1000 sq cm).

The rate of loss of excited molecules, by fluorescence and by non-radiative (monomolecular) energy dissipation, is given, for each layer with constant concentration of these molecules, by Eq. (3).

\[
- \frac{d[\text{UO}_2^{++*}]}{dt} = \alpha \cdot [\text{UO}_2^{++*}] = (a\varepsilon + k_d) [\text{UO}_2^{++*}] = \frac{[\text{UO}_2^{++*}]}{\tau}
\]

where

\[
a\varepsilon = \frac{N_A \lambda^2 10^{-3}}{8\pi} = 2.4 \times 10^{18} \varepsilon \lambda^2 = \frac{1}{\tau_0}
\]

The relation in parentheses is the universal relation between the natural lifetime of an excited state, the absorption coefficient of the spectral line that leads to this state, and its wave length (\(N_A\) is Avogadro's number).

According to Lewis and Kasha, this expression should be multiplied by a factor \(n^2\) if the process occurs in a medium with an index of refraction \(n\).

We assumed in equation (3) that both processes bring the excited molecules back into the ground state, and not into some long-lived metastable state,
and that dissipation, like fluorescence, is a first order process in respect to the concentration of the excited ions. The constant $k_d$ is the monomolecular velocity constant of the radiationless dissipation process. The total monomolecular deactivation constant, $\alpha^* (= \alpha_e + k_d)$, is the inverse of the actual mean lifetime of the excited state, $\tau$.

The concentration of excited ions, $[\text{UO}_2^{++}]$, present in an infinitely thin layer at depth $l$ after an illumination time of $t_f$ sec is obtained by integrating the difference between (1) and (3):

$$[\text{UO}_2^{++}]_{t_f} = \left(1 - e^{-\alpha^* t_f}\right) \frac{\epsilon I_l [\text{UO}_2^{++}]}{\alpha^*}$$

By integration of Eq. (5) over the depth $l_0$, we obtain, using (3.2),

$$\int_0^{l_0} [\text{UO}_2^{++}]_{t_f} \, dl_0 = \frac{1-e^{-\alpha^* t_f}}{\alpha^*} \int_0^{l_0} I_l \, dl$$

$$= \frac{1-e^{-\alpha^* t_f}}{\alpha^*} I_0 \left(1 - e^{-\epsilon [\text{UO}_2^{++}] l_0}\right) = \frac{1-e^{-\alpha^* t_f}}{\alpha^*} I_a$$

where $I_a$ is the amount of light absorbed in passage through the layer $l_0$.

At the beginning of illumination, as long as $t_f \ll \frac{1}{\alpha^*}$, the concentration of excited ions in each layer $dl$ increases proportional to $t_f$:

$$[\text{UO}_2^{++}]_t = \epsilon I_l \, t_f [\text{UO}_2^{++}]$$

and the same is true of the total number of excited molecules in the finite layer, $l_0$. When $t_f > \frac{1}{\alpha^*}$, the concentration of excited molecules in each thin layer reaches a steady value:

$$[\text{UO}_2^{++}] = \frac{\epsilon I_l}{\alpha^*} [\text{UO}_2^{++}] \text{ moles/liter}$$

and the same is true of the total amount of excited molecules in a finite layer, $l_0$:

$$\int_0^{l_0} [\text{UO}_2^{++}]_{\infty} \, dl = \frac{I_a}{\alpha^*}$$

The momentary local intensity of fluorescence at any given time is

$$F = a \epsilon \, [\text{UO}_2^{++}] \text{ einsteins/(sec liter)}$$
Immediately after the beginning of illumination, therefore, we have
for an optically thin layer:

\[ F = a \varepsilon^2 I \tau_f[UO_2^{++}] \text{ einsteins/(sec liter)} \]

and for a finite, optically dense layer \( l_0 \):

\[ F_0 = \int_0^{l_0} F \, dl = a \varepsilon I \tau_f \text{ einsteins/(sec 1000 sq cm)} \]

In the steady state, we have, for an optically thin layer:

\[ F_\infty = \frac{a \varepsilon^2 I \tau_f}{\alpha^*} [UO_2^{++}] \text{ einsteins/(sec liter)} \]

and for an optically dense layer:

\[ F_\infty = \int_0^l F_\infty \, dl = \frac{a \varepsilon}{\alpha^*} I_\alpha = \tau a \varepsilon I_\alpha \text{ einsteins/(sec 1000 sq cm)} \]

When illumination stops, the fluorescence decays exponentially as
function of the dark time, \( t_d \).

If the excitation period had been long (meaning "long enough to reach
the steady state") \( t_f \gg \frac{1}{\alpha^*} \), we have, for a thin layer, \( dl \):

\[ F_{td} = \frac{a \varepsilon^2 I \tau_f}{\alpha^*} [UO_2^{++}] e^{-\alpha^* t_d} = F_\theta e^{-\alpha^* t_d} \text{ einsteins/(sec liter)} \]

or, for a dense layer, \( l_0 \):

\[ F_{td} = \frac{a \varepsilon I}{\alpha^*} e^{-\alpha^* t_d} = F_\theta e^{-\alpha^* t_d} \text{ einsteins/(sec 1000 sq cm)} \]

where \( F_\theta \) is the fluorescence intensity immediately after the cessation of
illumination.

The (time) integral of the yield of fluorescence after the cessation
of "long" excitation is:

\[ L = \int_0^\infty F_{td} \, dt_d = \frac{a \varepsilon^2 I \tau_f}{\alpha^* 2} [UO_2^{++}] = \frac{F_\theta}{\alpha^*} \text{ einsteins/liter} \]

or

\[ L = \int_0^{l_0} L_d \, dl = \frac{a \varepsilon}{\alpha^* 2} I_\alpha = \frac{F_\theta}{\alpha^*} \text{ einsteins/1000 sq cm} \]
If the excitation was by a brief flash $t_f > \frac{1}{\alpha^*}$, the fluorescence immediately after the end of the flash is:

\[
F_0 = (1 - e^{-\alpha^* t_f}) \frac{ae^2 I_0}{\alpha^*} [\text{UO}_2^{++}] \text{ einsteins/(sec liter)}
\]

or

\[
F_0 = \int_0^L F_0 \, dl = (1 - e^{-\alpha^* t_f}) \frac{ae}{\alpha^*} I_a \text{ einsteins/(sec 1000 sq cm)}
\]

It then decays exponentially with time:

\[
F_{td} = (1 - e^{-\alpha^* t_f}) \frac{ae^2 I_0}{\alpha^*} [\text{UO}_2^{++}] e^{-\alpha^* t_d} = F_0 e^{-\alpha^* t_d} \text{ einsteins/(sec liter)}
\]

or

\[
F_{td} = (1 - e^{-\alpha^* t_f}) \frac{ae}{\alpha^*} I_a e^{-\alpha^* t_d} = F_0 e^{-\alpha^* t_d} \text{ einsteins/(sec 1000 sq cm)}
\]

The time-integrated emission is in this case:

\[
L \int_0^\infty F_{td} \, dt_d = (1 - e^{-\alpha^* t_f}) \frac{ae^2 I_0}{\alpha^*} [\text{UO}_2^{++}] = \frac{F_0}{\alpha^*} \text{ einsteins/liter}
\]

or

\[
L = \int_0^L L_\ell \, dl = (1 - e^{-\alpha^* t_f}) \frac{ae I_a}{\alpha^*} = \frac{F_0}{\alpha^*} \text{ einsteins/1000 sq cm}
\]

If the flash is very short ($t_f \ll \frac{1}{\alpha^*}$), we have:

\[
L = \frac{ae^2 I_0}{\alpha^*} [\text{UO}_2^{++}] = \frac{F_0}{\alpha^*} \text{ einsteins/liter}
\]

\[
L = \int_0^L L_\ell \, dl = \frac{ae I_0}{\alpha^*} = \frac{F_0}{\alpha^*} \text{ einsteins/1000 sq cm}
\]

When $k_d$ can be neglected (and $\alpha^*$ is therefore equal to $a \varepsilon$, meaning 100% fluorescence yield in the steady state!), we obtain, after long excitation:

\[
L = \frac{I_\ell}{a} [\text{UO}_2^{++}] \text{ einsteins/liter}
\]

and

\[
L = \int_0^L L_\ell \, dl = \frac{I_a}{ea} \text{ einsteins/1000 sq cm}
\]
After a "brief" flash:

\[ L = (1 - e^{-a \varepsilon_t}) \frac{I_a}{a} [\text{UO}_2^{++}] \text{ einsteins/liter (thin layer)} \]

\[ L = \int_0^{L_0} L \, dl = \frac{1 - e^{-a \varepsilon_t}}{a \varepsilon} I_a \text{ einsteins/1000 sq cm (dense layer)} \]

and after a "very brief" flash:

\[ L = t_f I_a [\text{UO}_2^{++}] \text{ einsteins/liter (thin layer)} \]

\[ L = \int_0^{L_0} L \, dl = t_f I_a \text{ einsteins/1000 sq cm (dense layer)} \]

The yield of fluorescence, measured by integrating the emission after a flash, can reach 100% only in the third case, i.e., if \( t_f \ll a \varepsilon \), because then practically no absorbed energy is re-emitted during the flash. The same applies generally to the relation between the fluorescence yield in steady light and the fluorescence yield after flash illumination: the latter is generally lower, but approaches the former when the duration of the flash becomes very short compared to the life time of the excited state.
2. INTENSITY AND DECAY OF URANYL FLUORESCENCE IN CRYSTALS

E. Becquerel (1872) first determined by means of a “phosphoroscope” the duration of light emission by illuminated solid uranium nitrate. He noted that the luminescence lasted for $3 - 4 \times 10^{-5}$ sec after the cessation of excitation - a value which agrees well with the more recent determinations. (As will be seen below, these determinations gave values of about $3 \times 10^{-4}$ sec for the “life time” of the excited state, i.e., the time required for the fluorescence intensity to decline by a factor of e; fluorescence remains visible - or detectable - for a considerably longer period, depending on its initial intensity and on the sensitivity of the eye, or of the measuring device.)

Nichols and Howes (1919) constructed a “synchrono-phosphoroscope” to study the law of decay of luminescence in uranium compounds. They began by establishing the identity of what they called “fluorescence spectrum” with what they designated as “phosphorescence spectrum,” i.e., of the spectrum of uranyl luminescence during excitation and that emitted at different times after the cessation of excitation. Sparks repeated 120 times per second served for excitation; observation was either synchronized with excitation, or shifted to different moments in the intervals between sparks. The same seven groups of bands were found in both cases, and they had the same relative brightness. This result is in agreement with the since well-established concept that light-excited uranyl salts are capable of only one kind of photoluminescence, namely, a slow-decaying fluorescence. (In other words, they exhibit no true phosphorescence.) The reason why the fluorescence of uranyl salts persists in the dark for several milliseconds (thus resembling phosphorescence), while the fluorescence of organic dyestuffs, such as fluorescein, disappears in less than a microsecond, is the low intensity of the absorption bands of the uranyl ion, as compared to the bands of organic dyestuffs and the consequent long life-time of the excited state (cf. Eq. 4). In true phosphorescence, according to the most appropriate definition of this term, delayed re-emission of absorbed light energy is caused by the conversion of the primarily excited state into another, metastable state (of somewhat lower energy), and not by the long life of the excited state itself. The emission of phosphorescent light can originate in the metastable state; in this case, the phosphorescence band is displaced towards the longer waves compared to the fluorescence band (which originates directly in the light-excited state). Alternatively, emission may be caused by return of the molecule from the metastable into the original excited state, caused by thermal agitation; in this case, the phosphorescence band will coincide with the fluorescence band (cf. Fig. 3.1).

The decay curves of luminescence of uranium salts after cessation of illumination were assumed by Nichols and Howes to follow the equation

$$
\sqrt{1/F_{td}} = \sqrt{1/F_0} + c_t \delta
$$
FIG. 3.1—FLUORESCENCE AND PHOSPHORESCENCE SCHEME.
G, ground state; F, fluorescent state; M, metastable state; A, absorption; E, fluorescence; NR, non-radiative transition; kT, thermal excitation; P, phosphorescence.
where $F_0$ is the intensity of fluorescence at time zero, and $C$ is a proportionality constant. Already before that time, when Eq. (24) was applied to other phosphorescent substances, deviations from this "law" had been found by Nichols and Howes. These had been interpreted by them by assuming two superimposed decay processes: the decay first followed equation (24) with the higher value of the constant, $C_1$, and later the same equation with a smaller decay constant, $C_2$. In the case of uranyl salts, an apparent change in the opposite direction was found: the constant $C$ appeared to become higher as the luminescence decayed. Three increasingly steep linear sections were found by Nichols and Howes in the fluorescence-time curves ($1/F_{td}$ as function of $t_d$) of several uranyl salts (Fig. 3.2). (For re-interpretation of these results, see below.)

The total periods over which the decay of uranyl salt fluorescence could be followed were found by Nichols and Howes to be of the order of $10^{-3}$ sec. This was noted with crystals of uranyl sulfate, ammonium uranyl sulfate, potassium uranyl sulfate, uranyl nitrate hexahydrate, and ammonium uranyl chloride. At constant intensity of illumination, the initial intensity of emission, $F_0$, was highest in ammonium uranyl and potassium uranyl double sulfates, and several times lower in uranyl nitrate, uranyl sulfate, and ammonium uranyl chloride. Potassium sulfate, freshly prepared in the dark, gave a much brighter fluorescence than a similar preparation exposed to light for a long time.

Simultaneous irradiation with red or infrared light, which enhances the phosphorescence of sulfide phosphors, had no effect on the luminescence of uranyl salts. This is in agreement with its interpretation as a long-lived fluorescence, rather than phosphorescence. (The phosphorescence of sulfide phosphors and similar luminous solids is caused by conversion into a metastable state, in which the originally excited electron wanders away from its nucleus and is caught in a "trap," often provided by an impurity; infrared radiation liberates the electron from the trap and thus accelerates the restoration of the initial excited state and the emission of phosphorescence.)

Excitation by quartz mercury arc gave the same decay curve as excitation by a spark.

Uranium glass, although its composition invites comparison with a phosphor made luminescent by an impurity, showed a decay curve similar to that of pure uranyl salts.

Viscous uranyl phosphate did not fluoresce at all until the water content was reduced so far that it became a plastic solid; in this state, the phosphate showed the same decay curve as crystalline uranyl salts.

Lowering of temperature from $+60^\circ$ to $-180^\circ$C made the decay slower, but the effect was irregular. In the ammonium uranyl sulfate, for example, the decay was faster at $-180^\circ$ than at $+20^\circ$C.
FIG. 3.2 - FLUORESCENCE DECAY OF RUBIDIUM URANYL NITRATE CRYSTALS AT FOUR LIGHT INTENSITIES (AFTER NICHOLS AND HOWES). (INTENSITY IS SUPPOSED TO DECLINE PROPORTIONALLY TO $t_d^{-2}$). (FROM S. VAVILOV AND V. LEVSHIN, ZEIT. F. PHYSIK., 48, 398 (1928)).
Intensity of excitation has no effect on the shape of the decay curve. (In the interpretation of Nichols and Howes, all three consecutive decay stages were prolonged in the same proportion; the duration of each stage was found to be proportional to the logarithm of the intensity of the exciting light.)

Decay was much slower in uranyl nitrate hydrate than in the corresponding anhydrous salt.

Double chlorides (such as rubidium uranyl chloride) exhibited a polarization of the fluorescent light. The components polarized in the two perpendicular planes had the same rate of decay.

Nichols and Howes also studied the luminescence of uranyl salts excited by cathode rays. Its spectrum was the same as that of light-excited luminescence, but the emission lasted minutes instead of milliseconds.

To measure the duration of rapidly decaying fluorescence of organic dyestuffs, Gaviola (1927) constructed an electro-optical "fluoroscope" based on the Kerr effect - an instrument suitable to observe changes in light intensity occurring within $10^{-8}$ sec or less. He applied it also to uranium salt solutions (uranyl sulfate, in methanol or in concentrated sulfuric acid) and obtained an unexpected result: He found the mean life-time $\tau$ to be even shorter than in dyestuff solutions - of the order of $10^{-9}$ sec! For a sample of uranium glass, on the other hand, he found $\tau > 15 \times 10^{-9}$ sec (the latter figure represented the upper limit of usefulness of his instrument). One could think at first that, perhaps, the fluorescence of uranyl salt solutions decays much faster than that of uranyl salt crystals, but Gaviola and Pringsheim (1927), using the same instrument, also found a value of $5.1 \times 10^{-9}$ sec for the decay constant of fluorescence of solid uranyl nitrate. They noted the wide disagreement between this value and the decay periods found for uranyl salts by phosphoroscopic methods ($10^{-4}$ to $10^{-2}$ sec) but could give no explanation of the discrepancy. Subsequent studies confirmed the observation of Becquerel and of Nichols and Howes that the visible fluorescence of uranyl salts lasts for about a thousandth of a second. The existence, in addition to this slow-decaying fluorescence, of a rapidly decaying fluorescence, such as was described by Gaviola, is very unlikely.

Two extensive investigations of the fluorescence of uranyl salts were carried out by Vavilov and Levshin (1927, 1928) and by Perrin and Delorme (1928, 1929). They studied crystals as well as solutions (for results obtained with the latter, see Sec. 3).

Vavilov and Levshin (1928) re-interpreted the above-described fluorescence measurements of Nichols and Howes by plotting the data on a semi-logarithmic scale, $\log F = f(t_d)$. In this way they obtained straight lines (Fig. 3.3), indicating that the true decay law is exponential:
FIG. 3.3 - SAME DATA AS IN FIG. 3.2 REPLOTTED BY
VAVILOV AND LEVSHIN (log F AS FUNCTION OF t).
(FROM S. VAVILOV AND LEVSHIN, ZEIT. F. PHYSIK.,
48, 399 (1928)).
as expected for a monomolecular process. From Nichols and Howes data, Vavilov and Levshin calculated the values of $\tau$ shown in the second column of Table 3.1.

Previous investigations by Vavilov and co-workers had shown that in dye solutions in glassy media, a long-living phosphorescence often was superimposed on short-lived fluorescence; while in liquid solutions, only the latter was observed. The luminescence of solid uranyl salts showed no such complexity and because of its long duration Vavilov and Levshin (similarly to Nichols and Howes) first classified it as a phosphorescence. They saw a confirmation of this view in an observation, that a dark interval intervened between the cessation of illumination and the beginning of emission in uranium glass - a phenomenon they had noted previously in typical phosphorescences. However, both arguments proved fallacious: the low intensity of the visible uranyl absorption bands indicates that the excited uranyl ions must have a long natural life time, $\tau_0$, so that no doubts need to arise as to the fluorescent character of its emission merely because of its long duration. As to the "dark interval" (again found in Vavilov and Levshin's second investigation, in 1928, where it was determined to last, in uranyl nitrate, for about $1 \times 10^{-4}$ sec), his observation was subsequently found to be erroneous (Levshin and Sheremetjev, 1947).

The decay constant measurements by Vavilov and Levshin are shown in the penultimate column of Table 3.1.

The shape of the decay curves found by Vavilov and Levshin for uranyl sulfate suggested that a second decay period, with $\tau = 0.8 \times 10^{-4}$ sec, is superimposed upon the main decay period ($2.6 \times 10^{-4}$ sec). Similarly, the $3.2 \times 10^{-4}$ sec decay period of "uranium glass 1" was combined with a second decay period of $0.5 \times 10^{-4}$ sec. This shorter-lived fluorescence was particularly strongly excited by far ultraviolet light (Fig 3.4) and was absent in fluorescence excited by visible (blue) light.

Nichols and Howes' data on cathode ray-excited fluorescence indicated a very slow decay, following a complex course (cf. above, p. 13); Vavilov and Levshin suggested that this phenomenon may be similar to long-lasting tribo-luminescence, which can be observed when uranyl salt crystals are broken by a hammer.

Vavilov and Levshin found no evidence of the extremely short-lived fluorescence described by Gaviola. The same conclusion was reached by Perrin and Delorme (1928, 1929).

Contrary to Vavilov and co-workers, Perrin and Delorme interpreted the long-lived emission of uranyl salts correctly as "fluorescence of long duration." Their phosphoroscopic measurements gave, for solid uranyl salts,
### TABLE 3.1

Decay Time Constants of the Fluorescence of Solid Uranyl Compounds

\( F = F_0 e^{-t/T} \)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \tau \times 10^4 ) sec, as observed by</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nichols and Howes*</td>
</tr>
<tr>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>( \text{UO}_2(\text{NO}_3)_2 )</td>
<td>5.6</td>
</tr>
<tr>
<td>( \text{RbUO}_2(\text{NO}_3)_3 )</td>
<td>6.7</td>
</tr>
<tr>
<td>( \text{UO}_2\text{SO}_4 )</td>
<td>2.55**</td>
</tr>
<tr>
<td>( (\text{NH}_4)_2\text{UO}_2(\text{SO}_4)_2 )</td>
<td>4.3</td>
</tr>
<tr>
<td>( \text{K}_2\text{UO}_2(\text{SO}_4)_2 )</td>
<td>4.15</td>
</tr>
<tr>
<td>( \text{UO}_2\text{Cl}_2 )</td>
<td>---</td>
</tr>
<tr>
<td>( \text{RbUO}_2\text{Cl}_4 )</td>
<td>4.2</td>
</tr>
<tr>
<td>( \text{K}_2\text{UO}_2\text{Cl}_4 )</td>
<td>---</td>
</tr>
<tr>
<td>Uranyl Phosphate</td>
<td>---</td>
</tr>
<tr>
<td>Uranyl ammonium phosphate</td>
<td>---</td>
</tr>
<tr>
<td>( \text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 )</td>
<td>---</td>
</tr>
<tr>
<td>( (\text{NH}_4)_2\text{UO}_2(\text{CO}_3)_2 )</td>
<td>---</td>
</tr>
<tr>
<td>Uranium glass†</td>
<td>4.45</td>
</tr>
</tbody>
</table>

*Calculated by Vavilov and Levshin.

**Another numerical example in Nichols and Howes monograph gave \( \tau = 0.44 \times 10^{-4} \) sec.

†Superimposed by a shorter decay period (cf. below p. 19). Levshin and Sheremetjev (1947) found later, by photographic methods, \( \tau = (2.7 \pm 0.2) \times 10^{-4} \) sec.

‡Sevchenko (1944) found values between \( 3.2 \times 10^{-4} \) sec and \( 11 \times 10^{-4} \) sec for a series of different composition.
FIG. 3.4—FLUORESCENCE DECAY OF URANYL SULFATE EXCITED WITH ULTRAVIOLET LIGHT. EMPIRICAL DECAY DATA (O) INTERPRETED AS SUPERPOSITION (- - ) OF TWO LOGARITHMIC DECAY CURVES, \( t = 2.6 \times 10^{-4} \) sec. (Curve I) AND \( t = 8 \times 10^{-5} \) sec. (Curve II).

FROM S. VAVILOV AND V. LEVSHIN, ZEIT. F. PHYSIK., 48, 404 (1928).
the values of \( \tau \) listed in the second columns of Table 3.1. They found that the decay required up to 2-1/2 times as much time in liquid air as at room temperature. This indicates that the actual lifetime of the fluorescent state is limited, or at least "co-limited," by a non-radiative energy dissipation process (i.e., that \( k_d \) in Eq. 3 is not zero); the rate of such processes can be expected to increase with temperature.

In uranyl compounds in which fluorescence was very weak, its lifetime was distinctly shorter than in strongly fluorescent salts, but no exact proportionality, or even consistent parallelism, was observed between the lifetime for emission, \( \tau \), and the initial intensity of emission, \( F_0 \). For example, uranyl sulfate was found to fluoresce stronger than nitrate, but its fluorescence decayed faster. (Below, we will quote examples of a parallelism of \( \tau \) and \( F_0 \)).

Hein and Retter (1928) were concerned only with the practical problem of analytical determination of various elements by their fluorescence, and gave figures for the minimum concentration of uranyl sulfate in a powder mixture at which the uranyl fluorescence (in the light of a quartz mercury lamp) is recognizable to the eye: 1 g UO_2SO_4 in 80-100 g CuO, 25-30 g Cr_2O_3, in 2-3 g Fe_2O_3, 5-8 g HgO, or 50-70 g azobenzene.

Anderson and Bird (1928) investigated the possibility of using the fluorescence of uranium glass (as well as that of esculin or fluorescein) for measuring the relative intensities of visible fluorescence excited by various mercury lines in the ultraviolet (253.7 to 366 m\( \mu \)), with the relative intensities of the same lines, measured by means of a thermopile. They found the two sets of values to be proportional to each other, showing that fluorescence can serve as measure of the intensity of exciting light. [The observed proportionality can be considered as proof of two things: (a) complete absorption of exciting lights at all wave lengths used, in a thin-layer of the fluorescent material; and (b) identical quantum yield of fluorescence at all these wave lengths.]

Gurevich and Chakhrov (1936) made a direct determination of the absolute yield of fluorescence of solid uranyl potassium sulfate [it probably was K_2UO_2(SO_4)_2 \cdot 2H_2O]. The method used was, however, rather inexact, since it involved visual photometry of colored light. Fluorescence was excited by filtered light from a carbon arc; the exciting band was assumed to be 325-410 m\( \mu \), with a maximum of 370 m\( \mu \). It fell on a screen covered with potassium uranyl sulfate powder, and the intensity of fluorescence was measured by a visual photometer, while the intensity of exciting light was measured simultaneously by a thermoelement. The fluorescent light was reduced in intensity and changed in color by a "pink" filter (which transmitted only about 3%), to permit convenient visual comparison with white light from a sheet of magnesium; the thermoelement was calibrated by a tungsten band lamp. The absorption of the exciting light in the fluorescent screen was determined by means of the same visual photometer.
In this way, a quantum yield of about 1.1 (quanta emitted per quantum absorbed), corresponding to an energy yield of 80% (ergs emitted per erg absorbed), was calculated. Not much significance can be attached to this result, in virtue of the crudeness of the method used, except that it indicates that the yield of fluorescence of solid potassium-uranyl sulfate is rather high.

Sevchenko (1944) investigated the polarization of fluorescence in uranium glass. Gaviola and Vavilov had found in this case no polarization at all, while Perrin (cf. above) had observed a polarization of up to 10%. Sevchenko showed that the degree of polarization depends on the specific composition of the glass and on the wave length of exciting light; furthermore, it changes as fluorescence decays.

Basic glasses, containing uranates, do not fluoresce at all. Acid glasses, which can be presumed to contain uranyl ions, fluoresce with more or less strongly polarized light, depending on the anions present. The glasses studied contained 1% uranium, in a boron, boron-silica, basic silica or phosphate glass.

Excitation with the light of the ordinary quartz mercury lamp (centered around 365 mȝ) gives the weakest polarization. Using a nickel arc and a monochromator, Sevchenko plotted the degree of polarization as function of the wave length of the exciting light. In BaO-P2O5 glass, the polarization was lowest (about 10%), and practically constant between 240 and 500 mȝ. In acid glass (K2O-7B2O3·10SiO2), the polarization varied between 15 and 25% and showed three maxima: at 240-250, 330-340, and 400-420 mȝ. The same three maxima also occurred, although less pronouncedly, in other silica glass.

The degree of polarization decreased with time after excitation; this is plausible, since the ions which emit later have more time to change their orientation in the crystal. The degree of polarization and the half-time of decay were independent of the uranyl concentration in glass between 4 x 10^{-6} g/cc and 2 x 10^{-3} g/cc showing that, in this concentration region, resonance exchange of excitation energy between ions is unimportant. The total yield of fluorescence, L, was found to be proportional to the life time, as it should be if the initial intensity, F0, is the same for all glasses [cf. Eqs. (16), (16a), etc. where a* is inversely proportional to τ]. Values of the actual life time, τ, between 0.32 x 10^{-3} and 1.1 x 10^{-3} sec were found by Sevchenko for the different glasses studied (cf. footnote to Table 3.1).

At 4 x 10^{-3} g/cc of [UO2^{2+}], polarization declined markedly (e.g., from 13 to 10%), and the yield became lower (e.g., 35 instead of 43 rel. units). This may perhaps be taken as evidence of incipient resonance exchange between adjacent uranyl ions.
Sevchenko discussed whether the uranyl emission is a dipole or a quadrupole radiation. Low intensity and long duration of fluorescence suggest a quadrupole radiation. On the other hand, Vavilov's criterion of polarization indicated dipole nature. (This argument is based on comparison of uranyl glass fluorescence with fluorescence of dyestuffs in aqueous glycerol, whose dipole character is certain. In both cases, measurements of the degree of polarization as a function of angle between the electric vector of incoming light and the direction of observation, gave the same maximum - about 12.5%.)

Randall and Wilkins (1945) studied the photoluminescence of various solids in relation to their photoconductivity. Theoretically, photoconductivity is expected when light absorption liberates an electron from its atom and transfers it into a "conductivity band." An external electric field affects the motion of the electrons in the conductivity band and thus causes an electric current to flow during illumination. In uranyl salts no photoconductivity was found, confirming that the excited electron remains within the attraction sphere of its original atom (or, rather, of the triatomic group UO$_2$$^+$$^+$$^+$$). This, too, is in agreement with the interpretation of the luminescence of uranyl salts as true fluorescence.

Fig. 3.5 shows the growth and decay curve of ammonium uranyl phosphate fluorescence, excited by constant ultraviolet light, as registered by an oscilloscope. It will be noted that in this case, the rate of decay appears the same at 90° and 300°K, indicating no temperature-dependent dissipation processes co-limiting the lifetime of the excited state and thus pointing to a fluorescence yield close to unity.

No time scale is given for this curve, but in phosphoroscopic measurements of Randall and Wilkins (made by means of a photocell rather than by visual comparison, as in the experiments from Vavilov's and Perrin's laboratories) the mean lifetime of fluorescence was found to be 1.42 x 10$^{-3}$ sec for the ammonium uranyl double phosphate; for uranyl nitrate, it was 7.19 x 10$^{-4}$ sec (cf. last column in Table 3.1). The precision with which the decay follows the exponential law is illustrated by Fig. 3.6. This figure also shows that the rate constant of decay is unaffected by a ten-fold change in the intensity of exciting light, a result which is to be expected if both fluorescence and radiationless de-activation are monomolecular processes.

Levshin and Sheremetjev (1947) re-investigated some topics not satisfactorily clarified in the study of Vavilov and Levshin (1928). In the first place, they analyzed the apparent delay in the beginning of fluorescent emission, mentioned on p. 15. They found an (at least qualitatively) satisfactory explanation of this delay in the gradual approach of fluorescence intensity to its stationary peak value (cf. Eq. 11). As shown in Sec. 1, the illumination time required to reach the stationary concentration of the excited atoms or molecules is greater the longer the life time of the latter
FIG. 3.5 - RISE AND DECAY OF FLUORESCENCE IN SOLID AMMONIUM URANYL PHOSPHATE. ABOVE, 90°K; BELOW, 300°K. (FROM J. RANDALL AND M. WILKINS, PROC. ROY. SOC. A, 184, 350a (1945)).
AMMONIUM URANYL PHOSPHATE

URANYL NITRATE

FIG. 3.6—URANYL SALT FLUORESCENCE DECAY CURVES. THE EXCITING INTENSITY FOR CURVES a IS TEN TIMES THAT FOR CURVES b. AMMONIUM URANYL PHOSPHATE, $\lambda = 703$ sec.$^{-1}$ URANYL NITRATE, $\lambda = 1390$ sec.$^{-1}$ (FROM J. RANDALL AND M. WILKINS, PROC. ROY. SOC. A, 184, 353(1945)).
(tf must be >> \(\frac{1}{\alpha_0}\) = \(\tau\)). With such slow emitters as uranyl ions (\(\tau = 5 \times 10^{-6}\) sec), fluorescence grows so slowly as to produce the impression that it does not begin at all until \(10^{-4}\) sec after the start of illumination. By experiments of higher precision, Levshin and Sheremetjev showed that if the beginning of uranyl fluorescence lags behind absorption at all, the lag is shorter than \(3 \times 10^{-6}\) sec.

Another point studied by Levshin and Sheremetjev was whether the spectral distribution of uranyl sulfate fluorescence changes in the course of its decay. Comparison of spectrophotograms made at the beginning of decay (1-2 \(\times 10^{-5}\) sec after cessation of illumination) with those taken 8 \(\times 10^{-4}\) sec later (when the intensity of fluorescence has decreased by a factor of 28) showed no difference (outside the limits of experimental error) in the relative intensity of the seven main bands, originating in the non-vibrating excited state, and of the eighth, short-wave band originating in the state with one quantum of symmetric bond vibration (cf. ANL-5173, Fig. 2.1). Also no significant change was noticeable in the energy distribution within each of the eight bands. These results indicate that the thermal equilibrium distribution of excited molecules over their vibrational levels is achieved, at room temperature, within a time that is short compared to the decay time of fluorescence so that this distribution already is present, to all practical purposes, when fluorescence first becomes observable, and is maintained throughout the emission. If the fluorescence decay constants of the different vibrational states are different - which is likely - the distribution of excited molecules over these levels must be maintained during the emission by exchange of vibrational quanta in collisions. This applies to the relatively large quanta of the bond vibrations \(\nu_s\) and \(\nu_a\), as well as to the smaller quanta of molecular and lattice vibrations, which determine the intensity distribution in the individual bands.

The uranyl sulfate preparation on which the decay measurements were made had a "doublet type" fluorescence spectrum; according to Chap. 1 (ANL-5122, p. 60), it must have consisted of two types of trihydrate crystals. The relative intensity of the two doublet components also did not change during the decay, showing that the transition probabilities are not significantly different in the two types of crystals.

Levshin and Sheremetjev also measured (by photographic comparison) the relative intensity of the total fluorescence of uranyl sulfate preparations as function of water content. Table 3.2 show the results. The anhydrous crystals are non-fluorescent, the monohydrates but weakly fluorescent. It was mentioned in ANL-5122, p. 60, that the bands of preparation I became double upon drying to dihydrate and even more strongly so upon conversion to monohydrate, indicating partial re-crystallization to forms derivable from form II of the trihydrate.
TABLE 3.2

Total Intensity of Fluorescence of Uranil Sulfate Crystals in Relation to Water Constant

<table>
<thead>
<tr>
<th>Preparation</th>
<th>$\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$</th>
<th>$\text{UO}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$</th>
<th>$\text{UO}_2\text{SO}_4 \cdot \text{H}_2\text{O}$</th>
<th>$\text{UO}_2\text{SO}_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I + II (doublet bands)</td>
<td>100</td>
<td>91</td>
<td>35</td>
<td>1</td>
</tr>
<tr>
<td>I (single bands)</td>
<td>75</td>
<td>43</td>
<td>38</td>
<td>9</td>
</tr>
</tbody>
</table>

A photographic re-determination of the decay constant of the fluorescence (determination of time needed to decrease fluorescence intensity by a factor of 4) by Levshin and Sheremetjev gave $\tau = (2.7 \pm 0.2) \times 10^{-4}$ sec, in good agreement with the earlier determinations (Table 3.1).
3. INTENSITY AND DECAY OF URANYL FLUORESCENCE IN SOLUTIONS

F. Perrin (1926) first measured the duration of fluorescence of uranyl salt solutions and compared it with that of crystals. The former he found to be much shorter; he pointed out that this does not mean that the one is a "fluorescence" and the other a "phosphorescence," as both can be due to the same mechanism and even have the same intrinsic decay constants, $\alpha e$. According to Eq. (2), this is possible if the radiationless decay constant, $k_d$, is higher for the liquid than for the solid state, thus increasing the total decay constant, $\alpha^*$. According to Eq. (1), the value of $F$ at any given time and its integral between two given times are inversely proportional to the "decay constant," $\alpha$. Perrin found that, among different uranyl salt solutions, the strongest and longest afterglow is exhibited by uranyl sulfate dissolved in concentrated sulfuric acid. Although the viscosity of sulfuric acid is only 20 times that of water, and thus much less than that of a "rigid" solvent, the lifetime of fluorescence in this solvent is as long as $5 \times 10^{-4}$ sec, or one-fourth of that in solid uranyl sulfate. Perrin concluded that rigidity is not a necessary condition for long-lived luminescence, as has been often asserted before. The occurrence of long-lived luminescence of uranyl sulfate solution in sulfuric acid was one of the reasons that caused Perrin to interpret the luminescence of uranyl ions as "fluorescence of long duration" rather than phosphorescence (p. 15). Perrin realized that according to the quantum theory of light absorption, this hypothesis is only permissible if the absorption bands are very weak and he was uncertain whether the uranyl absorption bands actually are sufficiently weak to permit a lifetime of the order of $10^{-4}$ or $10^{-3}$ sec. Subsequent measurements of the intensity of absorption have confirmed that this is in fact the case.

Perrin and Delorme (1928) gave experimental values for the lifetime of fluorescence in uranyl sulfate solutions, listed in Table 3.3. According to Table 3.3, the lifetime decreases with temperature and uranyl concentration. (The total yield of fluorescence after a flash should change in the same way.) This indicates that the rate is affected by deactivation ("quenching") processes and deactivation is accelerated by an increase in the concentration of $\text{UO}_2^{4+}$ ions (for explanation, see below, Sec. 4).

Dilution of sulfuric acid with water also had a quenching effect (e.g., $\tau$ declined to $0.55 \times 10^{-4}$ sec when sulfuric acid was diluted by 30 vol. % water).

In a second paper, Perrin and Delorme (1929) noted that the duration of fluorescence is very sensitive to small impurities, such as halogen ions, or certain organic substances. One part HCl in 30,000 parts of water reduced $L$ and $\tau$ by 50 percent.
TABLE 3.3

Lifetime of Fluorescence of UO_2SO_4 Solutions
(after Perrin and Delorme, 1928)

<table>
<thead>
<tr>
<th>UO_2SO_4 in conc. H_2SO_4</th>
<th>( T \times 10^4 ) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>28°C</td>
</tr>
<tr>
<td>7.2 \times 10^{-3} g in 1 cc</td>
<td>1.25</td>
</tr>
<tr>
<td>7.2 \times 10^{-2} g in 1 cc</td>
<td>-</td>
</tr>
<tr>
<td>7.2 \times 10^{-1} g in 1 cc</td>
<td>-</td>
</tr>
</tbody>
</table>

Perrin and Delorme also measured the fluorescence of uranyl phosphate in metaphosphoric acid, to observe the effect of changes in viscosity. Table 3.4 gives the results.

TABLE 3.4

Viscosity and Lifetime of Uranyl Fluorescence
(after Perrin and Delorme, 1929)

<table>
<thead>
<tr>
<th>( \eta ) (approx.)</th>
<th>( T \times 10^4 ) sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>cgs units</td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>0.9</td>
</tr>
<tr>
<td>1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>100</td>
<td>2.3</td>
</tr>
<tr>
<td>20,000</td>
<td>3.8</td>
</tr>
<tr>
<td>paste</td>
<td>5.6</td>
</tr>
<tr>
<td>glass</td>
<td>7.0</td>
</tr>
<tr>
<td>(pure acid)</td>
<td></td>
</tr>
</tbody>
</table>

Gaviola (1927) and Gaviola and Pringsheim (1927) used a fast Kerr-effect fluorometer (cf. p. 13) for the determination of the rate of decay of fluorescence of uranyl sulfate solutions, and found very low \( T \) values: \( 1.9 \times 10^{-9} \) sec for a solution in concentrated sulfuric acid, and \( 1.3 \times 10^{-9} \) sec for a solution in methanol. As mentioned previously, the existence of such a fast-decaying uranyl fluorescence (in addition to the slow-decaying fluorescence with a lifetime of \( 10^{-4} \) to \( 10^{-3} \) sec) is very doubtful.
Independently of Perrin and co-workers, Vavilov and Levshin (1927, 1928) also noticed the comparatively long life and high intensity of uranyl sulfate fluorescence in concentrated sulfuric acid, and proceeded to study this phenomenon under a great variety of conditions.

Since they considered the luminescence of solid uranyl compounds as a "phosphorescence" (cf. above, p. 15), they were astonished to find that the same phenomenon can be observed, with the same slow decay, also in solutions. (No "phosphorescence" was supposed at that time to occur in liquids.) They therefore made many tests to convince themselves that the systems studied were true solutions, and not colloidal suspensions.

Vavilov and Levshin measured the dependence of the decay constant, $\alpha^*$, on the concentration $[\text{UO}_2\text{SO}_4]$ (Table 3.5). At all three concentrations used, the decay followed the exponential law (Fig. 3.7).

**TABLE 3.5**

Fluorescence Decay Constants of Uranyl Sulfate in Concentrated Sulfuric Acid*
(after Vavilov and Levshin)

<table>
<thead>
<tr>
<th>$[\text{UO}_2\text{SO}_4]$ g/cc</th>
<th>$\tau \times 10^4$ sec</th>
<th>$L = \int_0^\infty Fdt$</th>
<th>$F_0 = L/\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.74</td>
<td>0.47</td>
<td>0.6</td>
<td>1.28</td>
</tr>
<tr>
<td>0.35</td>
<td>0.89</td>
<td>1.14</td>
<td>1.28</td>
</tr>
<tr>
<td>0.14</td>
<td>1.27</td>
<td>1.44</td>
<td>1.13</td>
</tr>
</tbody>
</table>

*All uranyl concentrations used sufficiently high for practically complete absorption.

In Table 3.5, $\tau$ and $L$ (the integrated intensity of fluorescence after "practically instantaneous" excitation by a spark) were measured directly, while $F_0$, the initial intensity of fluorescence, was calculated. In the range studied, $F_0$ turned out to be practically independent of concentration, as expected (cf. Eq. 12) when practically no deactivation by radiation has time to occur during the excitation period. (In other words, excitation is interrupted when the concentration of the excited ions still grows proportionally with time.) With longer excitation periods, the final steady concentration of excited ions will depend on the strength of the uranyl solution, since the rate constant of deactivation, $k_d$, and with it the constant $\alpha^* = \alpha c + k_d$, is increased by rise in concentration ("self-quenching").
FIG. 3.7–DECAY OF FLUORESCENCE IN URANYL SULFATE SOLUTION IN SULFURIC ACID. THREE CONCENTRATIONS: 0.74 g/ml (TRIANGLES), t = 4.7 x 10^{-5} sec; 0.35 g/ml (CROSSES), t = 8.9 x 10^{-5} sec; 0.14 g/ml (CIRCLES), t = 12.7 x 10^{-5} sec. (FROM S. VAVILOV AND V. LEVSHIN, ZEIT. F. PHYSIK., 48, 408 (1928)).
The initial intensity, $F_0$, also proved to be independent of temperature in the region between 18.5 and 67°C; the explanation must be the same as in the case of variations in concentration (no measurable dissipation during the flash). On the other hand, the decay of fluorescence is accelerated by increasing temperature, and the integral yield of fluorescence is consequently decreased (Table 3.6).

**TABLE 3.6**

Effect of Temperature on Uranyl Sulfate Fluorescence in Sulfuric Acid Solution

$\tau = 1/\alpha^* = \text{decay time}; \ L = \text{integrated intensity}$

<table>
<thead>
<tr>
<th>$t^\circ C$</th>
<th>$\tau \times 10^4$ sec</th>
<th>$L$</th>
<th>$F_0 = L/\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.5</td>
<td>1.08</td>
<td>3.9</td>
<td>3.6</td>
</tr>
<tr>
<td>27</td>
<td>0.81</td>
<td>3.1</td>
<td>3.8</td>
</tr>
<tr>
<td>45</td>
<td>0.58</td>
<td>2.0</td>
<td>3.4</td>
</tr>
<tr>
<td>52</td>
<td>0.46</td>
<td>1.6</td>
<td>3.5</td>
</tr>
<tr>
<td>67</td>
<td>0.33</td>
<td>1.1</td>
<td>3.3</td>
</tr>
</tbody>
</table>

The reason for accelerated dissipation of electronic energy at higher temperatures is (according to Franck) that the internal conversion of electronic into vibrational energy requires the co-operation of thermal agitation to bring the electronically excited molecule into a configuration identical with that of a strongly vibrating molecule in the ground state. The effect of uranyl salt concentration and temperature on the yield of fluorescence are illustrated by Fig. 3.8.

Aqueous solutions of $\text{UO}_2\text{SO}_4$ and $\text{UO}_2(\text{NO}_3)_2$ fluoresce too weakly for exact measurements of the mean lifetime; $\tau$ is, in any case, shorter than $10^{-5}$ sec. No fluorescence at all could be noticed in glycerol, alcohol and several other solvents.

$\text{UO}_2^{++}$ solutions in $(\text{H}_2\text{SO}_4 + \text{H}_2\text{O})$ mixtures showed an increase of with increasing concentration of the acid (Table 3.7).

The considerable difference between the fluorescence constants in the solid state and in fluid solution naturally leads to consideration of the effect that viscosity may have on the yield and the rate of decay of fluorescence. The higher yield and slower decay in concentrated sulfuric acid, compared to pure water, as well as the enhancing effect of lower temperature, can be interpreted, at least in part, as consequences of increased viscosity.
FIG. 3.8—YIELD OF FLUORESCENCE ($J^\infty_{F} dt$) OF URANYL SULFATE SOLUTIONS IN SULFURIC ACID AS FUNCTION OF TEMPERATURE. FIVE CONCENTRATIONS (READING FROM TOP TO BOTTOM CURVE): 0.1; 0.22; 0.40; 0.67; 1.0 g/ml. (FROM S. VAVILOV AND V. LEVSHIN, ZEIT. F. PHYSIK., 48, 412 (1928)).
TABLE 3.7

Fluorescent Decay of Uranium Ions in Sulfuric Acid of
Different Concentrations at 18°C
c = g UO₂SO₄ in 1 cc solvent

<table>
<thead>
<tr>
<th>Solvent: Aqueous Sulfuric Acid</th>
<th>c = 5 x 10⁻³ g</th>
<th>c = 5 x 10⁻¹ g</th>
</tr>
</thead>
<tbody>
<tr>
<td>90% H₂SO₄</td>
<td>1.6 x 10⁻⁴ sec</td>
<td>0.65 x 10⁻⁴ sec</td>
</tr>
<tr>
<td>75% H₂SO₄</td>
<td>1.4 x 10⁻⁴ sec</td>
<td>---</td>
</tr>
<tr>
<td>50% H₂SO₄</td>
<td>1.1 x 10⁻⁴ sec</td>
<td>0.20 x 10⁻⁴ sec</td>
</tr>
<tr>
<td>25% H₂SO₄</td>
<td>0.25 x 10⁻⁴ sec</td>
<td>---</td>
</tr>
<tr>
<td>0% H₂SO₄</td>
<td>&lt;0.1 x 10⁻⁴ sec</td>
<td>---</td>
</tr>
</tbody>
</table>

To investigate this possibility, Vavilov and Levshin replotted the data obtained by varying the temperature at a constant value of the concentration [UO₂⁺⁺] as function of viscosity. (For this purpose, the viscosity of solutions of uranyl sulfate had first to be determined for different concentrations and temperatures.) Fig. 3.9 shows the resulting plot. The total yield of fluorescence, L, at a given concentration appears to be directly proportional to viscosity, the points obtained at different temperatures falling on the same straight lines. This can be taken as indication that the temperature effect is due entirely to changes in viscosity.

Of course, the lines in Fig. 3.9 representing L as function of η, cannot remain linear indefinitely, since they must approach a finite limit for η = ∞. This is confirmed by figures in Table 3.8. At very low viscosities, too, L approaches a certain constant value and does not tend to become zero.

TABLE 3.8

Fluorescence Yield as Function of Viscosity at
Constant Concentration of Uranyl Sulfate

<table>
<thead>
<tr>
<th>t°C</th>
<th>103</th>
<th>83</th>
<th>63</th>
<th>47</th>
<th>35</th>
<th>26</th>
<th>14</th>
<th>7</th>
<th>4</th>
<th>-1</th>
<th>-2</th>
<th>-5</th>
<th>-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>η</td>
<td>0.043</td>
<td>0.058</td>
<td>0.067</td>
<td>0.095</td>
<td>0.135</td>
<td>0.170</td>
<td>0.250</td>
<td>0.350</td>
<td>0.375</td>
<td>0.425</td>
<td>0.485</td>
<td>0.580</td>
<td>0.625</td>
</tr>
<tr>
<td>L</td>
<td>0.030</td>
<td>0.78</td>
<td>1.26</td>
<td>2.02</td>
<td>2.60</td>
<td>3.45</td>
<td>4.5</td>
<td>5.6</td>
<td>6.0</td>
<td>6.5</td>
<td>7.0</td>
<td>7.2</td>
<td>7.8</td>
</tr>
</tbody>
</table>
FIG. 3.9—SAME DATA AS IN FIG. 3.8 PLOTTED AGAINST VISCOSITY. (FROM S. VAVILOV AND V. LEVSHIN, ZEIT. F. PHYSIK., 48, 413 (1928)).
The effect of changing concentration can be calculated from these data, for constant temperature (and changing viscosity), or for constant viscosity (and changing temperature). The results are represented in Fig. 3.10.

A separate set of measurements was made at low uranyl sulfate concentrations, from \(9 \times 10^{-3} \, \text{g/cc}\) to \(1 \times 10^{-3} \, \text{g/cc}\). (In the previously described measurements, the concentration was so high that the absorption of the exciting light could be assumed to be complete, independently of the uranyl salt concentration.) In the low concentration region, absorption could be assumed to be proportional to concentration. Table 3.9 shows the absolute yield of fluorescence, \(L\), in relation to concentration, in this region.

### Table 3.9

<table>
<thead>
<tr>
<th>([\text{UO}_2\text{SO}_4]) mg/cc</th>
<th>(L)</th>
<th>([\text{UO}_2\text{SO}_4]) mg/cc</th>
<th>(L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.93</td>
<td>0.28</td>
<td>0.096</td>
<td>0.81</td>
</tr>
<tr>
<td>1.7</td>
<td>0.26</td>
<td>0.166</td>
<td>0.73</td>
</tr>
<tr>
<td>3.0</td>
<td>0.26</td>
<td>0.23</td>
<td>0.59</td>
</tr>
<tr>
<td>5.8</td>
<td>0.23</td>
<td>0.333</td>
<td>0.47</td>
</tr>
<tr>
<td>14.0</td>
<td>0.22</td>
<td>0.47</td>
<td>0.42</td>
</tr>
<tr>
<td>36</td>
<td>0.21</td>
<td>0.595</td>
<td>0.40</td>
</tr>
<tr>
<td>79</td>
<td>0.21</td>
<td>0.695</td>
<td>0.35</td>
</tr>
<tr>
<td>147</td>
<td>0.21</td>
<td>0.77</td>
<td>0.31</td>
</tr>
<tr>
<td>265</td>
<td>0.19</td>
<td>1.00</td>
<td>0.25</td>
</tr>
<tr>
<td>365</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The last measurements in set 1 are affected by changing viscosity and by a deviation of absorption from proportionality with concentration.

The yield (quantum yield) of the fluorescence of uranyl sulfate solution in sulfuric acid was estimated by Vavilov and Levshin, for a solution containing \(10^{-2} \, \text{g/cc}\) (complete absorption!) at \(+10^\circ\text{C}\), by comparing it with that of a fluorescein solution excited by the same wave length (435 m\(\mu\)). (The emission peaks are at 520 m\(\mu\) in fluorescein, and at 530 m\(\mu\) in uranyl sulfate.) For fluorescein, a yield of 80\% was found previously; for the uranyl sulfate solution, a value of about 25\% (\(\phi = 0.25\)) was estimated by comparison. Since the yield at 5\(^\circ\)C is about one-fourth of the maximum yield (observed at liquid air temperature), the latter must be close to 100\%.
FIG. 3.10—FLUORESCENCE YIELD ($\int_0^t F dt$) AS FUNCTION OF CONCENTRATION AT CONSTANT VISCOSITY, $\eta \approx 0.3$ (SOLID LINE) AND AT CONSTANT TEMPERATURE, 40° (DASHED LINE).
(From S. Vavilov and V. Levshin, Zeit. f. Physik., 48, 414 (1928)).
Vavilov and Levshin calculated fluorescence yield isothermals (similar to those given in Fig. 3.10 for concentrated uranyl sulfate solutions) for the dilute solutions also. In Fig. 3.11, the 53°C isothermal shows no dependence on concentration at all; the 18°C isothermal and the curve showing fluorescence as function of [UO₂⁺⁺⁺] at constant viscosity (instead of temperature) are similar to those in Fig. 3.10.

In uranyl nitrate solutions, isothermals \( L = f [\text{UO}_2^{++}] \) at \( t = \text{const.} \) were horizontal even at room temperature.

Plotting the fluorescence data for dilute uranyl sulfate solutions in sulfuric acid as function of viscosity (by proper combination of temperature and concentration) again gave straight line (Fig. 3.12).

Fig. 3.13 shows a similar plot for four different uranyl salts. The curves for nitrate, sulfate and carbonate extrapolate linearly to the same limiting value of viscosity, \( \eta \approx 0.005 \), which would give \( L = 0 \), if the curves did not bend at low viscosities. The acetate line is curved in the opposite sense, probably because of photochemical decomposition.

The uranyl nitrate fluorescence in nitric acid is about as intense as in water. (The viscosities of the two solutions are similar.)

No polarization could be detected in the fluorescence of uranyl sulfate solution at various stages of decay, not even in very dilute uranyl solution in pure sulfuric acid at liquid air temperature.

Vavilov and Levshin also described experiments (made by Trapeznikov) showing that the luminescence of uranyl salts can be excited by x-rays. The decay period is \( <10^{-3} \) sec, the emission being invisible in Vavilov's phosphoroscope.

Vavilov and Levshin considered their experiments as establishing the luminescence of uranyl salts as a phosphorescence, involving a metastable state. They surmised that this state may be an electronic state produced by collisions of excited uranyl ions with the medium. (The monomolecular decay law excluded transient dissociation or ionization as explanation of the metastable state.) Without sufficient reason, Vavilov and Levshin rejected as "implausible" the attribution of the long-lived emission to the longevity of the original excited state itself; we have seen above that this interpretation (which we now know to be correct) was supplied by Perrin.

Vavilov and Levshin derived equations for the influence of concentrations of uranyl fluorescence. They attributed it to deactivating encounters between normal and excited uranyl ions: \( \text{UO}_2^{++} + \text{UO}_2^{++} \rightarrow 2\text{UO}_2^{++} \).
FIG. 3.11 - TOTAL YIELD \( L = \int_0^\infty F \, dt \) OF FLUORESCENCE OF URANYL SULFATE SOLUTIONS IN WATER AS FUNCTION OF CONCENTRATION AT CONSTANT TEMPERATURE, 18° AND 53 °C (DASHED LINES) AND CONSTANT VISCOSITY (SOLID LINE). (FROM S. VAVILOV AND V. LEVSHIN, ZEIT. F. PHYSIK., 48, 417 (1928)).
FIG. 3.12 — FLUORESCENCE YIELD \( \int_0^\infty F dt \) OF URANYL SULFATE SOLUTION IN WATER AS FUNCTION OF VISCOSITY. FOUR CONCENTRATIONS, COUNTING FROM ABOVE: 0.13; 0.256; 0.571; 1.15 g/ml. (FROM S. VAVILOV AND V. LEVSHIN, ZEIT. F. PHYSIK., 48, 416 (1928)).
FIG. 3.13—FLUORESCENCE YIELDS OF DILUTE AQUEOUS SOLUTIONS OF VARIOUS URANYL SALTS AS FUNCTION OF VISCOSITY. (FROM S. VAVILOV AND V. LEVSHIN, ZEIT. F. PHYSIK., 48, 418 (1928)).
The average interval between two such encounters (and also the average time between excitation and the first encounter) must be inversely proportional to the diffusion coefficient, and thus directly proportional to the coefficient of viscosity:

\[ \tau' = \frac{C\eta}{[\text{UO}_2^{2+}]} \]

when \( C \) is a constant. (This equation can be expected to be most satisfactory for high \( \eta \) values and low \([\text{UO}_2^{2+}]\) values.) Its validity was analysed in a subsequent paper by Vavilov (1928).

The probability that an excited molecule will suffer a quenching collision between the times \( t_d \) and \( t_d + dt \) is \((e^{-td/\tau'}) dt/\tau'\); the integral of this probability from 0 to \( t_d \) is \((1 - e^{-td/\tau'})\); the probability of survival after this time, \( e^{-td/\tau'} \). Without quenching, we would have:

\[ F_{t_d} = F_0 e^{-td/\tau_0} \]

while with quenching we have

\[ F_{t_d} = F_0 e^{-td} \left( \frac{1}{\tau_0} - \frac{1}{\tau'} \right) = F_0 e^{-td/\tau} \]

this gives

\[ \tau = \frac{\tau_0 \tau'}{\tau_0 + \tau'} = \frac{C\eta \tau_0/[\text{UO}_2^{2+}]}{(C\eta/[\text{UO}_2^{2+}]) + \tau_0} \]

Integration of \( F \) from \( t_d = 0 \) to \( t_d = \) gives

\[ L = \int_0^{\infty} F_{t_d} dt_d = \frac{F_0 \tau_0 C\eta/[\text{UO}_2^{2+}]}{(C\eta/[\text{UO}_2^{2+}]) + \tau_0} \]

When \( k\eta/[\text{UO}_2^{2+}] \ll \tau_0 \) (low viscosity, strong quenching), \( L \) becomes a linear function of viscosity, \( \eta \). When \( \eta \) approaches \( \infty \), Eq. (31) reduces itself to \( L = F_0 \tau_0 \); if we call this limiting value \( L_0 \),

\[ \frac{1}{L} = \frac{1}{L_0} + \frac{\tau'[\text{UO}_2^{2+}]}{C L_0 \eta} \]

For large \( \eta \), where \( \tau' \propto \eta/[\text{UO}_2^{2+}] \) is a good approximation, \( L \) must be a linear function of \( 1/\eta \). This is confirmed by Fig. 3.14.

Assuming that at \( \eta = \infty \) (i.e., \( 1/\eta = 0 \)) the yield of fluorescence has the maximum possible value (quantum yield 1, or energy yield 0.81, equal to the ratio of the wave lengths of the exciting light, 435 m\( \mu \), and of the
FIG. 3.14—INVERSE OF THE YIELD OF FLUORESCENCE OF URANYL SULFATE SOLUTIONS IN SULFURIC ACID AS FUNCTION OF INVERSE VISCOSITY. (FROM S. VAVILOV AND V. LEVSHIN, ZEIT. F. PHYSIK., 48, 423 (1928)).
fluorescent light, \( \lambda = 535 \text{ m\(\mu\)} \), a value of 23\% can be derived from Fig. 3.14 for the yield at 18\°C (dotted line), in agreement with Vavilov and Levshin's estimate (25\%). However, the assumption of a limiting quantum yield of fluorescence \( \phi = 1.0 \) at \( \eta = \infty \) (rigid solvent) probably is incorrect. It presupposes the absence of any quenching except that caused by encounters with other uranyl ions, neglecting, for example, the quenching by internal dissipation of energy in the excited uranyl ion itself (more exactly, in the complex formed by excited uranyl ion and the solvent).

Vavilov and Levshin noted that the Eqs. (27) to (32) do not apply to the data obtained at high temperature and high concentration and suggested "solvate effects" as an explanation.

Vavilov (1928) attempted to calculate the concentration quenching of uranyl fluorescence theoretically from a simple molecular model of diffusion (assuming that quenching occurs whenever an excited and a non-excited ion encounter each other by diffusion). He concluded that the constant \( 1/C \) in Eq. (32) must be equal to \( 8kTN/\delta \pi \), where \( N \) is the number of molecules in 1 g of the solute (\([\text{UO}_2^{2+}]\) being measured in g per cc), and \( \delta \) a numerical factor \( 1 < \delta < 2.83 \). The empirical coefficient \( 1/C \) (as determined in sulfuric acid at 291\°K, with \( \eta = 0.22, \tau_0 = 4.3 \times 10^{-4}, \) and \( L_0 = 0.82 \)) turns out, however, to be only 2\% of the theoretical value. Vavilov attributes this difference to solvation of the uranyl ions (that slows down diffusion) and perhaps also to not every encounter being effective. (One should, perhaps, think also of the effect of the ionic charge, which makes collisions of two \( \text{UO}_2^{2+} \) ions less likely than a collision between two neutral solute molecules of the same diameter.)

Alenzev (1951) described a calorimetric method of measurement of the yield of fluorescence. He used it primarily for fluorescent dyestuffs; but mentioned, without any details, that he found a figure of 63\% for the yield of fluorescence of a uranyl salt solution - not much lower than that he found for fluorescein (67-80\%).
4. QUENCHING OF URANYL FLUORESCENCE IN SOLUTIONS

Quenching is the decline in the probability of fluorescence of an excited molecule caused by presence of other molecules. If the quenching is caused by increased concentration of the fluorescent molecules themselves, it is called "concentration quenching" or "self-quenching."

Several different mechanisms of quenching (or self-quenching) are feasible. In the first place, one can distinguish between "chemical" and "physical" quenching, depending on whether the energy lost for fluorescence is used for chemical reaction, or is dissipated into vibrational energy (and finally converted into heat), without causing chemical change. In the second place, a distinction can be made between three mechanisms of quenching: quenching caused by association of the light-excited molecules with the quenching molecule preceding the excitation (quenching by complexing), quenching by proximity of the excited and the quenching molecule (quenching by resonance transfer), and quenching by kinetic encounter of the quencher with the excited molecule. (In all three cases, quenching can be either chemical or physical.)

The "self-quenching" data and theoretical considerations of Vavilov and Levshin (1928) and Vavilov (1928) were presented in Sec. 3.

Trumpler (1915) first observed the quenching of fluorescence of uranyl solutions by organic acids, which he attributed to their oxidation by light-excited uranyl ions ("chemical quenching"). The quenching by formic acid was described by Trümpler as "weaker than that by oxalic acid."

The quenching of $\text{UO}_2^{++}$ fluorescence by inorganic ions was first studied by West, Müller and Jette (1928) in connection with the effect of these ions on uranyl-sensitized photodecomposition of oxalate. Figure 4.7 (ANL-5202) shows the competition between fluorescence and sensitization of uranyl oxalate mixtures with different ratios of the components. Addition of $\text{Cl}^-$, $\text{Br}^-$, $\text{CNS}^-$ or $\text{I}^-$ ions depresses both the fluorescence and the decomposition, both effects increasing in strength with the size of the quion, from $\text{Cl}^-$ to $\text{I}^-$.\)

Volmar (1928) noted that solutions of uranyl sulfate, nitrate or acetate cease to be fluorescent at $\text{pH} \geq 7$. The disappearance of fluorescence is followed by precipitation of a hydroxide. (The formation of insoluble hydroxide probably is preceded by that of soluble, but non-fluorescent, complex ions, of the types discussed in Chapter 2, ANL-5173.) Uranyl halogenides do not fluoresce even in acid solution, because of the quenching effect of the halide ions, as first noted by Perrin (1926).

Volmar and Mathis (1933) investigated the possibility of using the quenching of uranyl fluorescence for analytical determination of the anions. Using uranyl nitrate as fluorescent material, exciting it with 350 mμ, and adding various salt solutions, they found that the strongest quenchers were the following anions:
I\textsuperscript{-}, Br\textsuperscript{-}, CNS\textsuperscript{-}, Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2-}, Fe(CN)\textsubscript{6}\textsuperscript{4-}, As\textsubscript{3}\textsuperscript{5-}, S\textsuperscript{-} (in decreasing order)

Other "active" anions were NO\textsubscript{3}\textsuperscript{-}, S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}, CrO\textsubscript{4}\textsuperscript{2-}, MnO\textsubscript{4}\textsuperscript{2-}.

"Inactive" were the anions F\textsuperscript{-}, ClO\textsubscript{3}\textsuperscript{-}, BrO\textsubscript{3}\textsuperscript{-}, IO\textsubscript{3}\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, SO\textsubscript{5}\textsuperscript{2-}, PO\textsubscript{4}\textsuperscript{3-}, AsO\textsubscript{4}\textsuperscript{3-}, formate, acetate, oxalate, tartrate, citrate, borate and palmitate.

Among cations, only one, Ag\textsuperscript{+}, was found to quench the fluorescence of uranyl ions. All the other cations tested (Na\textsuperscript{+}, K\textsuperscript{+}, Li\textsuperscript{+}, NH\textsubscript{4}, Ca\textsuperscript{++}, Ba\textsuperscript{+++}, Zn\textsuperscript{++}, Mg\textsuperscript{2+}, Al\textsuperscript{3+}, Fe\textsuperscript{3+}, Bi\textsuperscript{3+}, Pb\textsuperscript{++}, Cu\textsuperscript{++}, Hg\textsuperscript{++}) proved inactive.

Fluorescence was not affected by small changes in pH, temperature, and uranyl ion concentration.

In plotting the number of drops (n) required to produce quenching, as function of concentration (c) of the quencher in them, Volmar and Mathis were baffled not to find inverse proportionality. At a certain (low) concentration, c\textsubscript{b}, the curve n = f(c) became vertical; no complete quenching could be obtained with still lower concentrations, c < c\textsubscript{b}. This result is, however, trivial. If what matters for complete quenching is not the amount of the quencher added, but its final concentration, c\textsubscript{f} (which must exceed a certain value c\textsubscript{0}), then we have (V being the initial volume of the uranyl solution and v the volume of a drop)

\[ c_0 = \frac{n_0cv}{V + n_0v} \quad \text{and} \quad n_0 = \frac{c_0V}{v(c - c_0)} \]

When c approaches c\textsubscript{b} (from above), the number n\textsubscript{0} of drops needed to quench the fluorescence in a given volume of uranyl solution approaches infinity; at c < c\textsubscript{b}, complete quenching becomes impossible. This relationship indicates that the quenching of uranyl fluorescence by anions is not due to stable complexing, e.g., \( UO_2^{2+} + Cl^- \rightarrow UO_2Cl^- \). Because of the weakness of the absorption, it is also unlikely to be due to a resonance transfer of energy; the most probable mechanism of quenching is therefore by kinetic encounters. The most likely effect of these encounters is, in turn, a reversible oxidation reduction, e.g.,

\begin{align*}
(33a) & \quad UO_2^{2+} + I^- \rightarrow UO_2^+ + I^- \\
(33b) & \quad I + UO_2^+ \rightarrow I^- + UO_2^{2+} \\
(33) & \quad UO_2^{2+} + e^- \rightarrow UO_2^{++} 
\end{align*}

Practically all quenching ions (I\textsuperscript{-}, Ag\textsuperscript{+}, Fe(CN)\textsubscript{6}\textsuperscript{4-}, etc.) are, in fact, reductants, i.e., have a tendency to acquire electrons. The question remains open whether reaction (33a) is reversed immediately, even before the two products have separated in solution, the net result being an internal conversion
of electronic energy into heat in the complex \( \{ \text{UO}_2^{+++} \} \) or whether
the products react back only after a certain free life in solution, in which
the case partial irreversibility and net/photochemical transformation become
possible, e.g.,

\[
\text{(34) } \text{UO}_2^{+++} + 21^- + 4H^+ \rightarrow \text{U}^{4+} + I_2 + 2H_2O
\]

This, in fact, is the probable mechanism of the photochemical reaction of
uranyl ions with iodine (cf. ANL-5202).

Carter and Weiss (1940) measured the quenching of fluorescence
of uranyl nitrate solution by potassium iodide. Figure 3.15 shows the results.
The curve is from the equation

\[
\text{(35) } 1 = \frac{I_0}{1 + 5 \times 10^3 [I^-]}
\]

This indicates "half-quenching" \( F = \frac{1}{2} F_0 \) at \([I^-] = 2 \times 10^{-4} \text{ m/l} \); assuming \( 10^4 \text{ sec}^{-1} \) for the rate constant of fluorescence, we obtain a value of
\( 10^4 / (2 \times 10^{-4}) = 5 \times 10^7 \) for the rate constant of the quenching reaction, which
we may tentatively assume to be identical with the first step in the reaction
of uranyl and iodide ions:

\[
\text{(36) } \text{UO}_2^{+++} + I^- \rightarrow \text{UO}_2^{+} + I (\text{cf. Chapter 4, ANL-5202, p. 12}).
\]

However, quenching could also be associated with the formation of nonfluorescent complexes, \( \{ \text{UO}_2^{+++} \} \), an alternative which could only be excluded by
more extensive and systematic measurements.

Galanin (1951) looked for a proof of resonance quenching of uranyl
fluorescence. He pointed out that the long life of the excited state (which
is associated with the weakness of the absorption band) makes this proof
difficult, since its facilitates the quenching by encounters. To distinguish
between the two quenching mechanisms, Galanin measured the lifetime of
the fluorescence (which, according to Eq. 14, is proportional to the yield
of fluorescence as function of concentration of the quencher at different
viscosities). (Increased viscosity reduces the quenching by encounters,
but leaves unaffected the quenching by resonance transfer.)

Figure 3.16 shows the lifetime, \( \tau \), as function of temperature for
uranyl sulfate in sulfuric acid, with potassium bichromate and chrysoidine
as quenchers. The quenching by bichromate, which is complete at room
temperature, almost disappears at -185°C, while the quenching by the dye
remains strong even in liquid air (as expected for a resonance effect).

Figure 3.17 represents \( \tau_0 / \tau \) as function of the concentration of the
quencher, at -185°C. The effect of quencher concentration \([Q]\) (molecules/cc)
can be represented by equations of the Stern-Volmer type, \( \tau_0 / \tau = 1 + [Q] \)
with \( \beta = 0.2 \times 10^{-18} \) for chrysoidine and 0.04 \( \times 10^{-18} \) for bichromate. If these
FIG. 3.15-QUENCHING OF THE FLUORESCENCE OF URANIVUM IONS BY IODIDE IONS (KI). J. CARTER AND J. WEISS, PROD. ROY. SOC.
FIG. 3.16—RELATION BETWEEN TEMPERATURE AND DURATION OF
PHOSPHORESCENCE OF A SOLUTION OF URANYL SULFATE IN SULFURIC ACID (FROM GALANIN, 1951).
Curve 1: Pure solution.
Curve 2: Solution with the addition of 10% sodium chloride.
Curve 3: Solution quenched with chrysoidine \( (c = 5 \times 10^{-4} \text{ g/cc}) \).
Curve 4: Solution quenched with potassium bichromate \( (c = 5 \times 10^{-3} \text{ g/cc}) \).

FIG. 3.17—CHANGE OF FLUORESCENCE DURATION \( (T) \) OF THE
SOLUTION OF URANYL SULFATE IN SULFURIC ACID
(AT THE TEMPERATURE OF LIQUID NITROGEN) IN
RELATION TO THE CONCENTRATION OF THE QUENCHER
(FROM GALANIN, 1951).
Curve 1: Chrysoidine; Curve 2: Potassium bichromate.
constants are compared with the overlap $\tilde{a}$ of the absorption spectra of the fluorescer and the quencher, $\beta/\tilde{a}$ values of 5 and 57, respectively, are obtained for bichromate and chrysoidine respectively. These ratios are of the same order of magnitude as found for resonance quenching of the fluorescence of dyestuffs, where the natural lifetime is of the order $10^{-8}$ sec. (as compared to $10^{-4}$ sec. for uranyl ions!).
REFERENCES


1929  R. Delorme and F. Perrin, J. phys. radium, 10: 177-86.


