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LUMINESCENCE OF CRYSTALLINE CELL-NUCLEAR CHEMICALS UNDER IONIZING RADIATION

Berkeley, California

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Richard L. Lehman and Roger W. Wallace

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ABSTRACT

An experimental study has been made of the delayed phosphorescence and thermoluminescence properties of 34 separate cell-nuclear chemicals exposed as crystalline powders to cobalt-60 rays at 77°K. In addition, the luminescence of the nucleic acid bases and related compounds was studied under irradiation with intense heavy-ion and electron beams. Under electron bombardment, the effects of ambient gases at various pressures have been examined at 77 and 295°K. The biological significance of these measurements is discussed.

The thermoluminescence-glow peak location, temperature-widths, and yields have been reported. The location in no case exceeded 180°K, and in most cases stood in the region 100 to 150°K. It was found that a given chemical may have several peaks, and similar chemicals may have glow peaks that differ in width, location, and intensity. Adenine and cytosine samples released 0.2 and 0.1%, respectively, of the absorbed gamma energy as thermoluminescence. In each case, the

yields of molecular compounds that contained conjugated π-molecular orbitals approached these; other compounds such as lecithin had yields of the order of 10^{-7}. The activation enthalpies for thermoluminescence glows have been examined in detail, and a new method for their determination based on phosphorescence decay at 77°K has been used.

For those substances exposed to the particle beams, the emission spectra and yields at 250 to 600 nm under various gas pressures have been reported. Radiofluorescence energy yields up to 13% were measured for adenine at 77°K when the ambient oxygen gas pressure was 300 μ Hg. At 286°K the yield was 0.2%. Yields for the other nucleic acid bases were roughly 1/10 of these. The emission spectra were found to be bell-shaped bands in the region 350 to 540 nm with widths of about 100 nm. When adenine was exposed at 77°K in the presence of > 100 μ Hg of gas, the emission spectrum peaked at 490 nm. Under vacuum at 77°K, or at 286°K under all conditions, the spectrum peak shifted to 520 nm. Similar shifts were observed for the other compounds. A conceptual model, the exciton hypothesis, has been advanced to interpret the temperature and gas pressure effects on radioluminescence.

List of Symbols

β	Warming rate ($^{o}K/sec$) in thermoluminescence measurements.
ΔF	Free energy change in thermoluminescence reaction.
J	Rate of excitation of molecules by incident radiation.
K	Equals $\nu_t x$.
k	Boltzmann constant
L(t)	Intensity of luminescence at time t.
n(t)	Number of excited molecules at time t.
p	Equals $1/\tau$, the probability for radiative transition.
ΔS	Entropy change for thermoluminescence reaction.
s	Frequency factor--related to the natural vibration frequency of the system, to the entropy change in the thermoluminescence reaction, and to the transition coefficient.
T^*	Temperature at thermoluminescence glow peak.
T	Temperature as a variable.
t	Time as a variable.
τ	Meantime for luminescence decay.
ΔU	Thermal activation enthalpy for thermoluminescence reaction.
ν_t	Crystal vibration frequency.
x	The transmission coefficient.

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I. INTRODUCTION

There is now considerable support for the view that the basis of cell energy dynamics is the electron, and that the complex structure of biomolecules and their aggregates provides simply the scaffolding for handling electron excitation energy (Szent-Gyorgyi, 1941 and 1957; Augenstine, 1960). The electron energy transistions associated with crystalline luminescence amount to a few electron volts. This is the same order of magnitude as is handled in normal molecular energy transfer in living cells, and as is found in the primary chemical bonds.

This work starts from the point of view that ionizing radiation leads ultimately to electron excited states of the same size (a few

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electron volts), and that the mode of deexcitation determines the biological damage. It is held that such excitations, within a molecule or within an aggregate of molecules, may be stabilized as a change in a chemical bond, they may be dissipated as molecular vibration exchanges, or they may be released as luminescence. It thus becomes of interest to study the conditions that determine which deexcitation mode a molecule in a condensed system will take.

Crystalline luminescence is largely an empirical science, and interpretations in terms of basic principles has barely begun (Garlick, 1958; Curie, 1960). Optical transitions in organic molecules involve π and n electron orbitals. Such transitions are capable of modification by local interaction, for example with hydrogen bonds and with molecular vibrations, and in fact in condensed systems optical transitions occur in general only from the first excited singlet and triplet states because any excess energy of excitation is rapidly lost by means of such vibrations (Hochstrasser, 1962).

It is known that oxygen may strongly influence the luminescence of irradiated organic powders. Hamano (1926) reported that cholesterol and certain other dry substances were able, following x-ray or ultraviolet irradiation in the presence of oxygen, to expose photographic plates. Grosswiener and Matheson (1954) found that oxygen has no effect on the x-ray fluorescence of pure ice, but that

ice frozen in 0.2 atm of oxygen gives a broad thermoluminescence. Small quantities of hydrogen peroxide, however, quenched both the fluorescence and the thermoluminescence.

Other phenomena that are based upon electron action may be strongly modified by local interaction. A 0.1% tetracene-doped single crystal of anthracene was found by Bryant et al. (1959) to give a completely different conductivity glow curve than a crystal of pure anthracene. Vartanyan and Rozenshtein (1961) reported that the dark conductivity of certain xanthene dyes is increased in the presence of oxygen at lower temperatures, but not at temperatures of 50-100°C. The gaseous and water environments during and after irradiation have marked effects upon free radical yield, quality, and lifetime (Smith, 1962).

Some earlier investigations have concerned the low temperature thermoluminescence of organic powders. Emission spectra were found to consist of one or more bell-shaped bands of width 80-150 nm (Sharma, 1956; Weinberg et al., 1962). The glow peaks themselves, when recorded vs. temperature, also are roughly bell shaped, and they occur mainly in the temperature region 100 to 170°K (Augenstine et al., 1960). A given chemical may have several such peaks, and similar chemicals may have glow peaks differing in width, location, and intensity. The thermoluminescence glow peaks of the ring-

structure amino acids are 1000 times as intense as those of the other amino acids. Further, the crystalline system and chemical impurities are relatively unimportant in these glows; and the glow curve of a protein is not the composite sum of its amino acid glows (Carter, 1960).

In the experimental study reported herein, most of the chemicals present in the cell nucleus have been subjected to luminescence analysis in pure crystalline powder form. The preliminary work consisted of a study of the delayed phosphorescence and thermoluminescence properties of a wide variety of chemicals following irradiation at 77°K by cobalt-60 rays. The glow-peak location, temperature widths, and yields are reported.

The second phase of this work consisted of examining the luminescence of the nucleic acid bases and related compounds under irradiation with intense electron and heavy-ion beams. Under electron bombardment, the effect of ambient gases at various pressures on their luminescence has been studied. The energy yields and emission spectra for fluorescence, thermoluminescence, and delayed phosphorescence are reported.

II. EXPERIMENTAL METHOD

A. Equipment and Methods for the Gamma Irradiations.

1. Irradiation Facility.

The Lawrence Radiation Laboratory cobalt-60 gamma irradiation facility was used. It consists of two cobalt-60 sources, which at the time of these studies contained totals of about 700 curies and 25 curies, respectively. These sources have been described in detail elsewhere (Tolbert et al., 1957; Nielsen, 1957).

2. Chemicals.

The special cell-nuclear biochemicals were supplied in the purest commercial grades by Sigma Chemical Company of St. Louis, Missouri (Mr. Louis Berger, of this company, has written that the nucleic acid bases were crystallized from hot aqueous solutions without use of organic solvents.) The more common chemicals were of analytic reagent grade. The dry chemicals were in polycrystalline powdered form, and were stored in a freezer.

3. Sample Holder.

The sample holder for the irradiations may be seen in Fig. 1. It consisted of a base assembly and sample cup, a brass V-tube barrel, a heavy Teflon coupling mount, and end windows. Details of the base assembly are given in Fig. 2. All the metal parts were blackened by the "Ebonal C" process of alkaline oxidation. The smaller-diameter arm of the V-tube barrel is so oriented

that infrared light may be put on the sample through the small germanium end window. The larger-diameter arm serves as the light tube from the sample through the quartz end window to the photomultiplier apparatus. The V-tube arms are segmented so that Teflon gaskets may thermally insulate the end-windows. The Teflon gaskets provided air- and liquidtight seals.

4. Photomultiplier

Several RCA 1P28 quartz-window photomultiplier tubes were used. The light-sensitive photocathode material of these tubes is Cs_3Sb, which has an S-5 spectral response that peaks at 340 mμ and has a useful wavelength range from 220 to 600 mμ. The tubes used were carefully selected to have a dark-current output of 0.3 to 0.4 nA when operated at 980 V. The photomultiplier housing consisted of a Teflon coupling mount, a camera shutter, and the aluminum tube-head mount. The metal parts were black-anodized and the outer Teflon surface was covered with black tape.

5. Amplifier and the Recording Equipment.

The photomultiplier tube was supplied with 980 V via a standard voltage-divider box from the regulated 2-kV voltage supply. The light signal was amplified by the E-H Company model 215-RL electrometer-voltmeter fitted with a 10^8-ohm

precision resistor. The amplified light signal was displayed in the Leeds-Northrup $X_1 X_2$ model G type-S potentiometer strip-chart recorder. The temperature of the sample cup (Fig. 2) was simultaneously recorded on the strip chart by use of the copper-constantan thermocouple leads and coupling jacks.

6. Experimental Procedure.

A 10- to 200-mg sample of the chemical to be tested was weighed on a precision balance and put into the sample cup. The cup assembly was screwed into the body of the holder until the Teflon gasket was tight, so that the sample was sealed in air at 292°K at 40 to 60% relative humidity. The bottom two-thirds of the sample-holder assembly was then immersed in liquid nitrogen contained in a one-pint vacuum Dewar. Three minutes was required for the sample to reach liquid-nitrogen temperature.

Next, the Dewar holding the vacuum flask was remotely carried to the irradiation position inside the cobalt-60 source. Approximately 2 min elapsed during the process of getting the sample into and out of the large source housing. When the irradiation was completed, the photomultiplier assemby was coupled to the sample holder, and the latter was quickly taken from the liquid-nitrogen-immersion Dewar and seated in the heater. The heater consisted of wire coils housed in a ceramic base. From

it heat was delivered to the lower two-thirds of the sample holder. the heater base contained the sockets for the thermocouple jacks. By varying the ac voltage to the heater coils a constant rate of sample warm-up was obtained. The rate could be varied between 8 and 70°C per minute.

7. Dosimetry

The radiation fields within the cobalt-60 sources were measured with polished cobalt glass pieces 1.5×6×1.4 mm. The reading equipment was the Bausch and Lomb spectrophotometer type 33-29-40 together with the Sorenson and Company ac voltage regulator model 1000-3. The measured radiation field at the sample location was 93 roentgens/sec. This was found to be in agreement with interpolated values obtained by the Fricke ferrous sulfate method and by special colored-liquid dosimeters (Lehman, 1962) supplied by the Edgerton, Germeshausen and Grier Company. In each case it was assumed that an exposure dose of 1 roentgen delivered an absorbed dose of 1 rad, or 100 ergs/g.

B. Equipment and Methods for the Particle Irradiations

1. Heavy-Ion Accelerator

The Lawrence Radiation Laboratory heavy-ion accelerator can produce variable-intensity ion beams of atoms of mass between

helium and argon at fixed energy of about 10 MeV per nucleon. Its use in biophysics irradiation has been described by Brustad (1960).

For this work oxygen (+6) and carbon (+4) ion beams were used at beam intensity levels of 1.2 to 4 nA, measured by a 0.1-mil insulated aluminum foil mounted behind a 3/8-in.-diam collimating hole, immediately in front of the target sample holder. The beams were delivered in 2-msec pulses at the rate of 12 to 15 pulses/sec.

2. Electron Linear Accelerator

The Lawrence Radiation Laboratory Linear Accelerator produced intense beams of 5-MeV electrons. The beams were delivered in 6-μsec pulses at rates between 7.5 and 30 pulses/sec.

3. Chemicals

The chemicals were the same as those used in the γ irradiations. For use in the target sample holder it was necessary to press the powdered polycrystalline chemicals into 3/4-in.-diam 1-g pellets by use of a hydraulic ram. The pellets were stored at $0^{\circ}C$ over a desiccant ($CaSO_4$). A new pellet was prepared and put into use when its predecessor had accumulated 10^7 rads.

4. Target-Sample Holder

The target sample holder was designed so that particle beams

would play on the pellet directly. The holder may be described with the aid of Fig. 3. The particle beam entered brass port B and struck the pellet, which was mounted by means of double-sided masking tape on the copper target mount D. The target luminescence passed through quartz window C and coupling mount A to the spectrometer-analyzer and phototube. The copper-constantan thermocouple leads E passed through the brass base plate to the target mount. A stream of liquid nitrogen flowed from F to D to G to cool the target mount during the low-temperature measurements. Dry nitrogen gas, flowing under roughly 10 to 30 psi along the same path, warmed the target mount during thermoluminescence runs.

All the metal parts in the optical end of the holder were blackened by the "Ebonal C" process of alkaline oxidation. The holder had vacuum-tight rubber O-ring seals at all coupling surfaces. Hidden in the brass port B and located 1 in. from the target mount was an aluminum collimator-plug with a 1/2-in.-diam central hole drilled along the beam axis. This plug allowed the beam to play exclusively on the mounted pellet.

5. Conditions During Irradiation

At the linear accelerator, the target sample holder and support assembly were separated from the end of the accelerator beam tube by 3 in. The beam-port tube of the holder slipped past an O-ring vacuum seal into the support assembly. The support assem-

bly was fitted with a National Research Corporation vacuum ion gauge mount above, and with a vacuum mount below.

A needle valve in the vacuum line allowed variable quantities of dry nitrogen, oxygen, or helium from commercial cylinders to enter the target sample holder via the support assembly. The high-vacuum system consisted of a mechanical roughing pump backed by a mercury diffusion pump.

For the work at the heavy-ion accelerator, the beam-port arm of the target holder entered a support assembly mounted on the end of the accelerator-tank beam tube. There the pellets were irradiated in the vacuum of the accelerator tank itself.

6. Dosimetry

Pellet-sized cobalt-glass dosimeter plates were exposed at the target site to the electron beams. The reading technique and equipment are given in Subsec. II-A.7. It was found that the dose rate was 3800 rad/sec when the accelerator was operated at 0.05 V and 30 pulses/sec. When a piece of microslide glass was mounted at the target site and irradiated, a circular area just slightly less than the 3/4-in. pellet was darkened.

No dosimetry was attempted at the heavy-ion accelerator. It was assumed that the readings of the foil beam monitor (Part A) gave a true measure of the beam current on the pellets. The heavy

ions were of course stopped in the first 0.40 mm of the pellet and the local rad dose was unknown but very high. However, a certain amount of beam energy was put into the pellet surface and a certain amount of light energy was emitted. The luminescence yields in this case were simply the latter divided by the former.

7. Calibration of the Photomultiplier-Amplifier-Recorder System.

A Sylvania Company 0.02-W electroluminescent disk was used as a distributed constant low-intensity light source to simulate the experimental glow. The disk and the blackened-brass light tube are shown in Fig. 4. The brass tube has the diameter of the light orifice in the sample holders, and the exact length of the pellet-to-spectrometer coupling distance. Thus, when the brass tube was inserted into the spectrometer coupling and the face of the disk was held tight against the open end, the experimental optical geometry obtained.

The electroluminescent disk, with 30.0 volts 60-cycle ac applied to it, was found to glow with total radiant intensity of 0.82 μ watts/steradian, and to have a bell-shaped emission spectrum of 500 nm, 80 nm wide at half intensity. The luminous

and radiant intensity of the disk were measured at the National Bureau of Standards by use of a calibrated vacuum photoelectric tube fitted with a removable luminosity filter. The measured intensity is believed to be accurate to ±20%.

The elctroluminescent disk intensity was strongly dependent on voltage: it changed at a rate of 2.5% per 0.10-volt shift from 30.0 V, and the total decrease in intensity in going from 120 V to 10 V ac was by a factor of one million. The emission spectrum did not shift over this range of intensities. These properties coincide with those of an electroluminescent ZnS phosphor described by Butler and Waymouth (1955).

8. Spectrometer

The spectrometer consisted of the monochromator analyzer of a Beckman model DU. A simple flat-mirror coupling input was used, and an RCA 1P28 phototube was the output light detector. The phototube housing was identical to that used in the gamma-irradiation studies, but without the light shutter and Teflon collar. The housing was permanently attached to the face plate of the DU. The optical band-pass width of the DU at 2.0 mm (wide open) entrance slit varies with wavelength, as given in Fig. 5. In the same figure may be seen the IP28 phototube relative spectral response, and the "total" relative phototube-DU response.

The high-voltage supply, electrometer-voltmeter, and strip-chart recorder were the same as in the gamma-irradiation studies.

III. EXPERIMENTAL RESULTS

The luminescence properties of thirty-four organic chemicals irradiated at 77°K by cobalt-60 rays, and those of the nucleic acid bases and related compounds irradiated by heavy-ion and electron beams, are reported in this section.

A. Luminescence Following Low-Temperature Gamma Irradiation

1. Thermoluminescence

The glow-peak temperature, duration, and yield of radiant energy for three dozen chemicals in powdered or quick-frozen-liquid form are presented in Table I. Because all the glow peaks are roughly bell-shaped, the three given measured parameters (temperature-location, duration at half maximum, and yield) are sufficient to describe them. In each case the glow measurements were begun between 2.5 and 4 min after the end of the exposure.

On the basis of Table I, two things may be emphasized:

a. The glow-peak temperatures stand without exception in the region below 180°K.

b. Certain cell-nuclear chemicals under suitable conditions may release 0.1 to 0.2% of the locally absorbed gamma dose as thermoluminescence.

From Fig. 6 it can be seen that in each case of high glow yield, the molecular structure contains conjugated double bonds (π orbitals),

or, in the case of inorganic crystals, electronic excited states common to the entire crystal. For comparison we have found that $PbCl_2$ crystals have a low-temperature glow-peak yield of about 0.02. The starred chemicals have been entered in Fig. 6 at their approximately correct places as estimated from relative intensity values reported by Augenstine et al. (1960).

The yields were obtained by comparison of the glow intensities of the samples with the radiant intensity of a calibrated electroluminescent disk at the same optical location. It was found that the average glow-peak intensity of 1 μwatt could be duplicated when the calibrated disk was operated at 30 V (60 cycles).

2. Phosphorescence

Those chemicals that, 3 minutes after the end of the gamma-irradiation, glowed with at least 0.1 the glow-peak intensity have been noted "LNp" in Table I. In histone and protamine sulfate, this "phosphorescence" was observed to be simply the emptying of traps (via the low-temperature end of the Boltzmann distribution tail) which belong to broad low-temperature glow peaks of small thermal activation energy (<0.15 eV). The same mechanism was observed in sucrose and sodium chloride, except that sharp peaks (>0.2 eV) in the region 77 to 85°K caused the phosphorescence.

Strong delayed phosphorescence was observed in 5'-adenosine

diphosphate (ADP) crystals and in a piece of sheet polyethylene. When these substances were warmed at 8°K/min a phosphorescence of mean life about 6.6 min was found in the time region 4 to 22 min after irradiation. Typical glow peaks were superimposed on this phosphorescence. However, at a heating rate of 70°K/min, the mean life of the phosphorescences dropped to about 0.8 min (the glow peaks were still clearly superimposed). The 4- to 22-min phosphorescence yields (140 and 50×10^{-6} for ADP and polyethylene respectively) remained constant at both warming rates.

B. Luminescence Following Irradiation by Heavy-Ion Beams

Oxygen ions at 10 MeV/nucleon give up their energy locally as dense spikes of excitation along their paths. And because these ions come to rest in the region that they have excited, they are a particularly interesting tool for the study of the local oxygen effect. These measurements allow comparison of the effects of two different excitation modes on luminescence.

1. Fluorescence

The fluorescence yields and spectra of eight cell-nuclear chemicals under irradiation with heavy ions at 77° and 295°K may be seen in Table II. (The term "fluorescence" is used here to describe luminescence emitted during irradiation. It includes all the phosphorescence with mean life <1 second and the initial few seconds of phosphorescence of longer duration.) It should be noted that the yields are minimum estimates, not corrected for that portion of the fluorescence which is self-absorbed, in pressed crystalline pellets. This correction could amount to a factor of 10 or more.

Nonetheless all values are of the order of 2×10^{-5}, and there is no consistent pattern. Considerably different spectra and yields were observed when adenine was irradiated at 77°K with carbon and with oxygen beams.

In each case the emission spectrum consisted of a single sharp or broad peak located in the 350- to 525-nm region. With oxygen beams the peak widths at half maximum intensity varied from 90 to 225 nm, but most were in the neighborhood of 100 to 130 nm.

An unexpected transient fluorescence "buildup," which may be related to the on-off method of taking measurements, was observed in about one-half the runs. During this work the heavy-ion beam was turned on for 5 sec (12 pulses/sec), then off for 5 sec while the monochromator dial was changed to the next wavelength band. The "buildup" was a fluorescence during the first few 5-sec exposures that was 1.5 to 2 times the intensity obtained by subsequent exposure at the same wavelength setting.

2. Phosphorescence

An exceedingly small phosphorescence of mean life between 0.5 and 2 sec was observed in all samples irradiated at 77°K and in all but guanine, thymine, and adenosine triphosphate (ATP) at 295°K. The yields amounted to approximately 0.01 the fluorescence yields, and the phosphorescence emission spectra lay in the region

450 to 600 nm. The absence of this afterglow was quite evident on the declining edges of the 320-to-450-nm fluorescence "spikes" of thymine and guanine.

3. Thermoluminescence

Attempts were made to generate the 120°K adenine glow by use of heavy-ion energy inputs up to 2000 joules. Neither with oxygen nor with carbon beams was there any evidence of a low-temperature glow. Under the experimental conditions of 1 to 5 μ Hg residual vacuum the glow yield did not exceed 10^{-10}. Similarly, no glow was observed in sucrose irradiated by doses to 500 joules.

When the photomultiplier is coupled directly to the optical arm of the sample holder and the DU is eliminated, sensitivity is increased about 300 times. A guanine pellet was irradiated at 77°K with such a setup to an energy input of 70 joules of oxygen beam. An initial phosphorescence fell, by a factor of 100, to approx zero during the first 40 sec postirradiation. Upon heating, a small sharp glow peak appeared at 93°K and a broad peak at 124°K that had a tail to 200°K. The total yield was 0.32×10^{-9}, with the residual gas pressure of 1 to 5 μ Hg.

C. Luminescence Following Irradiation by 5-MeV Electrons

Measurements were begun at the electron linear accelerator in order to obtain the high irradiation dose rates required to study the

luminescence spectra of organic crystals. The studies with heavy-ion beams and preliminary work with electrons had revealed that the ambient gas pressure during irradiation has a profound effect on radio-luminescence. For this reason, during these runs the sample holder and mount were separated from the electron-beam tube and had an independent high-vacuum system that admitted controlled amounts of gas.

1. Fluorescence

The radiofluoresence yields and spectra of the five nucleic acid bases are reported in Table III. (Again, "fluorescence" refers to luminescence emitted during irradiation.) As with the heavy-ion beams, the yields are the ratios of the radiant (visible) energy to the energy taken from the electron beam by the pellets. An experimentally determined factor of 10 has been applied in all cases to compensate for the self-absorbed light deep in the pellet. There was no fluorescence "buildup" with the 5-sec-on; 15-sec-off routine.

The maximum fluorescence yields occurred at 100 to 300 μ Hg of oxygen pressure, and the yields were in general greater at the lower temperatures. Otherwise there were no general patterns. Under certain conditions adenine was observed to release up to 13% of the absorbed dose from 5-MeV electrons as visible radiation.

The emission spectra were found to be bell-shaped with peaks in the region 440 to 540 nm and widths from 65 to 160 nm. The spectrum of a sample at constant temperature was not strongly altered by a change in gas pressure. A change in the quality of the gas or in the temperature of the sample, however, did modify the emission.

2. Phosphorescence

a. Adenine. The data for measurements of the 77°K afterglow of adenine under widely different conditions of gas quality and pressure may be simply stated: at pressures greater than 30 μ Hg the adenine phosphorescence yield and spectrum are identical with the thermoluminescence yield and spectra for the given conditions. With good precision it was possible to estimate the magnitude of the 120°K glow peak from that of the 77°K afterglow. A number of careful spectral measurements also failed to reveal a difference from the glow peak spectrum, 440-490-550 nm (see Table IV).

The decay of the adenine afterglow was quite special also: the intensity followed

$$I \propto 1/t, \qquad \text{for} \quad t > 1 \text{ sec.} \tag{1}$$

That is, the decay is logarithmic, with slope of -1. This decay has the interesting property that its instantaneous "mean

life" always equals the time elapsed since the end of the irradiation.

As the pressure drops below 30 μ Hg, the phosphorescence persists in the absence of thermoluminescence, but with decreasing yield. No measurements were taken at room temperature.

b. Cytosine. The 77°K phosphorescence of cytosine followed the same pattern, except that the yield never exceeded 0.1 of the thermoluminescence yield at pressures above 200 μ Hg. At lower pressures a weak afterglow persisted in the absence of a glow peak. Here also the decay obeyed Eq. (1), and the afterglow spectrum coincided with the glow-peak spectrum.

c. Uracil. At 77°K the uracil afterglow yield was about 1/20 of the 140°K glow-peak yield under all conditions. The emission spectrum was measured, 420-470-520 nm, and found to coincide with that of the glow peak. The decay also obeyed Eq. (1).

d. Thymine and guanine. The low-temperature phosphorescence of these substances was weak but measurable. In no case did the yield for thymine exceed 0.1 the 121°K glow peak yield.

3. Thermoluminescence.

The glow-peak yields and emission spectra for the nucleic acid bases are presented in Table IV, and a typical glow curve may be

seen in Fig. 7. Although the yields varied widely between the different samples, the emission spectra were remarkably similar and constant under different gases and pressures. However, in each case there was a definite and measurable shift to the longer wavelengths as the glow-peak temperature was exceeded, i.e., on the descending part of the glow peak. This shift amounted to about 20 nm.

The pressure dependence of the glow-peak yield for adenine may be seen in Fig. 8. In no case was a measurable thermoluminescence glow observed when the ambient pressure was less than 20 μ Hg. When dry nitrogen or oxygen gas or air was present, there was a remarkable drop in the glow-peak yield in the region 20 to 30 μ Hg. A similar drop occurred with helium at somewhat higher pressure. An optimum gas pressure for thermoluminescence was found at about 100 μ hg: at this point the yields were 5 times those at 1 atm N_2 and 1.5 times those at 1 atm O_2. At 1 atm pressure, the yields in oxygen were consistently twice those in nitrogen.

A similar pressure dependence was observed for the glow-peak yields in cytosine, except that the sharp drop occurred in the region 100 to 200 μ Hg, and the dependence on oxygen and nitrogen differed. The cytosine pressure dependence as well as that of uracil

and thymine may be seen in Fig. 9. The latter substances exhibited the same glow-peak yields at all pressures. In a single attempt to measure the guanine glow in 110 μ Hg of oxygen, none was observed.

The adenine, uracil, and thymine glow-peak yields at 1 atm pressure was found to roughly coincide with yields obtained from cobalt-60 irradiation. However, with electrons, the cyctosine peak was only 1/20 that with γ rays. The giant 130°K cytosine peak was never observed following electron bombardment.

IV. DISCUSSION

A. Interpretation of the Thermoluminescence Data

1. The Problem

The principal value of glow-curve measurements is in the study of trap depths. The problem that arises in interpeting glow curves is therefore: after obtaining by experiment the temperature T^* of the maximum glow, to derive from it the depth ΔU of the traps. The glow-curve equation

$$L(T) = n_0 \, s \exp(-\Delta U/kT) \exp\left\{-\int_{T_i}^{T} \frac{s}{\beta} \exp(-\Delta U/kT')dT'\right\} \qquad (2)$$

reveals that ΔU is proportional to T^*, but only for given values of the frequency factor s and the heating rate β. The frequency factor is at the heart of the problem, and the remainder of this section concerns its relation to T^* and ΔU.

By use of Eq. (2) the entire glow curve may be computed, point by point, by numerical integration. However, such calculations are very tiresome, so it is desirable to find ΔU directly from T^*. Now, T^* is determined by setting $\frac{dL}{dT} = 0$. This gives

$$\beta \frac{\Delta U}{kT^*} = s\, T^* \exp\left(-\frac{\Delta U}{kT^*}\right), \tag{3}$$

in which ΔU is defined as an implicit function of T^*. Equation (3) has been solved by the technique of successive approximation for certain values of s/β, and the solutions have been presented graphically in Fig. 10. The full nature of the problem is revealed by these graphs.

For example, when adenine crystals are irradiated at $77^{\circ}K$ and then warmed at $1^{\circ}K/sec$, a glow-peak is observed at $120^{\circ}K$. It can be seen with the help of Fig. 10 that ΔU may lie between 0.07 and 0.32 eV, <u>depending on the value of s selected.</u> The same figure shows that there is a strong dependence of ΔU upon s for any T^*.

The determination of ΔU without knowledge of s by use of

$$L \approx n_0 s \exp(-\Delta U/kT), \tag{4}$$

a simplification of Eq. (2) that is valid at low temperatures, is equally unsatisfactory. For instance, Sims (1962), using Eq. (2), found that values of $s = 10^{11}$ and $\Delta U = 0.485$ were

required in order to duplicate the 195°K glow peak of KH_2PO_4 crystals. Yet for the same peak, an Arrhenius plot of Eq. (4) gives $\Delta U = 0.30$; this corresponds to $s = 2\times10^8$ according to Fig. 10.

2. The Solution

The problem is that Eq. (3) contains four variables, and only two (β and T^*) are known from a single glow-curve measurement. A second independent observation of the relationship between s and ΔU is therefore required if the equation is to be solved. Measuring the phosphorescent decay at 77°K and using

$$P = s \exp(-\Delta U/kT) \tag{5}$$

provides such an independent measurement. Determination of ΔU for adenine is an example of this method.

When an adenine sample was allowed to remain 22 minutes in the dark at 77°K prior to the glow measurement, there was no appreciable attenuation of the glow peak yield. If there had been a slow phosphorescence during this time ($\approx$ 1300 sec) at the expense of the glow peak, then such a decay (of $\tau < 1000$ sec) would have been evident by a reduction in the yield. Therefore $\tau_{77°}$ for the 120°K adenine peak is greater than 10^3 sec. This observation sets a lower limit of 10^8 sec^{-1} for s, and of 0.17 eV for ΔU for the adenine glow.

The relationship between the phosphorescence decay times $\tau = 10^2, 10^3, 10^4, 10^5$ sec) at 77°K and the dependence of various

glow-peak temperatures upon s and ΔU is presented in Fig. 11. A careful examination of this plot is helpful in the interpretation of the thermoluminescence data:

a. The glow-peak temperature of 100°K must be associated with a frequency exceeding 3×10^{10} sec^{-1} in order to have $\tau_{77} > 100$ sec. This no doubt is the principal reason that very few glow peaks were observed at $T^* < 100°K$ in this work: the low-temperature peaks decayed away in the 3- to 4-minute delay between irradiation and heating.

b. For the same reason, the trap depths associated with $T^* < 100°$ must exceed 0.16 eV in this work.

c. Histone and protamine sulfate, which were observed to have a 77°K phosphorescence 200 sec after irradiation and whose glow peaks are approx 115°K, may be placed with $s = 10^8$ sec^{-1} and $\Delta U = 0.16$ eV.

d. For all the other glow peaks, the trap depths may be limited to ±0.05 eV by using Figs. 10 and 11. For instance, take the 105°K aniline peak. It is known that $\tau > 10^3$ sec, otherwise a measureable 77°K phosphorescence would have been recorded. Therefore, from Fig. 11, $s > 5 \times 10^{11}$ sec^{-1} and $\Delta U > 0.22$ eV. From Fig. 10, with $s = 10^{14}$ sec^{-1} (the maximum conceivable value), $\Delta U_{max} = 0.27$ eV. In this case,

therefore, the limits on ΔU are 0.22 to 0.27 eV, and on s are 5×10^{11} and $10^{14}\,sec^{-1}$.

e. The paucity of glow peaks in organic powder samples of $T^* > 170^oK$ remains to be explained. It is possible that in these substances trapping sites of depth > 0.30 eV are not present in appreciable numbers. If such relatively high-temperature peaks are found, it is likely that the τ_{77o} will be great--the order of years or more.

3. Relation Between τ and β.

In Sec III.B.2 the strong 77°K phosphorescence of ADP and polyethylene was mentioned. When these substances were heated at two different rates, the mean life of the phosphorescence changed. This is of course expected of temperature-dependent phosphorescence: during constant heating the exponential form remains, but the "mean life" shortens directly as the heating rate is increased.

It was in fact discovered that the parameter s/β in Fig. 10 very nearly equals $10\ s\tau$ for every T^* and ΔU as obtained from Fig. 11. Setting $10\ s\tau = s/\beta$ gives the relation $\beta\tau = 0.1$. That is to say, for $\beta = 1^oK/sec$ we have $\tau = 0.1$ sec. In thermoluminescence this is of some interest in that when $\beta = 1$, then at T^* the mean life of the emptying traps is about 0.1 sec. And of course when $\beta = 0.1$, then $\tau = 1$ sec at T^*. This relationship gives a quantitative basis for the

well-known phenomenon of intensification of glow-peak height by means of increased heating rate.

4. Comparison of Gamma- and Electron-Induced Glow Peaks

The adenine peak location, yield, and emission spectrum remained remarkably constant under excitation by these different modes. However, there was when cytosine was irradiated with electrons a surprising reduction in yield, and the giant glow peak was absent.

In no case did the glow-peak temperature exceed 180°K, and with the exception listed above, the glow curves for electrons resembled those for γ rays. This implies that the elctrons behave similarly to cobalt-60 rays in their interaction with organic crystals. It is noteworthy that the strong electron beams were capable neither of grossly modifying the luminous centers nor of creating new ones.

B. The Role of Gas Pressure

1. The Dependence of Glow Yields Upon Gas Pressure and Quality

The observations to be explained are:

a. The thermoluminescence of adenine, cytosine, and guanine vanished at low gas pressures (< 20 μ Hg), while that of thymine and uracil remained unchanged to pressures < 0.1 μ Hg.

b. The 120°K adenine peak shifted to 140°K at low pressures, (about 100 μ Hg), and to 112°K when the ambient gas was oxygen at 1 atm.

c. The thermoluminescence and 77°K phosphorescence emission spectra coincided, although there was a definite but small shift to longer wavelengths as T^* was exceeded.

d. The glow-peak emission did not change when nitrogen gas was replaced by oxygen or helium.

2. Dependence of Fluorescence Yields Upon Gas Pressure and Temperature

The observations to be explained are:

a. With the exception of cytosine, the fluorescence yield at room temperature roughly equalled the low-temperature glow-peak yield. For cytosine, this holds true if the γ-ray glow yield is used.

b. The 77°K optimum fluorescence yield (at 200 μ Hg O_2) was roughly 100 times the glow yield except for uracil, for which the factor was only 12.

3. Clues from the Emission Spectra

The measured emission spectrum for a given substance was found to have the same shape under the different experimental conditions. Remarkably, the wavelength peak was at either one of two positions.

a. At room temperature, and at 77°K under vacuum, the peak locations coincided. The emission peak under heavy-ion

irradiation also generally occupied this spectral position.

b. At 77°K, under gas pressure exceeding 100 μ Hg, the emission spectrum was the same as that for the thermoluminescence (and the 77°K phosphorescence).

4. Exciton Hypothesis

The dependence of luminescence yields and emission spectra upon temperature and local gas pressure requires an explanation. To meet this requirement the following hypothesis for the role of gases in the radioluminescence of organic crystals is advanced.

a. The ionizing radiation produces electronic excitations in the crystals with energy packets of a few electron volts. Some of these excitations are "localized" below the conduction bands and give up their energy to lattice vibrations. Another portion has sufficient energy to enter the conduction bands and travel to discrete molecular luminescence centers or to sites where nonradiative deactivation may occur.

b. The ambient gas penetrates into the crystal lattice, thereby increasing the characteristic lattice vibration frequency, and changing the potential-energy states of the luminescence centers.

c. At low temperature, the excitons formed below the conduction band have a greatly reduced probability for vibrational energy loss. They therefore are effectively trapped, although

they do not necessarily remain at one location.

d. The heat applied in thermoluminescence serves as the activation enthalpy for the diffusion (release) of the trapped excitons. This enthalpy is slightly decreased (0.04 eV) by the local presence of gas molecules.

e. The major effect of the gas, however, is the perturbation of the potential-energy states of the luminescence centers. One of the many possible perturbations that is consistent with the observations is given in Fig. 12. In excited state 1, the probability for nonradiative transitions via CC' is great. This probability is reduced in favor of a radiative loss in state 2. Also, in accordance with measurement, the emission peak frequency DD' is slightly greater than that for BB'.

5. Implications of Exciton Hypothesis

It must be emphasized that this model is simply an interpretation and that there is no compelling evidence for it. None the less the hypothesis usefully predicts the following things:

a. Increased conductivity at T^*.

b. Indifference of the molecular emitter to the type of gas present.

c. Reduced molecular deactivation yield (broken chemical bonds, etc.) at low temperature when gas is present.

d. Thermoluminescence potentiated after irradiation *in vacuo* by a penetrating gas.

e. Bimolecular reaction kinetics.

C. Comparison of Measurements

No energy yields for thermoluminescence of organic compounds have been reported; that for LiF was less than 10^{-4} (Daniels et al., 1953). Here it was also found that in general the low-temperature glows had yields less than 10^{-4}. However, the yields of crystalline powders of adenine and cytosine were 1 to 2×10^{-3}. There was confirmation of the earlier observations that organic conjugated ring molecules have yields 1000 times as great as other molecular types, that the glow peaks of similar compounds differ in width, location, and intensity, and the glow peaks occur generally below 170°K, and that the emission spectra are bell-shaped and about 100 nm broad.

During thermoluminescence of single crystals of the hygroscopic substances phenol and KF, a series of sharp < 1-sec spikes was recorded instead of the normal glow at low temperatures. Sharma (1956) and Sims (1962) have reported similar phenomena. The latter author believes these spikes are a form of triboluminescence.

The fluorescence energy yields under electron bombardment at certain local gas pressures and temperatures exceeded 10% for adenine, but generally stood in the region 0.1 to 5.0%. These yields

are comparable to those observed in organic solid and liquid scintillators.

The discovery that organic thermoluminescence may be strongly influenced by the local gas pressure has been independently confirmed by measurements using tyrosine and certain other substances (Carter, 1962). The reproducibility extremes for the glow yield of a given chemical batch were found to be about ±50%.

Optical de-excitation of irradiated material at 77°K was found (in agreement with the data of Bryant et al., 1959) to be inefficient at wavelengths exceeding 2 μ. Large exposures with an infrared lamp did not reduce the glow yield by more than the normal ±50% fluctuations.

The exciton hypothesis may be compared to a model proposed by Voevodskii and Molin (1962), which predicts a reciprocal relation between the radiolytic yield of H atoms and luminescence yield. Briefly, their model attempts to explain the low yields for the organic compounds that possess resonance stability. They feel that the energy position of the lowest excited state is critical. If this exceeds the dissociation energy for the C-H bond, then the probability for bond rupture is high. If it does not, then radiative de-excitation becomes more probable. The exciton hypothesis has no provision for bond rupture once the exciton has reached the luminescence center. The only nonradiative decay mode from the lowest excited state envisaged in the configuration

coordinate model is vibration exchange. However, it is a simple matter to add a third potential surface (to Fig. 12) representing a bond-rupture decay mode. In such a figure all three possible modes would then be pictured, and the probabilities for each would depend upon the relative positions of the potential surfaces as determined by local configuration and the liquid and gas environment. Such a tripotential figure, however, will be rather difficult to precisely construct for a given substance.

There is a recent observation that supports the basic feature of the exciton hypothesis. Brocklehurst and Pimentel (1962) recorded glow peaks at 10, 14.5, and 19°K when solid notrogen had been irradiated with electrons at 4.2°K. In this case it is difficult to conceive of the diffusion of anything except excitons upon thermal release.

D. Future Investigations

Several future biophysics investigations by use of luminescence technique suggest themselves:

(a) Yeast cells quick-frozen in solutions containing β-Mercapto-ethylamine (MEA) provide a simple system for radiation protection studies (Smaller and Avery, 1959). These authors observed that when this system was irradiated at 77°K and then warmed, at 125°K the water radicals vanished without interaction with the yeast and MEA radicals. It will be of interest to determine if this disappearance

is associated with luminescence, and is unique for ice at this temperature; 125°K is near T^* for the strongest thermoluminescence in organic crystals.

(b) The study of single organic crystals under various environmental conditions in order to obtain dark-, photo-, and radioconductivity data for correlation with luminescence.

(c) The study of the nature of the initial excitation energy of organic crystals by extending measurements into the 4-77°K region.

(d) The work of Vladimirov (1961) and of Zadorozhnyĭ and Naboikin (1960) has suggested that hydrogen bonds may be of importance in luminescence phenomena.

(e) The examination of luminescence decay of organic crystals by use of fast-pulse electronics. Knowledge of the fluorescence decay kinetics will allow greater understanding of this mode of electronic de-excitation.

(f) The testing by luminescence analysis of crystals grown under conditions whereby gases and other impurities have been vigorously excluded.

(g) Further studies designed to determine the necessary conditions for change in the relative heat, luminescence, and chemical yields.

V. SUMMARY AND CONCLUSIONS

Organic crystalline powders have been exposed to high-energy radiations and examined by luminescence analysis. It was observed that temperature and gas pressure have profound effect upon luminescence yields. The fluorescence energy yields under certain conditions may rise to 13%, the phosphorescence and low-temperature thermoluminescence yields may rise to 0.01 of this. The emission spectra under various conditions and excitation modes were found to be bell-shaped in the region 350-550 nm and 100 nm wide. The activation enthalpies for thermoluminescence glows have been examined in detail and a new method for their determination, based on luminescence decay at 77°K, has been used. A rather broad conceptual model for the interpretation of the observations--the exciton hypothesis--has been advanced.

It is argued that luminescence is one of the three fundamental de-excitation modes in radiation biology, that there is justification for analogy between the electronic states of condensed systems in living cells and those in molecular crystals, and that luminescence analysis may stand with electron spin resonance as a new window through which unique aspects of radiation biology may be studied.

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Table 1. Thermoluminescence of various gamma-irradiated chemicals[a]

Chemical	Heating rate (°K/m)	T (°K)	Duration (sec)	Yield $\times 10^{-6}$	Comments	Sigma Chemical Company lot number
Adenine	70	120±10	31±5	2400	480±50 nm width	A-12B-255
5' ADP-Na salt	6	98	420	35[b]	LNp	121B-790
	70	120	45	37[b]		
ATP-di-Na salt	54	80	≈20	16	two peaks	121B-785
	54	125	36	200		
ATP-di-Na salt	70	95-114	40	24	dissolved in H_2O	
Aniline	54	105	66	240		
Anthracene	54	98-111	27	28		
Benzene	54	95	10	17	lesser peaks 80°, 118°, 145°	
Carbon tetrachloride	32	135	70	0.016		
Catalase	70	80-147	60	8	hint of peak at 185°K	
Cephalin	70	90-105	≈15	0.16	two peaks	C-40B-65
	70	148	60	0.28		
Cholesterol	70	124	20	28	two peaks	C-121B-95
	70	183	26	17		
Cytosine	70	115	15	72	three peaks	C-80B-58
	70	130	25	640		
	70	180	35	360		
Sodium chloride	70	200	35	600	two peaks	
	70	250	40	180		
DNA - Calf thymus	70	138	29	2.8	highly polymerized	Type I
DNA-tetra-Na Salt	70	153	30	1.5		Type II
DNA-Grade III	70	120	29	22.		Grade III
DNA-free acid	70	125	33	6.1	tail to 210°K	Type IV
	70	~110	~30	6.4	sat. sol'n	

(cont.)

Table 1. Thermoluminescence of various gamma-irradiated chemicals (cont.)

Chemical	Heating rate (°K/m)	T^{0} (°K)	Duration (sec)	Yield×10^{-6}	Comments	Sigma Chemical company lot number
β-DPN	12	115	135	11.		111B-692-7
β-DPN	70	132	12	12		
β-DPNH	70	83	6	0.56		121B-625
Ether, anhyd.	70	93	11	4.4	lesser peaks 50°, 100°, 150°; two peaks	
	70	135	12	2.8		
Glycine	36	77-150	150	0.032		
Guanine	70	106±4	24±6	10.	pk. 510 nm; LNp	
Histone-calf thymus	70	113	50	14.	LNp	H-101B-96
Lecithin	70	77-160	70	0.28		2-120B-51
Linoleic acid	54	100	90	1.9	tail to 185°K	
Naphthalene	54	102	14	7.5	lesser peaks at 60°, 164°K, 202°K, two peaks	
	54	132	22	22.		
Phenanthrene	70	102-225	110	~160Q		
Phenol (single crystal)	54	100-230	150	?	about 100 sharp spikes	
Polyethylene	70	118±4	31±3	400	LNp; transparent sheet; two peaks.	
	70	155±5	24±3	105		
Protamine-SO_4	70	77-150	60	1.6	LNp (salmine)	
Pyrimidine	70	105	45	1.2	long tail	Cal Bio. 5481
Sucrose	54	120	30	1.2	LNp; lesser peaks at 150°, 220°	
Sucrose	70	175	12	0.0080	sat. sol'n	
Sucrose	70	105	30	1.4	hot syrup cooled in air	
Thymine	70	105	22	30	tail to 265°K	T81B-267
Toluene	70	110	60	160	two peaks	
	70	153	18	20		
Uracil	70	120	35	36	resembles thymine glow; two peaks	
	70	160	54	28		
Tap water	11	174	60	0.0040	required 10^5 rad exp.	

[a] Exposures at 93 rad/sec to Co^{60} γ rays. Exposure range 0.3 to 50 krad. Samples sealed at 1 atm air, 21°C, 40 to 60% RH.

[b] Partly engulfed in a temperature-independent phosphorescence of 4X this yield.

Table II. Luminescence of certain chemicals during heavy-ion irradiation.[a]

Chemical	Temp. (°K)	Yield[b] ($\times 10^{+6}$)	Spectrum[c] (nm)
Adenine	77	17.	505-525-562[a]
Adenine	77	1.2	425-470-525
Adenine	295	55.	465-522-575
ATP	77	8.0	393 ⟨430, 445⟩ 530[d]
ATP	295	8.0	396-460-550[d]
Cytosine	77	18.	452-504-556
Cytosine	295	33.	465-505-555
DNA	295	3.4	465-525-585
Guanine	77	8.8	360 ⟨410, 520⟩ 585
Guanine	295	5.0	360 ⟨375, 500⟩ 585
Sucrose	295	3.2	405-463-545
Thymine	77	28.	315-350-470[d]
Thymine	295	23.	315-354-440[d]
Uracil	77	24.	440-511-576
Uracil	295	15.	435-500-572

[a] The first entry was irradiated with 120-MeV C^{+4} ions at 43 mW intensity--all others with 160-MeV O^{+6} ions at 33 to 95 mW. All samples irradiated at residual air pressure of 1 to 5 μ Hg.

[b] Ratio of mW of measured light energy emitted to mW of heavy-ion energy put into the surface of the 1-g chemical pellets. Not corrected against E-L disk standard spectrum, 465-500-535 nm.

[c] Wavelength at peak intensity--and that on each side of peak at half intensity.

[d] Spectrum tail to 680 nm.

Table III. Luminescence of certain chemicals during 5-MeV electron irradiation.

Chemical	Temp (°K)	Gas pressure	Yield ($\times 10^3$)	Spectrum (nm)
Adenine	77	< 1 μ Hg air	5.8	490-520-590
Adenine	77	5 μ Hg O_2	80.	435 475 500 550
Adenine	77	300 μ Hg O_2	130.	438 475 500 550
Adenine	220	25 μ Hg O_2	3.4	480-530-580
Adenine	245	25 μ Hg O_2	2.4	490-540-580
Adenine	283	<1 μ Hg air	2.1	495-535-580
Adenine	286	26 μ Hg air	2.1	490-535-593
Adenine	286	110 μ Hg O_2	2.1	485-525-615
Cytosine	77	<1 μ Hg air	0.62	450-500-555
Cytosine	77	200 μ Hg O_2	4.8	425-480-535
Cytosine	80	1 atm O_2	0.80	450-480-532
Cytosine	100-125	130 μ Hg O_2	1.40	447-480-537
Cytosine	290	3 μ Hg air	0.80	495-520-560
Cytosine	290	110 μ Hg N_2	0.13	470 500 520 545
Cytosine	290	1 atm N_2	0.16	475-510-545
Guanine	77	10 μ Hg air	5.3	462-510-565
Guanine	77	110 μ Hg O_2	11.0	460-507-560
Guanine	280	30 μ Hg O_2	0.17	-- 525 --
Guanine	275	1 atm O_2	0.09	-- 500 --
Thymine	77	150 μ Hg O_2	52.	430-460-535
Thymine	294	16 μ Hg air	0.032	-- 480 --
Uracil	77	<1 μ Hg air	1.2	410-450-520
Uracil	77	200 μ Hg O_2	1.2	415-460-515
Uracil	77	200 μ Hg N_2	1.2	395-440-520
Uracil	290	<1 μ Hg air	0.008	400 440 520 560

Table IV. Thermoluminescence of electron-irradiated chemicals[a]

Chemical	Heating rate (°K/m)	Gas pressure	Peak temperature T^*(°K)	Duration (sec)	Yield $\times 10^{+6}$	Spectrum (nm)[b]	Comments
Adenine	44	1 atm N_2	124	38	1200	none	No DU
	44	1 atm O_2	112	30	2400	440-490-550	
	55	1 atm He	120	33	1200	440-490-550	
	55	<100 μ, any gas	140	45	See Fig. 15	440-490-550	
ATP	44	30 μ air	--	0	0.24 max.	none	No DU
Cytosine	55	all conditions	177±7	95	See Fig. 16	445-490-545	
Guanine	55	110 μ O_2	--	0	16.	-- 500 --	
Thymine	55	220 μ O_2	121	91	32.	430-460-530	
	55	< 220 μ N_2	110±2	72	25.	430-460-530	
Uracil	55	all conditions	139±6	101±10	100.	425-465-525	

[a] Dose rates varied, but were near 3300 rad/sec

[b] Peak wavelength, and wavelength at half maximum on each side, at T^*.

FIGURES

1. Sample holder for gamma irradiations.
2. Details of base assembly.
   a. Copper cup, blackened by "Ebonal C" process.
   b. Thermocouple leads--and junction.
   c. Stainless steel.
   d. Teflon gasket.
   e. Pressed wood plastic.
   f. Copper-constantan thermocouple jacks.
3. Target sample holder.
4. Electroluminescent disk and accessory tube.
5. Spectral response of detectors.
   A. RCA 1P28, S-5 response.
   B. "Total" DU and S-5 response.
   C. DU response.
   D. Emission spectrum of electroluminescent disk light standard.
6. The low-temperature glow-peak yields. (Starred values from Augenstine et al., (1960))
7. Glow and phosphorescence decay at 430 μ Hg N_2 pressure. (Adenine pellet, 1 g; 7×10^4 rad 5-MeV electrons.)
8. Thermoluminescence yield of adenine at low gas pressure
   o oxygen ▲ nitrogen
   ● air △ helium
   □ blank run (no adenine)
9. Thermoluminescence of uracil, thymine, and cytosine at low gas pressures.
   ● air ▲ nitrogen o oxygen
10. Solutions of the glow-peak equation (3).

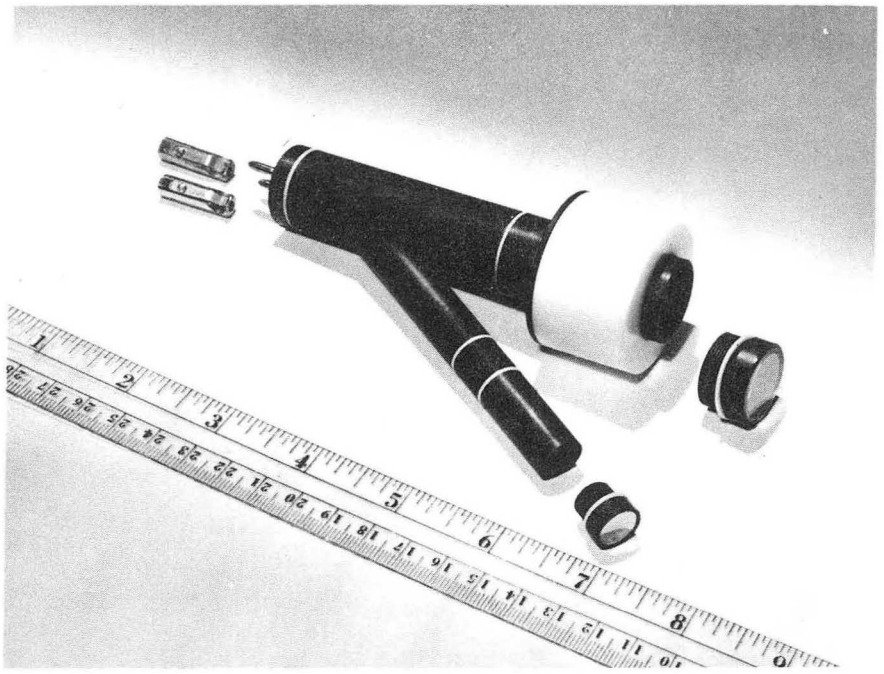
11. Solutions of the phosphorescence equation (5).

    see dashed curves for $\tau = 0.1$ sec.

    see solid curves for $T = 77^{\circ}$ K.

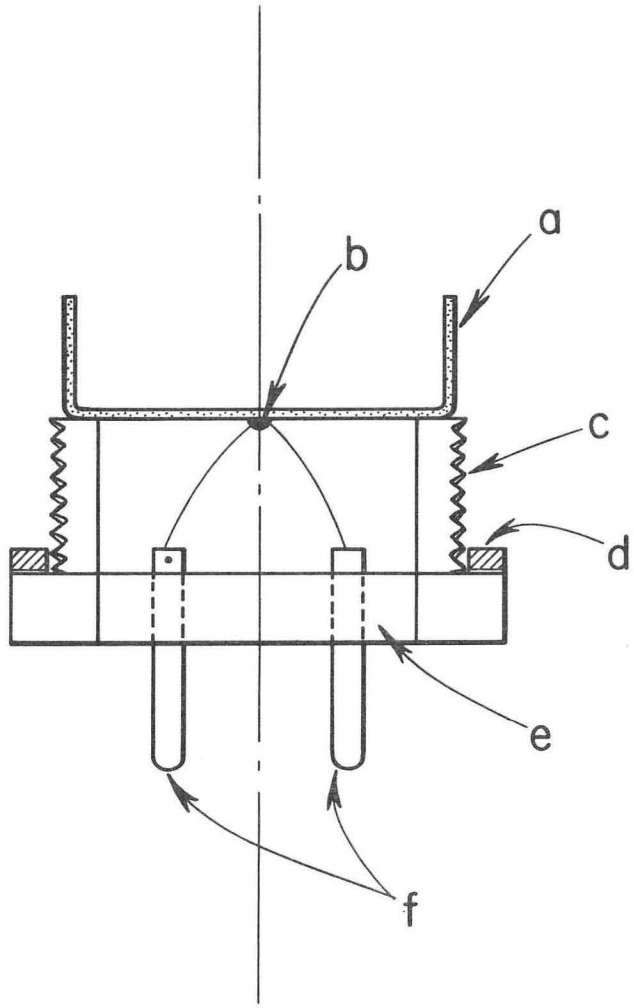
12. Hypothetical coordinate shift.

    1. Position of excited state in pure crystal.
    2. Position when gas molecules have entered the crystal.



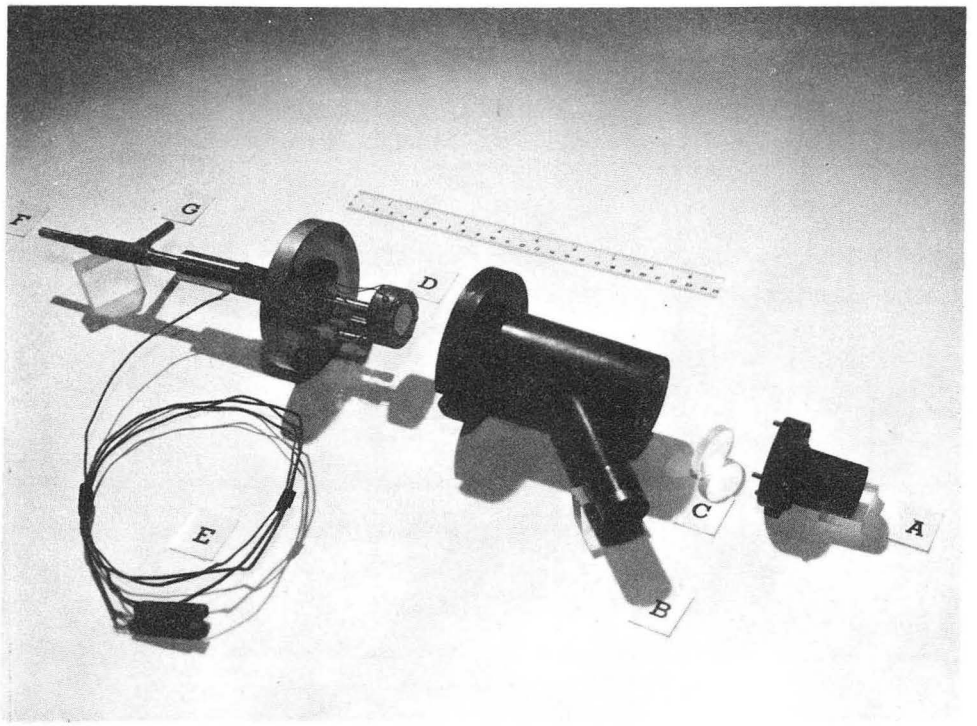
ZN-3674

Fig. 1.



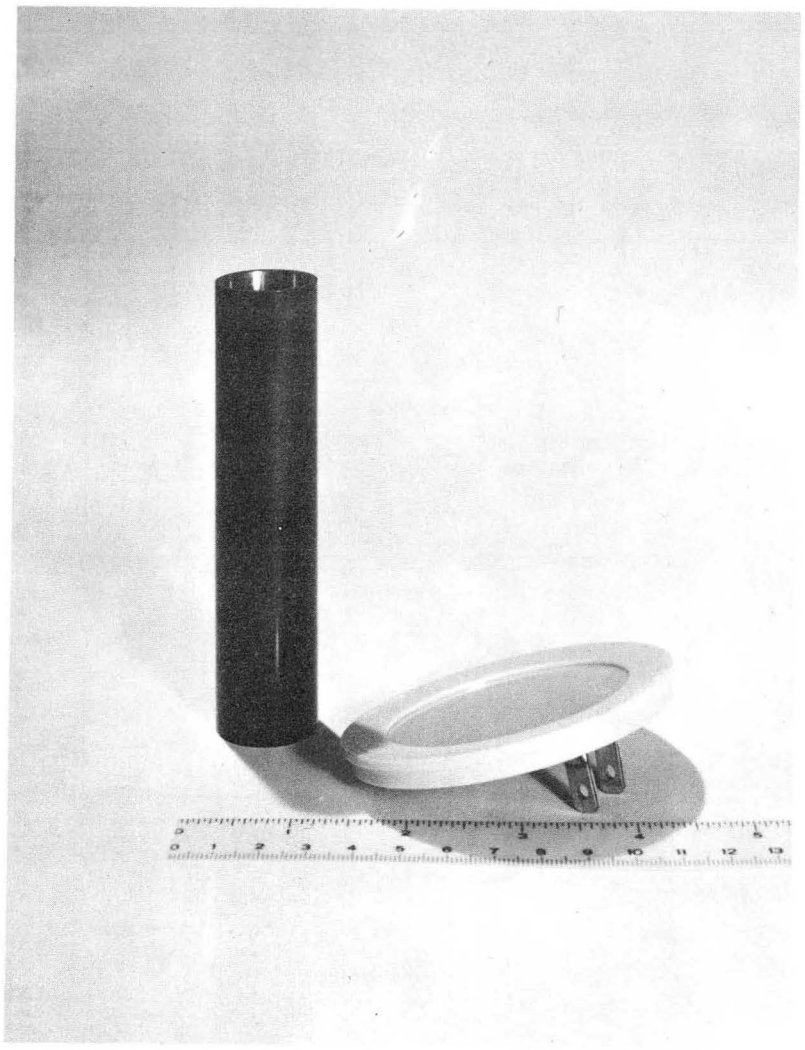
MU-30288

Fig. 2.



ZN-3679

Fig. 3.



ZN-3677

Fig. 4.

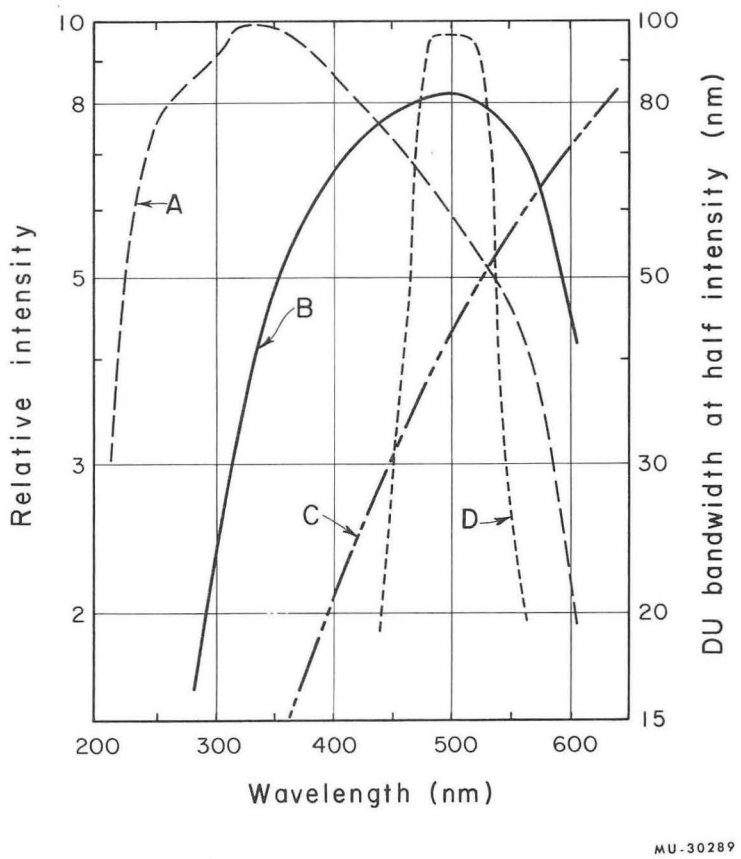

10
8
5
3
2
100
80
50
30
20
15
200
300
400
500
600
Wavelength (nm)
Relative intensity
DU bandwidth at half intensity (nm)
A
B
C
D
MU-30289

Fig. 5.

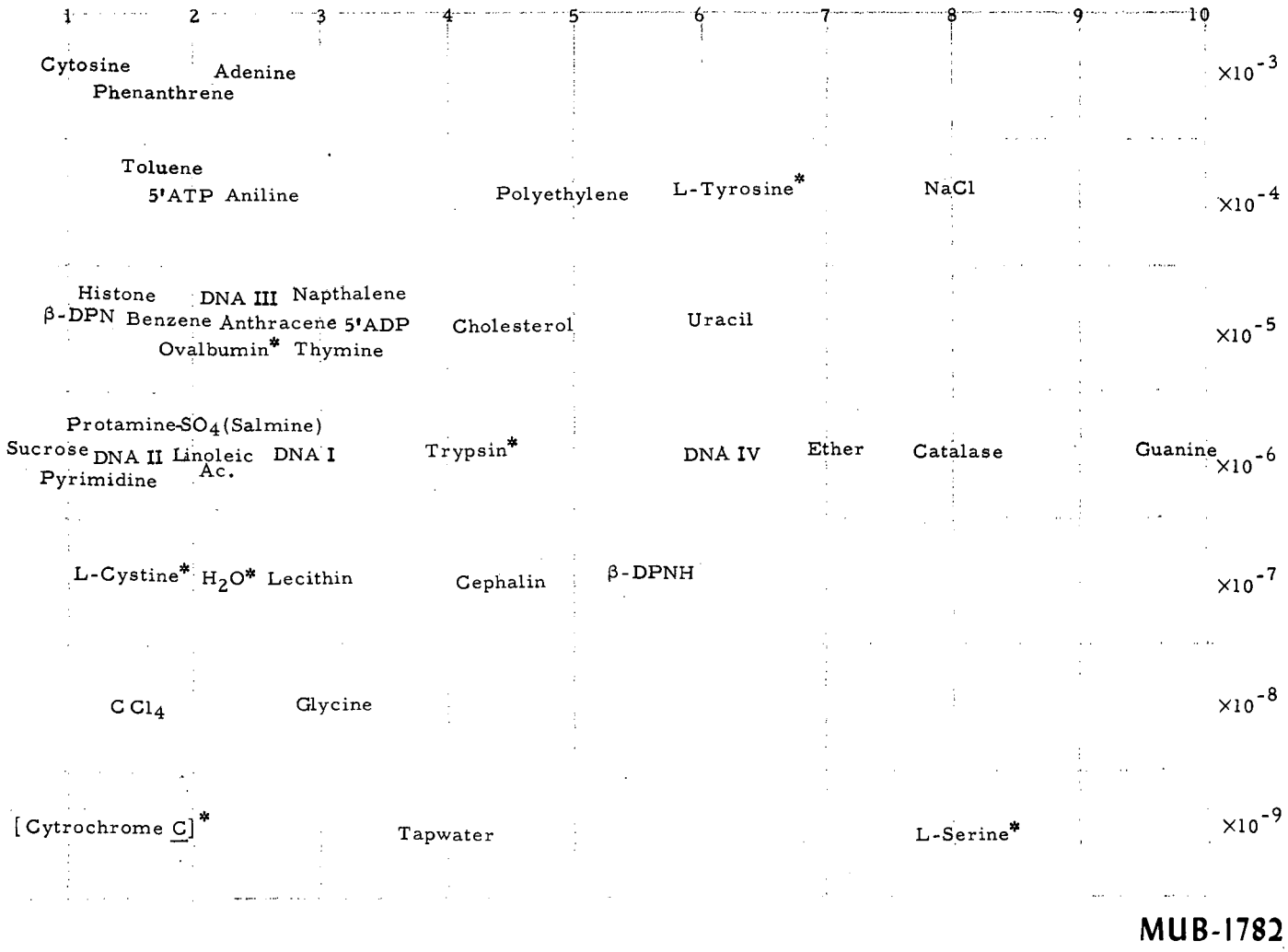

1 2 3 4 5 6 7 8 9 10
Cytosine
Adenine
Phenanthrene
×10^-3
Toluene
5'ATP Aniline
Polyethylene
L-Tyrosine*
NaCl
×10^-4
Histone
DNA III Napthalene
β-DPN Benzene Anthracene 5'ADP
Cholesterol
Uracil
Ovalbumin* Thymine
×10^-5
Protamine-SO4(Salmine)
Sucrose DNA II Linoleic Ac. DNA I
Trypsin*
DNA IV
Ether
Catalase
Guanine
Pyrimidine
×10^-6
L-Cystine* H2O* Lecithin
Cephalin
β-DPNH
×10^-7
C Cl4
Glycine
×10^-8
[Cytrochrome C]*
Tapwater
L-Serine*
×10^-9
MUB-1782

Fig. 6.

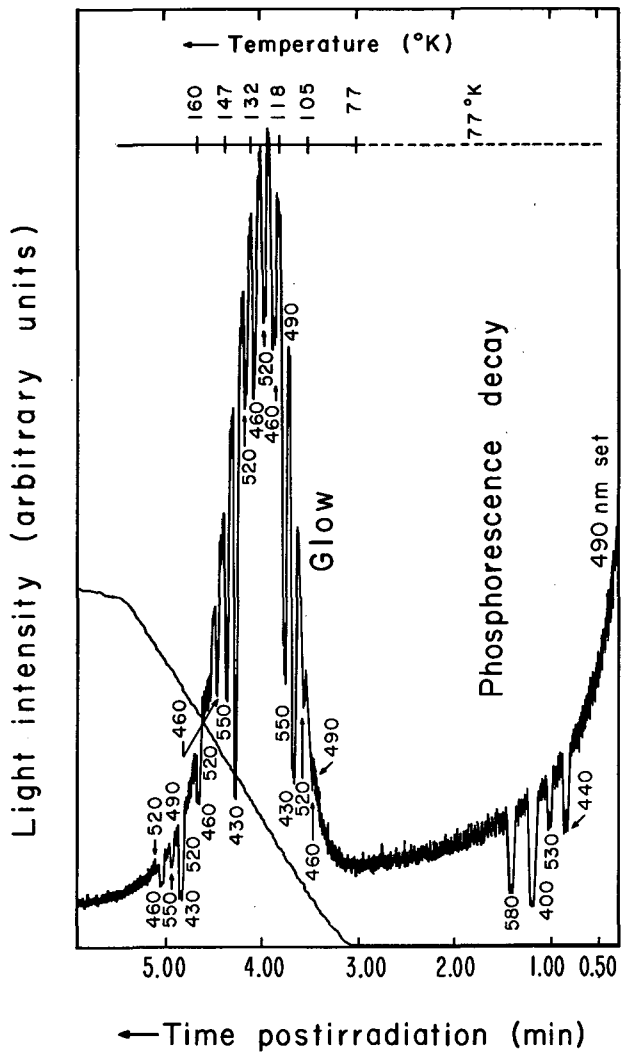

Temperature (°K)
160
147
132
118
105
77
77°K
Light intensity (arbitrary units)
Glow
Phosphorescence decay
490 nm set
5.00
4.00
3.00
2.00
1.00
0.50
Time postirradiation (min)
MU-30290

Fig. 7.

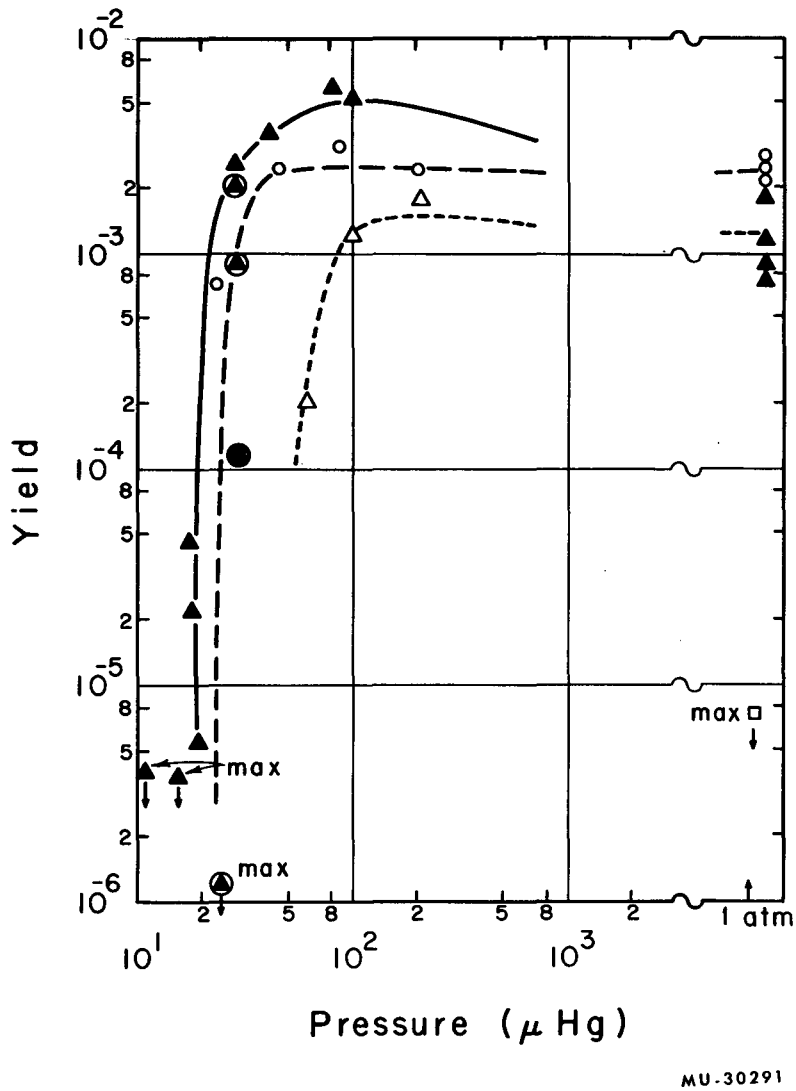


Fig. 8.

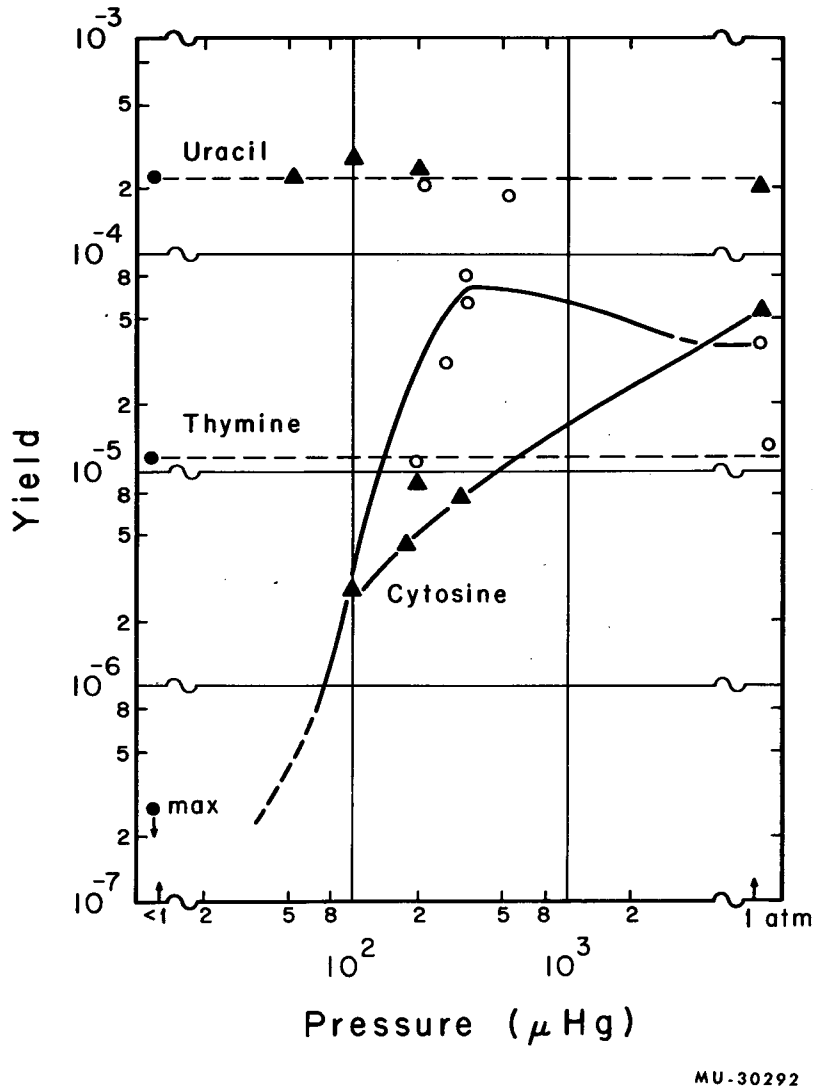

Uracil
Thymine
Cytosine
max
Yield
Pressure (μHg)
1 atm
MU-30292

Fig. 9.

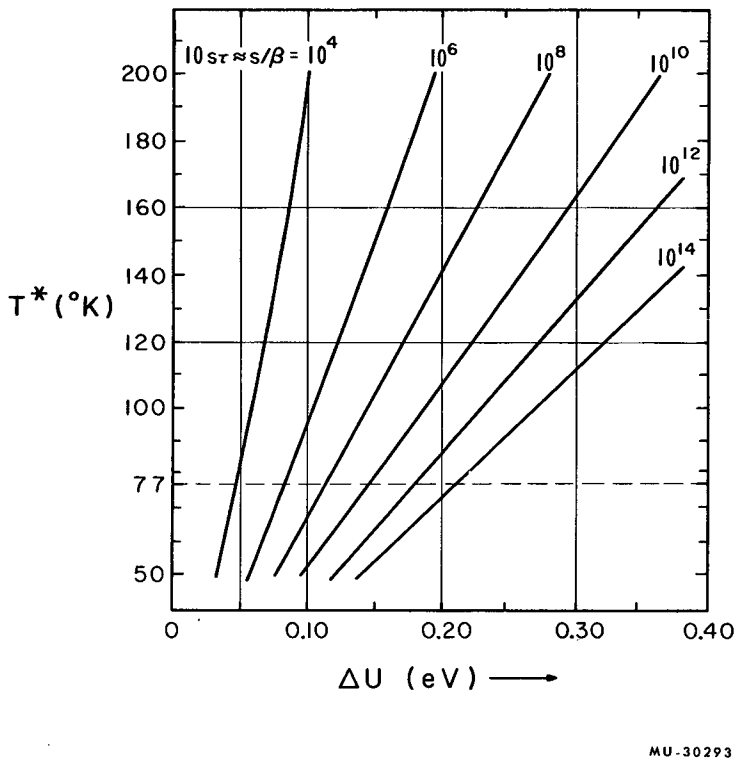
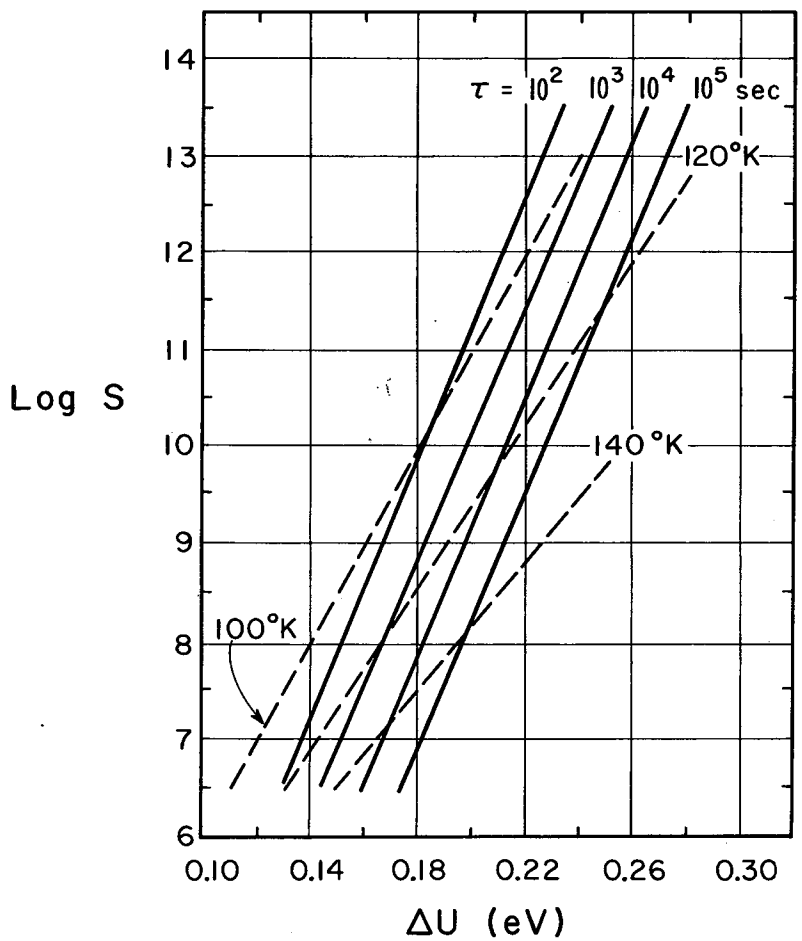

$10 s\tau \approx s/\beta = 10^4$
10^6
10^8
10^{10}
10^{12}
10^{14}
200
180
160
140
120
100
77
50
T* (°K)
0
0.10
0.20
0.30
0.40
ΔU (eV)
MU-30293

Fig. 10.



MU-30294

Fig. 11.

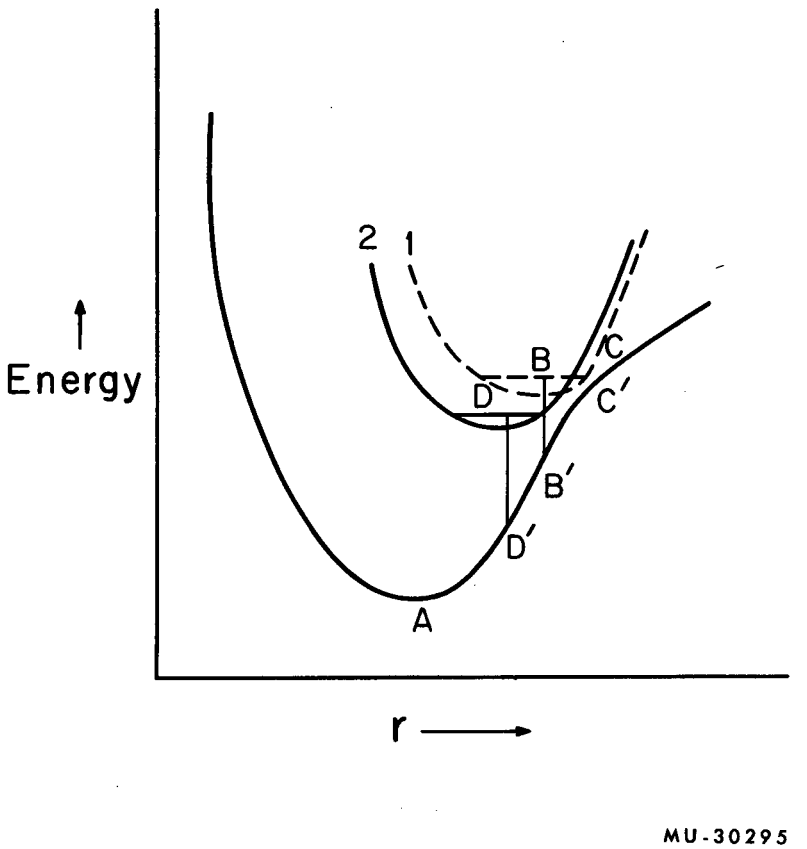


Fig. 12

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