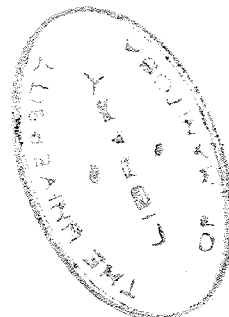Kinetics of Luminescence Quenching

In Liquid Scintillators

by

Edward Neparko

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ABSTRACT

The kinetics of luminescence quenching in liquid scintillator solutions containing dissolved oxygen have been studied. The mechanisms involved in the quenching process can be either static or collisional. According to the experimental data for the systems investigated, the quenching process is found to be a collisional one and the kinetics of this collisional process may be explained by use of the Stern-Volmer equation. Using the Stern-Volmer equation, the quenching constants have been evaluated for the solutions and using the quenching constants, the rate constants have been evaluated and compared with rates of collision obtained from simple kinetic theory approximation. Such a comparison indicates an extremely efficient collisional mechanism with almost every collision effectively deactivating the solute molecule during its lifetime.

The effect of gases other than Oxygen have been investigated. Gases like Sulphur Dioxide exhibit almost total quenching of luminescence whereas gases like Hydrogen and Nitrogen do not exhibit quenching properties. The effect of change of solution viscosity on the quenching constant and rate constant were also investigated. As predicted by the encounter theory, both the quenching constant and the rate constant are inversely proportional to the solution viscosity. The increased viscosity of the solution causes a decrease in the collisional quenching process.

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INTRODUCTION

Kinetic studies carried out by Bowen[1-2] on the fluorescence quenching of solutions and vapors by gases like O_2 and SO_2 showed that the process could be explained by an extremely rapid and efficient collisional mechanism. Although there are some differences between the fluorescence and scintillation processes, the similarity between the two warranted a similar investigation on liquid scintillators. This would be of both theoretical and practical value in view of the important discovery made by Pringle[3] et al. that dissolved O_2 gas caused a considerable decrease in the efficiency of liquid scintillator solutions. Up to now, no quantitative measurements had been made on the O_2 quenching and no quantitative relation had been established for this quenching effect.

It is important that one distinguish between internal and external quenching processes. In the first case, the degradation of the incident energy in a solution is achieved by solvent and solute molecule interaction. In the second case, the non-emissive degradation is achieved by the interaction of the fluorescent molecules with some foreign molecules like O_2 gas. Some mention of the ideas of internal quenching will be made later. In this investigation, the most important quenching process is the external quenching of liquid scintillators by gases such as O_2 or SO_2.

In addition to the quantitative measurements of O_2 quenching and the establishment of a suitable mechanism for the quenching process in liquid scintillators, the effect of viscosity was also investigated according to the modern encounter theory. The effect of other gases on the luminescent output of liquid scintillators was checked as well.

HISTORICAL

Nuclear reactions occur with the emission of energetic particles, radiation, or a combination of both. In order to be able to characterise these particular phenomena, some means must be used to determine the energy associated with the particles and radiation. When a charged particle passes through matter, it causes excitation and ionisation of the molecules of the medium. It is the ionisation which is the basis of nearly all the methods used for the measurement and detection of such particles. In the case of uncharged radiation such as gamma rays or X-rays, the secondary ionising particles serve to characterise the radiation which produced them.

When the charged particle or radiation hits certain liquids or solids known as phosphors (luminescent materials), part of the energy is lost in molecular excitation and ionisation and may then be emitted as U. V. or visible light. The observation and the counting of these light pulses is the basis of the scintillation counter. The classical example of the scintillation counter was the activated ZnS screen used by Rutherford in his experiments with alpha particles. In this instance, the light pulses produced by the alpha particles were observed and counted with the aid of a microscope in a darkened room. A counter of this type would be insensitive to beta and gamma rays because of the weak ionisation produced in the thin phosphor screen. As a result, the scintillation counter dropped into relative disuse after this time and the Geiger-Müller type of counter was the type most widely used in the investigation of nuclear phenomena. With the development of efficient photo multiplier tubes of high gain and good sensitivity to small light intensities the interest in scintillation counters became quite pronounced. A very important advance in this field was made by Kallmann[4] who found that a large crystal of naphthalene could be used to detect the

scintillations produced by beta and gamma rays. Then, Bell[5] showed that a
crystal of anthracene was even better since it yielded a pulse whose ampli-
tude was five times that of a comparable naphthalene crystal. The work of
Hofstadter[6] showed that a crystal of NaI, activated by thallium, gave pulses
even larger than those from anthracene. Reynolds, Harrison and Salvini[7]
were able to show that certain organic solutions emitted pulses, under suit-
able excitation, which were comparable in magnitude to those obtained from
an anthracene crystal. Thus, these organic scintillating solutions could be
used as gamma ray detectors with an efficiency relatively the same as anthra-
cene. With these initial important discoveries, the technique involving
liquid scintillators has steadily advanced until today, liquid scintillators
are used in many and various fields. Indeed, there are numerous problems
which, as far as the physicist is concerned are over once a suitable solution
is found. For a chemist, however, they present a very interesting piece of
work since some of the problems - particularly the quenching of the mechanism
of light emission - can be explained along the lines of modern chemical
theories.

Inorganic Scintillators

There are two main classes of scintillators - inorganic and organic.
Historically, ZnS is the most interesting of the phosphors since various
forms of the substance were used in the earliest visual scintillation counters.
However, at the present time, its use is somewhat curtailed due to the inabil-
ity to prepare crystals of large dimensions. The most important group of in-
organic phosphors is the Alkali Halides. The high density of crystals such
as NaI, KI and RbI makes them very efficient absorbers of electromagnetic
radiation. A point of interest is that these crystals must be impregnated
with an "impurity" - usually thallium. This thallium activation is found

necessary in order for the crystal to function as a suitable detector. The theories which have been put forward to explain the processes by which the crystal emits energy and the role that the activator plays in the process are too complicated and advanced for an introduction such as this. However, Curran[8] gives an excellent account of the present theories of the luminescence of ionic solids and their properties.

Organic Crystal Scintillators

The other important group of scintillators are the large number of organic compounds. The organic group of scintillators may be divided into three classes: organic crystals, plastic scintillators and liquid scintillators. Many of the ideas which have been developed for ionic crystals are applicable, with some modification, to the field of organic crystals. Plastics and liquid scintillators, on the other hand, require new theories and explanations. These will be discussed later. As far as the migration of energy is concerned, there are a number of processes which are discussed for inorganic crystals[8]. Most authors agree that the same general type of mechanism can be used to explain the migration of energy through the organic crystal lattice. The majority of the work has been done on ionic crystals, but there is reason to believe that the phenomena of luminescence are more easily explained by examination of organic crystals and liquids. Although there has been a limited study of the properties of organic crystals, there is much material available and Bowen[9] has made use of potential energy diagrams in discussing the activation and de-activation of organic molecules.

It is found that the organic crystals, although differing markedly in structure, do, nevertheless, possess remarkable similarity. Both Bowen and Sangster[10] have carried out studies on this point and the results of the latter can be summarised very briefly as follows. The best crystalline

organic phosphors are colorless and possess a high melting point. The structure is fairly simple and the molecules should possess extensive ring structure with numerous double bonds and other structures giving extended interlocked systems. In fact, it is thought that the whole emissive and absorptive process is due to the resonance of the π electrons in the benzene like ring structure of the organic scintillators. The extensive studies carried out by Sangster on a large number of compounds have led him to these conclusions. The crystals were excited by Co^{60} γ -rays and U. V. radiation as well. This latter point is of great importance since much of our knowledge about fluorescence has been due to studies using U. V. excitation.

In the case of inorganic crystals, activators had to be used. With organic crystals, no activator is necessary and stress is placed on absolute purity and freedom from imperfections. Even traces of impurity present in the crystal can cause very serious quenching. The quenching of fluorescence is discussed very fully by Bowen[9]. No attempt will be made here to give these theories or discuss their relative merits.

Plastic Scintillators

Solid solutions of fluorescent organic compounds in a suitably transparent material have been found to yield pulse heights which are relatively high compared to anthracene. The most suitable materials used at present are polystyrene and poly vinyl toluene. These plastic scintillators offer some advantages in that they may be prepared in large volumes with relative ease and may be machined or cut to a shape or size desired for some particular problem. The mechanism of energy absorption and emission has not yet been fully resolved. However, since the plastic has no definite crystalline structure, it would appear that the plastics should be grouped with liquid scintillators rather than with the ionic crystals. Since the decay times are

of the order of 10^{-9} seconds, plastics find use in systems requiring fast
detection without regard to energy evaluation.

Liquid Scintillators

Organic solvents such as benzene, toluene and xylene show very weak
fluorescent properties when exposed to gamma rays or other exciting radia-
tion. However, the fluorescent excitations produced in the molecules would
nearly all be quenched by internal conversion of the energy into heat. The
quenching is due to some process whereby the non-excited molecules rob the
excited molecules of their energy and use it up in a non-radiative process
such as conversion into heat. When the solvent contains a solute like p-
terphenyl, whose molecule is highly conjugated, the fluorescent excitations
of the solvent molecules can be transferred to the solute before solvent
quenching can set in. This transfer of energy must occur in a time which
is short enough compared to the solvent quenching time. The trapped energy
of the solute is then degraded to some extent; but the quantum efficiency
(photons emitted / photons absorbed) - is quite high. It should be pointed
out that the emission spectrum of the solution corresponds to that of the
solute and not the solvent. There are a number of mechanisms which account
for the energy transfer from solvent to solute and the subsequent emission
process. These will be discussed in some detail at a later stage.

With the advent of the modern photo multiplier, the use of liquid scin-
tillators has increased very rapidly. The moderate cost of the solutions
and their stability makes them very attractive for use in research - parti-
cularly in nuclear physics where large volume solutions are used as particle
detectors. They are readily adaptable as regards size and shape. Their
emissive spectrum can be matched very closely to most commercial tubes by the
addition of very small amounts of secondary solutes known as spectrum shifters.

These spectrum shifters can shift the emissive spectrum of a solution to a more favorable position when added to the solution in quantities as small as 1 part in a thousand.

The luminescence efficiency of organic solvents like benzene, toluene and xylene is very low. However, when a solid like p-terphenyl or anthracene is added to the solvent, the resulting solution has a pulse height comparable with an anthracene crystal. These primary solutes, as they are usually called, are characterised by a number of benzene-like rings being joined together thus giving rise to a highly conjugated system. The presence of double bonds and the non-localised π electrons allows resonance structures to be set up and it is thought that the mechanism of energy absorption and emission is due to the excitation and de-excitation of these electrons and their associated resonance structures. Use of a two dimensional potential energy curve has been made by Bowen in explaining the mechanism of energy absorption and emission. Although the various primary solutes are different in properties, their structural properties are very similar. They all exhibit structures in which there are double bonds and conjugation of rings yielding extended and rigid interlocked systems.

The pioneer work on liquid scintillators and the mechanisms involved was done by Kallmann[11] and Kallmann and Furst[12-13]. They conducted a large number of experiments using various solutes and solvents. An important discovery was that the pulse height of a solution varied with the primary solute concentration. Furthermore, there was a certain optimum concentration of primary solute which would yield the maximum pulse height. Amounts in excess or deficiency of this quantity would yield pulse heights less than the maximum. These authors state that in the case where the primary solute is in excess of the optimum value, the decrease in pulse height is due to the concentration or self-quenching effect. Besides other processes involved,

like primary solute molecules can decrease the pulse height by a non-emissive degradatory process. It was also found that the emissive spectrum of the solution was characteristic of the primary solute and not that of the solvent even with solute concentrations as low as 10^{-4} parts. Another characteristic feature of liquid scintillators is the relative ease with which the emissive spectrum of the solution can be matched to the responsive spectrum of the commercially available photo multipliers. This is achieved by the addition of compounds known as spectrum shifters. Thus, in the case of a solid, anthracene containing naphthacene as an impurity, will show an emissive spectrum displaced to the green of the naphthacene. The optimum concentrations lie in the region 0.01 - 0.1 gms. / liter of solution. The displacement of the spectrum will occur only if the fluorescent spectrum of the "contaminant" is located at longer wave lengths than that of the bulk material. A typical spectrum shifter is 2-5-diphenyloxazole (PPO). This substance can play a dual role since it acts equally well as either a spectrum shifter or a primary solute. As with the primary solute, there is also an optimum concentration of spectrum shifter.

It is known that there are certain atoms or groups of atoms which act as quenching agents. The presence of Cl_2, COOH and NO_2 groups in a substance will suppress the fluorescence of a solution[14]. These atoms or atomic groups are competing with the radiative process and are able to de-activate a number of fluorescent molecules and convert the energy to heat. Another good quenching agent is O_2 gas. A typical scintillator solution will have its luminescence efficiency decreased by almost 50 percent when a fine stream of O_2 gas is bubbled through the solution. Bowen and Norton[15] found that bubbling a fine stream of N_2 gas through a solution would have a marked effect on the fluorescent emission. Thus a solution which was prepared under atmospheric

conditions would yield a pulse height of 50 percent of anthracene. This value would increase to 70 percent when the solution was bubbled with N_2 for a period of 15 minutes. The quenching of fluorescence is of great importance not only from the point of obtaining high efficiency solutions, but also from the point of elucidating the mechanisms by which the process of quenching occurs. A solution, whose pulse height has been decreased by O_2 bubbling, can be returned to its former state by bubbling with N_2 a second time. The quenching of fluorescence is not confined solely to the above mentioned substances. Traces of impurities in the solvent or in the apparatus would be sufficient to cause a noticeable quenching effect. Thus it is imperative that chemicals of the highest purity be used in the preparation of liquid scintillator solutions and that the apparatus used in the investigations be scrupulously clean.

Analogy With Fluorescence

Fluorescence of solutions has been known for a long time. One of the earliest references made was by Boyle who gave detailed instructions on how to prepare aqueous solutions. Stokes was able to show that the phenomenon depended upon absorption and re-emission at a different wave length. Fluorescence, like the light produced from a liquid scintillator, is one of the effects of interaction between light or energetic particles with matter. The emission of energy in both cases may be explained by the use of potential energy diagrams. Liquid scintillator solutions do show strong fluorescence when exposed to U. V. radiation whereas substances which exhibit fluorescent properties are not, in most cases, capable of acting as scintillators when dissolved in solution. Most authors agree that although there are a number of differences between the fluorescence and scintillation processes, there are nonetheless certain similarities as well. The fluorescence process and

the scintillation process can be distinguished by the fact that the latter's emissive process is caused by a single event in the solution or crystal. Another point of importance is that the decay time of the scintillation process is of the order of 10^{-9} seconds. Because of this and the weak intensity of the emitted light, a photo multiplier is needed as a detector. The study of either process will give valuable information to the other as well.

Scintillation Mechanisms

The mechanism involved in the scintillation process is given very fully by Kallmann and Furst[12-13] in their two excellent papers on liquid scintillators. By means of fluorescent experiments, it is well known that a transport of energy through solids can occur over distances which are of the order of 100 atomic diameters. This can be done by the free electrons of the crystal or by migration of excitation energy from one molecule to another. This idea led the authors to hope that a similar process would occur in solutions. Here the energy would be transferred from the bulk material to the dissolved molecules. Because of the fact that the molecules of a liquid have such considerable freedom of motion, the fluorescence of a pure solvent would be small due to the fact that the collisions between molecules would cause a non-luminescent degradation of energy. Should the liquid contain foreign molecules which can trap the excitation energy, it may be that the excitation energy is transported to the dissolved molecules before it is quenched.

From their experiments, the authors found that the energy emitted by the fluorescent substances in a solution comes originally from the solvent. Along with the energy transported from solvent to solute, the process of quenching by solvent molecules must also be considered. When the solute is added, the transport of energy must be fast enough to avoid the process of quenching of the excitation energy by the solvent. Two additional conditions must now be

fulfilled at the solute molecule for large light emission to occur. These are: (1) the excitation energy of solute cannot be quenched too much by internal conversion or interaction with solvent molecules and (2) the concentration of the solute molecules must be low enough to avoid self quenching. The emission can be thought of as a competition between emission and quenching processes. Along with these we still have the quenching of energy by solvent, the transport of energy to the solute and the trapping of the energy by the solute molecules. The probability of transporting to and trapping the excitation energy by the fluorescent molecule is proportional to the concentration of the fluorescent molecule.

Thus, there are five separate mechanisms involved in the luminescence of solutions:

1. Trapping the excitation energy of the solvent at the fluorescent molecule;

2. Quenching of the excitation energy in the solvent;

3. Light emission of the fluorescent molecule;

4. Internal quenching at the fluorescent molecule;

5. Concentration quenching between similar molecules.

The authors consider the various probabilities of these processes. In terms of the characteristic lifetimes, we can write $1/\tau_{q(b)} \equiv$ reaction probability of quenching the excitation in the solvent, $1/\tau_t \equiv$ reaction probability of trapping the excitation energy at the fluorescent molecules, $1/\tau_e \equiv$ probability than an excited molecule emits light in unit time, $1/\tau_i \equiv$ probability for internal quenching and $1/\tau_s \equiv$ same for self quenching. Noting that τ_s and τ_t depend upon the concentration c so that $\tau_t/\tau_q \equiv k/c$ and $\tau_e/\tau_s \equiv k'c$ and $\tau_e/\tau_i \neq 1 = k''$, the emission intensity is found to be

given by:

$$I = \left[c/(k \neq c) \right] \left[1/(\acute{k}c \neq \acute{k}) \right] Ne \qquad 1$$

Where Ne is the number of excited molecules produced per second by the external radiation within the solvent. The radiation from the solvent itself is neglected in equation 1. The investigations of various substances showed the following general characteristics. A sharp rise in intensity at small concentrations, then a slower increase or almost constant intensity over a larger range of concentrations, and finally a slow decrease in intensity. Self-quenching is regarded as a resonance interaction between the excited molecule and an unexcited molecule of the same kind whereas internal quenching is regarded as leading to a rapid transformation of excitation energy into heat by interaction wiht the surroundings. If a small amount of contaminant is present which quenches internally, equation (1) is modified and for larger concentrations can be shown to decrease exponentially. In solvents such as benzene, toluene and xylene, the molecule consists of a basic benzene ring type structure. These are fluorescent to some extent, but they differ with regard to the dissolved solute in regard to the position of the absorption and emission spectrum. In the case of heptane and paraffin oil, there are no double bonds and no substantial fluorescence has been reported. Nevertheless, in solution a considerable amount of the excitation energy of the bulk material is transferred to the solute molecules. This proves that energy transport is not limited to benzene like substances, but depends on a much more general property of the solvents.

From their extensive work Kallmann and Furst were able to conclude that self quenching plays an important role in the reaction process. There were two mechanisms by which this could be explained. If an excited mole-

cule approaches an unexcited molecule of the same kind, the excitation ener-
gy will oscillate between the two molecules and the energy state of the two
will split into two states. The state with the higher energy has a greater
probability of light emission than one of lower energy. Thus the isolated
molecule will have a greater probability of light emission than the double
state. When an excited and unexcited molecule collide, both states are pre-
sent; but the higher energy goes to the lower state and the excess energy
is degraded as heat. In the lower state, the molecules may be close enough
to dissipate the energy by vibrations. In the second case, the two mole-
cules may form an excited double molecule with a certain binding energy and
this excited double molecule will live until the excitation energy is
quenched by interaction with the surroundings. During the lifetime of the
double molecule, no emission occurs. From this, the probability of trans-
forming the excitation energy into heat is increased.

From fluorescence studies, the transport of energy in crystals is well
known and analogous ideas are used here as well. Immediately after the
excitation, the molecules of the solvent, are raised to highly excited
electron levels and atomic vibrations. In a very short time, these ener-
gies are transformed into heat and the molecules return to their lowest
excitation level. The excitation energy - (purely electronic) is of the
order of several volts and cannot be transformed as easily into heat as
the energies of the higher states, since the difference between energy
levels in the higher states are smaller than from the lowest excited level
to the ground state. Thus a very short time after the excitation, most of
the excited molecules are to be found in the first excited states. Then
the migration of this energy occurs. The transport theory must satisfy two
conditions:

1. the mechanism must explain the weak emissive character-
   istics of the solvent but the lifetime of the excitation
   energy must be long enough to allow a large portion of
   the energy to be trapped by the solute molecules;

2. the process must result in a trapping of the excitation
   energy by the solute molecules;

There are three possible mechanisms for the transport of the energy
considered by Kallmann and Furst. These are:

1. The excitation energy jumps from one molecule to another
   by the mechanism of energy exchange. If the average ener-
   gy associated with this energy exchange is described by
   Vex, then the time, τ_d which the energy takes to jump from
   one molecule to another is given by: τ_d = h/Vex. If
   the mole concentration of the fluorescent molecule is
   given by Nf/Ns where Nf is the number of fluorescent mole-
   cules / unit volume and Ns the number of solvent molecules
   / unit volume, then the average time τ_c required for the
   excitation energy to hit the fluorescent molecule is given
   by:

$$\tau_c = \tau_d \; (Ns/Nf)$$

If we assume each collision affects the trapping of energy
then τ_c is identical with τ_d . If not every collision is
effective, $1/\tau_c$ is multiplied by a factor $\alpha, (\alpha < 1)$ which
gives the probability that the excitation energy is trapped
at such a collision and we get for τ_f the reaction proba-
bility of energy transport

$$\tau_f = \tau_d \; Ns / \alpha \, c$$

where c is written for Nf and $\overrightarrow{Id}$ is a constant inherent
in the solvent. In this picture the energy transfer may
be described as a diffusion process through the bulk
material. In this treatment, the details of energy trans-
fer through solvent are omitted and may be considered as
a first approximation.

2. Between the purely electronic excited levels in the sol-
vent molecules and the excitation levels of the dissolved
solute molecules there exists a sort of a resonance when
the spectrum emitted from the solvent molecule can be ab-
sorbed by the dissolved molecule. Energy exchange between
these molecules can occur over fairly large distances and
resonance can exist between these two molecules with a
definite probability. But this energy exchange takes place
in such a way that the dissolved molecule, since its energy
level is lower than that of the solvent molecule is excited
with some nuclear as well as electronic vibrations. These
nuclear vibrations are at once transferred to other vibra-
tions and molecules and thus only the pure electronic ex-
cited states of the dissolved molecules remain. A similar
process has been calculated by Foerster[16] for the interaction
of certain dye molecules. The calculations involve the
assumption of dipole interaction between the excited solvent
molecule and the unexcited fluorescent molecule.

3. In this case one assumes that the excited solvent molecule
interacts with its neighboring molecules and thus forms
two energy states in which the lower one does not radiate

energy. If these excited solvent molecules are not strong-
ly quenched by solvent molecules, they may have a long
enough lifetime to undergo a collision with a solute mole-
cule in a way similar to the first process. The excitation
energy is again trapped in the fluorescent molecule.

With the work done up to the present, it is impossible to decide which
of the three processes is the correct one. Some substances which have a
high output would tend to favor the third process.

The remaining mechanism is the trapping mechanism. The excited mole-
cule of the solvent has an excitation level (exclusive of excitation of
atomic vibrations) which has a higher energy than the pure electronic level
of the fluorescent molecules. When such an excited solvent molecule inter-
acts with a fluorescent molecule, it will transfer its energy to the fluor-
escent molecule and give it a state in which the atomic vibrations are
excited as well. These will be transferred almost immediately to other
molecules and to other atomic vibrations and will be decoupled from the
electronic excitation in the fluorescent molecule. The remaining energy is
purely electronic. This energy is not enough to re-excite the solvent mole-
cule and so the energy is trapped. This trapping mechanism is a most essen-
tial part of the energy transport from the solvent to fluorescent contaminant.
It explains the experimental fact that addition of a small amount of a cer-
tain substance not only shifts the spectrum of the fluorescent light almost
totally to the spectrum of the added molecules but also increases the light
output in some cases. This latter effect occurs because the excitation
energy is trapped in the added molecules and restrained from being quenched
by the bulk material. The trapping of the excitation energy in the fluor-

escent molecules prevents the energy from being quenched in the solvent and increases the probability that the excitation energy is emitted as light by the fluorescent molecule.

There are a number of different theoretical interpretations which have been put forth by different authors. One of the best known is that of Johnson and Williams[17] which gives the luminescent efficiency as a function of activator concentration. This theory was first applied to activated crystals, but has now been generalized to liquids as well. Application to liquids involves consideration of internal radiationless processes, radiationless interaction with nearly unexcited activators and emission, the three ways in which the activators lose their energy. Further work has been done by Reynolds[18] who has laid stress on the low intensity of the observed radiation and the fact that the observed scintillation times are too short to permit the energy to be carried about by a particular solvent molecule or dimer. The work of Reynolds and his group at Princeton shows general agreement with that of Kallmann and Furst.

The applications of liquid scintillators are quite numerous and are increasing very rapidly. One important application is in the field of carbon dating. In some cases the C^{14} atom may be incorporated into the solvent of the solution. In other cases, compounds containing C^{14} such as methanol or methylborate may be dissolved in the solution without any serious quenching.[19] Knowing the half life of the C^{14} isotope, the number of counts from the unknown sample is compared with the number from a sample whose age is known. In this way, the age of the unknown sample can be found. The technique of carbon dating employing liquid scintillators has reached a high degree of perfection and depends only upon the compounds available incorporating the C^{14} atoms.

Up to now we have only considered internal quenching of luminescence. Internal quenching occurs when the activated solvent and solute molecules interact amongst themselves to cause a non-emissive energy degration. Another case of quenching is known where the activated solvent and solute molecules interact with foreign molecules to cause a decrease in the luminescence output of a solution. A good example is the decrease of the pulse height of a liquid scintillator solution by the dissolved O_2 of the air. Although some ideas concerning internal quenching have been made, this investigation will be solely concerned with the elucidation of the process of external quenching of liquid scintillators.

The presence of dissolved oxygen has been shown to decrease the luminescence of liquid scintillator solutions[3-20] and to cause the fluorescence quenching of solutions[1-2] under U. V. excitation. The majority of the work done on the quenching of fluorescence is by Bowen[9,1,2,21,22]. The study of the kinetics of the quenching process would be of considerable theoretical interest[2] since the quenching process can be considered as a typical fast reaction in which most collisions are effective. A fairly detailed study of the kinetics of oxygen quenching would be quite important to test the validity of the proposed mechanism. Although liquid scintillators show oxygen quenching, there was no experimental data which showed that the solutions would obey the Stern - Volmer[23] equation or would exhibit the rapid collisional mechanisms proposed by Bowen[24] to account for the decrease in luminescent output. It was the object of this work to do a quantitative study of the quenching by O_2 and to try and elucidate the mechanism by which the process occurs. The effect of other gases on the luminescent output was to be checked as well.

A number of mechanisms for the quenching process have been developed.

The earliest one is that of Stern and Volmer[23]. Bowen[24] has given a number
of mechanisms which he uses in explaining the various cases of quenching
which are observed. These mechanisms will be discussed in further detail in
the discussion of results. In order to show the validity of the mechanisms,
calculations can be made of the number of collisions necessary to cause
quenching. There are two methods that one can use. These are the simple
kinetic theory and the more complex encounter theory. In connection with
the encounter theory, one can show the dependency of the quenching constant
on the viscosity of the solution. The results of measurements in which the
solution viscosity was changed will also be discussed.

The quantitative measurement of quenching by O_2 in liquid scintillators
and the evaluation of certain results from these data was the chief concern
of this investigation.

Object of the Investigation

The extensive work carried out by Bowen on both fluorescent solutions and vapors have shown that gases like O_2 and SO_2 and atomic groupings like COOH and NO_2 exhibit quenching effects. By quenching, it is meant that the fluorescent intensity is decreased in proportion to the quencher concentration. The relative pulse height of liquid scintillator solutions is decreased by the quenching effect of O_2 gas as well. Although both static and collisional mechanisms were proposed for fluorescent quenching, no attempt was made to show whether these same mechanisms were applicable to liquid scintillators.

The present investigation was primarily concerned in showing the quantitative behavior of typical scintillator solutions containing known amounts of O_2 gas. With this knowledge two things could be done. One could establish whether the mechanism involved was static or collisional and if collisional, calculate the number of effective collisions using the kinetic theory as a simple approximation. The effect of viscosity on both the relative pulse height and quenching was also determined to find if the effect was the same as predicted by the encounter theory.

Experimental

The liquid scintillator solution was placed in a flat bottomed, cylind-rical cell A, (Figure 1) of 25 mm.o.d., 100 mm. in length provided with a stopcock. The solution was then degassed by alternate freezing and thawing on the vacuum line. The solution was evacuated under a pressure of 1.0×10^{-3} cm; this pressure being measured by means of the McLeod Gage in-corporated in the system. A minimum of four freezing and thawing cycles were found to be sufficient for the removal of dissolved gases. In some early cases, up to 10 freezing and thawing cycles were used, but it was found that after four complete cycles, there was no change in the resultant pulse height of the solution. The evacuated solution was then allowed to return to room temperature and increments of oxygen were introduced by a low pressure gas burette system B. Dow Corning Silicone vacuum grease was used throughout the system and had no quenching effect on the solution as was verified by measuring the pulse height of a typical solution containing a small amount of silicone grease.

A typical run would proceed as follows. The solution in cell A was de-gassed by four vacuum freezing and thawing cycles. Keeping stopcock 1 closed, the solution was brought to room temperature. Oxygen was admitted to the system by means of stopcock 4 and the pressure was read directly from the manometer. During the admission of gas, stopcock 1 was opened to fill the space above the solution. With stopcocks 4 and 5 closed, the mercury level in the tube was read on the scale. The solution was shaken vigorously to allow absorption to take place, the mercury was levelled and the differ-ence in the two readings was converted to the volume of oxygen absorbed by the solution under the given temperature and pressure. Table I shows the results for two typical solutions.

During the freezing and thawing cycles, it was found that the solutes came out of solution. However, by shaking the solution vigorously at room temperature, solution would soon be complete. Another point of importance was that the evacuated solution would not absorb any gas unless it were shaken vigorously. Fifteen minutes were usually allowed for complete saturation with gas at that particular pressure. Initially, absorption would be quite large, but as equilibrium approached, the absorption would decrease and after fifteen minutes, further shaking of the solution showed no further absorption.

The pulse height of the resultant solution was then determined relative to an anthracene crystal of approximately the same weight. The anthracene was arbitrarily assigned the value of 100 and the solutions were expressed as percent of anthracene. There were a number of methods that could be used to determine the relative efficiency of a solution. One method used was a comparison of the total number of counts for a given time for the solution and the anthracene crystal at zero bias on the discriminator. Another method was comparing the solution and the crystal at the discriminator setting corresponding to the end point. Another possibility was to choose some arbitrary value of the counting rate like 40c/15 sec. and compare the solution and crystal on both an integral and differential basis. However, since a differential and integral count at the end point are too time consuming, the 40c/15 sec. (integral) was chosen not only because of the ease and rapidity with which the measurements could be made but also because comparison of a standard solution by the four methods above yielded values of the relative efficiency which had a maximum deviation of only 2 percent from the mean value. One minute counts were used in order to average out the statistical variation. In each case, 25 ml. of solution were used and the geometry of the solutions was as far as possible identical in each case. The comparison of the solutions to the anthracene crystal by means of the 40c/15 sec. (integral) method was thought to be

justified since the four methods showed good agreement as mentioned earlier
and since the investigation was concerned with relative values of the solu-
tion efficiencies only and not absolute values. A typical pulse height de-
termination curve for a solution is shown below.
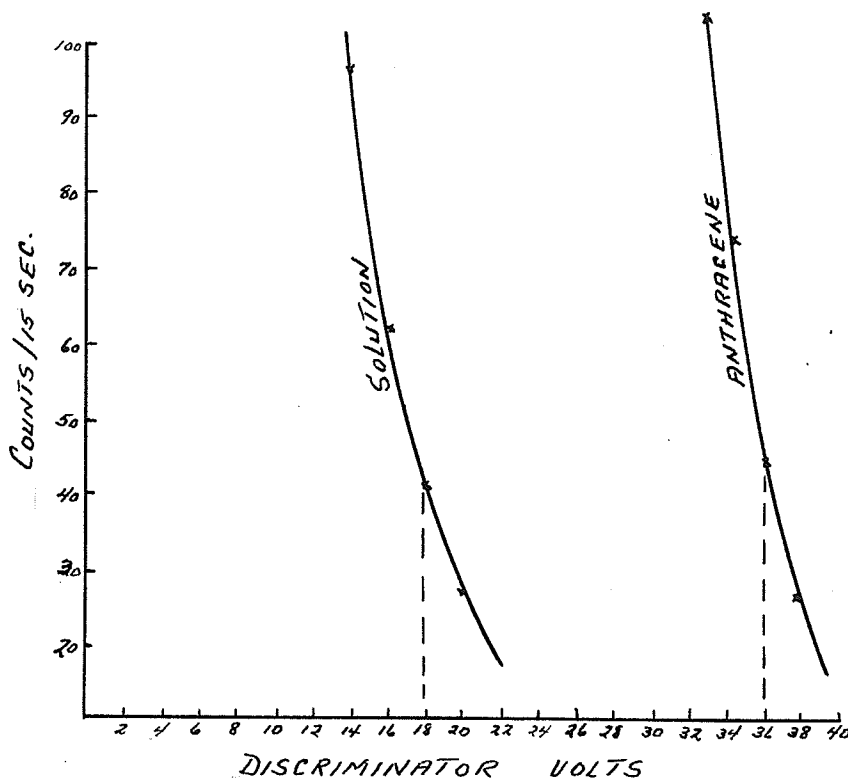
The pulse height of the solution was determined by mounting the cell on
an E.M.I. No. 1361 VX5055 photo tube operated at 1000 volts. The solution
was excited by the gamma radiation from a Cs^{137} source. The pulses were fed
to an Atomic Instrument No. 204-C amplifier, then to a Dynatron N/101 pulse
analyser and finally to an Atomic Instrument 162-A glow transfer counter
(Figure 2). Finely powdered, dry MgO was used as a reflector for the cell.
The cell was mounted in a glass jacket and the MgO was then packed around it
until the cell was completely covered, except for the stem. The geometry of
the liquid scintillator cells did not provide a very effective means of light
collection, and as a result, the pulse heights obtained were about 10 percent
lower than those obtained with wider and shorter cells of the same volume.
Nonetheless, the same geometry was used throughout the work and it is quite

probable that the relative pulse heights are comparable and the advantages of the long cells in the vacuum procedure compensated for their poorer light collection properties. In order to assure a good optical contact between the face of the photo tube and the cell, Dow Corning Silicone Fluid was used in all measurements of pulse heights.

There are a number of factors which would contribute to the error in the measurements. The stability of the electronic apparatus was checked during the course of each experiment by means of the discriminator setting for which 40c/15 sec. occurred for the anthracene. The maximum variation for a 10 hour period was found to be .5 volt giving rise to an error of 1.0 percent. The error due to statistical variation of the counting rate would have a maximum value of 2.0 percent at the point of comparison (40c/15 sec.). A further

2.0 percent error would arise in reading the level of the mercury in the manometer and levelling tube. This gives a total of 5.0 percent error for each point. Checking a number of points on the graphs shows that the maximum error found is 5.4 percent. There are some indeterminate factors such as the packing of the reflector which would add some further error. However, the distribution of the points about the curves is well within experimental error.

Chemicals

Scintillation grade chemicals obtained from the Arapahoe Chemicals, Inc. Boulder, Colorado, were used without further purification. These were: p - diphenyl benzene $C_{18}H_{14}$, (p - terphenyl), phenylbiphenylyloxadiazole - 1, 3, 4, $C_{20}H_{14}ON_2$ (PBD), 2,5 diphenyloxazole $C_{15}H_{11}ON$ (PPO), p-bis (2, 5- phenyloxazolylbenzene $C_{24}H_{16}O_2N_2$ (POPOP) and 2 - (1-naphthyl) -5-phenyl- oxazole $C_{19}H_{13}ON$ (NPO). Baker Analysed reagent grade xylene, p-xylene and toluene were employed.
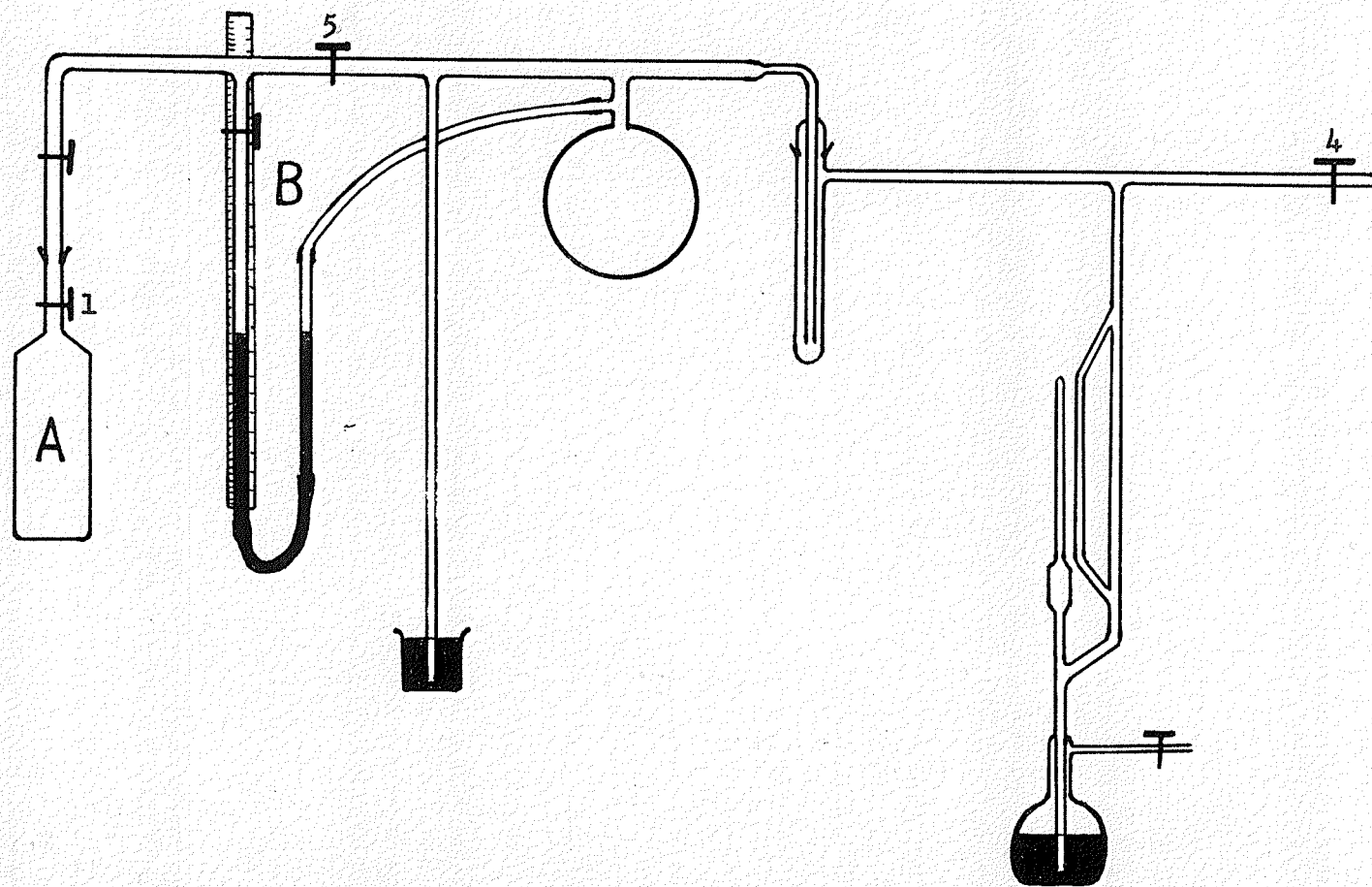
Figure 1. Apparatus for Degassing and Addition of Oxygen
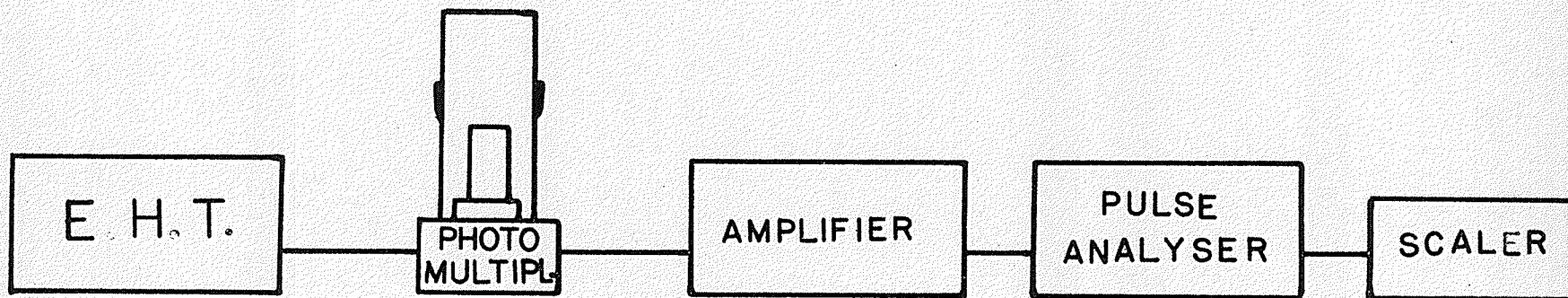
Figure 2. BLOCK DIAGRAM OF ELECTRONIC APPARATUS.

TABLE I

xylene: 4 gm./l. terphenyl
         .1 gm./l. POPOP

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_o/F - 1$
0	53.0	0
3.2	50.8	.04
7.6	47.5	.12
20.2	38.4	.37
28.0	35.0	.51
36.6	30.0	.76
49.2	25.4	1.08
59.2	23.8	1.22

p-xylene: 4 gm./l. terphenyl

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_o/F - 1$
0	36.8	0
4.20	33.1	.11
9.10	31.6	.16
20.9	26.3	.40
35.6	21.0	.76
39.7	20.4	.80
47.6	19.3	.91
54.8	17.9	1.06
69.6	15.0	1.46

Discussion and Results

There are two types of bimolecular processes which quench fluorescence and these have been divided into two groups - collisional and static quench-ing. In the former case, quenching begins after the molecule absorbs energy quanta whereas in the latter, the process begins previous to the absorption of energy. In the very simple case where quenching depends on collisions, we can write the following scheme:

$$S + h\nu \longrightarrow S^* \qquad K_A$$

$$S^* \longrightarrow S \qquad K_D$$

$$S^* + M \longrightarrow S + M^* \qquad K_T$$

$$M^* \longrightarrow M + h\nu' \qquad K_F$$

$$M^* + Q \longrightarrow M + Q \qquad K_Q$$
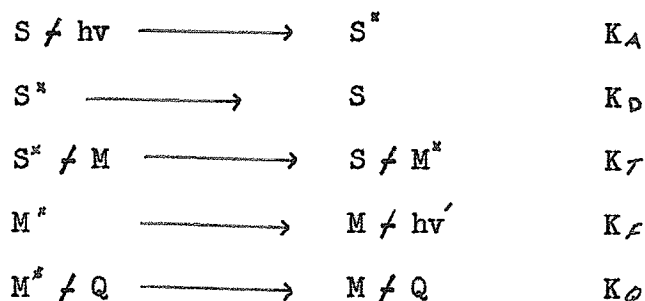
Using the steady state treatment, we can write the following scheme:
For no quenching we have:

$$F_o = K_F(M^*)$$

$$\frac{d(M^*)}{dt} = 0 = K_T(S^*)(M) - K_F(M^*)$$

$$(M^*) = \frac{K_T}{K_F}(S^*)(M)$$

$$F_o = K_T(M)(S^*)$$

For quenching we have:

$$F = K_F(M^*)$$

$$\frac{d(M^*)}{dt} = 0 = K_T(S^*)(M) - K_F(M^*) - K_Q(M^*)Q$$

$$(M^*) = \frac{K_T(M)(S^*)}{K_F + K_Q(Q)}$$

$$F = \frac{K_F \, K_T \, (S^*)(M)}{K_F + K_Q(Q)}$$

$$Fo = K_T(S^*)(M)$$

Thus:

$$\frac{Fo}{F} = K_T(S^*)(M) \; \frac{K_F + K_Q(Q)}{K_F \; K_T(S^*)(M)}$$

$$\frac{Fo}{F} = \frac{K_F + K_Q(Q)}{K_F}$$

$$\frac{Fo}{F} = 1 + K(Q)$$

And finally:

$$\frac{Fo}{F} - 1 = KQ \quad (1) \quad \text{where} \quad K = \frac{K_Q}{K_F}$$

S represents the solvent molecule, M the solute molecule, Q the quencher molecule, K the quenching constant, Fo the luminescent output in the absence of quencher and F, the luminescent output in the presence of quencher. In this mechanism, the transfer steps from solvent to solute have been added according to the present theories[12,13,25,26,27,28]. However, these additional steps do not change the final form of equation (1) from that obtained by the original Stern-Volmer mechanism[23]. Equation (1) is in the form of a straight line and thus a plot of the relative luminescent efficiency $\frac{(Fo-F)}{F}$ vs the concentration (Q) of quencher should yield a straight line whose slope will be equal to K; the quenching constant. It should be noted that K_F is the reciprocal of the mean life of the fluorescent molecule and its value may be found by fast circuit technique. Consequently, knowing the values of K and K_F, one can easily evaluate the constant KQ. The value of K_F for liquid scintillators is around 5×10^8 sec.$^{-1}$ [29] and since the measured values of K are of the order of magnitude 10 - 200; K_Q has values up to 10^{10} and larger.

This is a quantity which is very much larger than bimolecular velocity constants measured for ordinary thermal reactions. Experiments on quenching in the gaseous state of anthracene by oxygen or sulphur dioxide[1] gives quenching constants of magnitude 1000-2000. This is just what kinetic theory predicts for quenching on nearly every collision. Thus, it appears that the quenching processes can be very efficient under certain conditions. As a good approximation, the collision frequency between dissolved molecules in solution may be taken to be nearly the same as that for the molecules occupying the same volume in the gaseous state. Thus, with this assumption in mind, one may use the simple kinetic theory to calculate the number of collisions between solute and quencher molecules to a good degree of approximation. Such calculations have been made[24] and the results show that at fairly low quencher concentrations, the collisional process is very effective. Indeed, the results of this investigation show this to be the case for the solutions studied.

In the reaction scheme postulated for this work, the energy transfer step from solvent to solute was taken into account, but no mention was made of solvent quenching. Thus, we could have the following kinetic scheme as well:

$$S + h\nu \longrightarrow S^x \qquad\qquad K_A$$

$$S^x + Q_1 \longrightarrow S + Q_1 \qquad\qquad K_{Q_1}$$

$$S^x + M \longrightarrow S + M^x \qquad\qquad K_T$$

$$M^x \longrightarrow M + h\nu' \qquad\qquad K_F$$

$$M^x + Q \longrightarrow M + Q \qquad\qquad K_Q$$
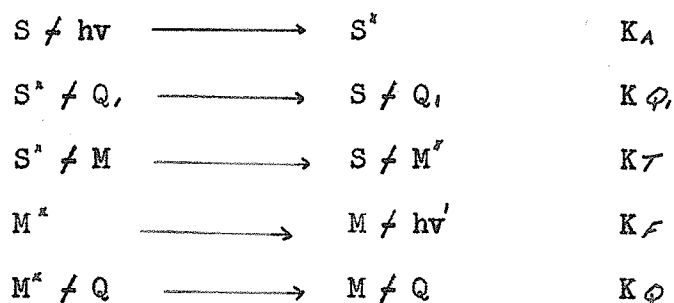
In this scheme a distinction is made between the two quenching processes by designating the quencher molecules as Q^1 and Q. Indeed it is very probable, that the same quencher will act on both the solvent and fluorescence molecules.

This is so especially when the system under study is subject to only one quencher - in this case oxygen gas. The distinction Q and Q^1 is made merely to allow ease in manipulation of the equations. One could perhaps, consider the step $S^* \neq M \longrightarrow S \neq M^x$ as a quenching of the solvent fluorescence. However, most authors agree that this is a true transfer step rather than a quenching step. Furthermore, the fluorescence emission of most solvents is very low in the absence of a primary solute, so that we can consider this step as a true energy transfer step rather than a solvent quenching step.

Using the steady state treatment as before, we again get the result that:

$$\frac{Fo - F}{F} = K \ (Q) \qquad \qquad (2)$$

The symbols have the same meaning as before. The mechanism which has been postulated for the quenching of luminescence seems to be dependent only upon the quenching of the excited solute molecule and independent of quenching of solvent. This does not mean to say that solvent quenching is not present. However, the final result of the kinetic scheme contains no expression involving solvent quenching. Nonetheless, it is quite possible that solvent quenching occurs to some degree and that its effect would add to that of the solute quenching and cause a further drop in the luminescent output which would be attributed to solute quenching only on the basis of this kinetic scheme.

Another important fact that has not been taken into account in our kinetic scheme is concentration or self quenching. It is well known that there are certain optimum concentrations of primary solute and spectrum shifter which will give the maximum pulse height for that particular system. Beyond this optimum concentration, a decrease in the pulse height of the solution is observed. Presumably, the mechanism of concentration quenching is

some non-radiative process such as degradation of the luminescence energy into heat. In this investigation, concentration quenching has been omitted; but as the results show, there is some variation of KQ with concentration of primary solute. This variation can, in all probability, be attributed to the effects of concentration quenching.

A number of examples of fluorescence quenching show features that cannot be explained by a collisional mechanism. Some of these are an increase in fluorescence intensity with an increase in temperature and the failure of some systems to obey the Stern-Volmer equation[1,30,31]. These can be explained satisfactorily by using the following kinetic scheme:

$$M + hv \longrightarrow M^{x} \qquad K_{1}$$

$$MQ + hv \longrightarrow degradation \qquad K_{2}$$

$$M + Q \longrightarrow MQ \qquad K_{3}$$

$$M^{x} \longrightarrow M + hv' \qquad K_{4}$$
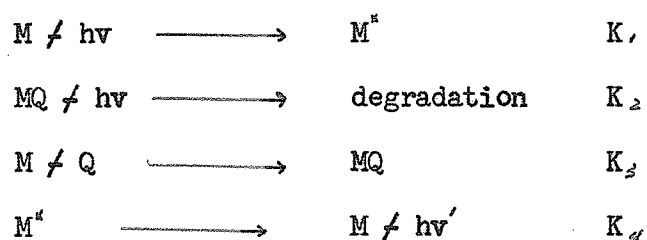
In this kinetic scheme, the fluorescent molecule M is thought to interact with the quencher molecule Q to form a sort of a loose "compound" possessing an equilibrium or mass action constant K_3. If the force between this compound is of a van der Waals nature, then we can assume that the compound will not interfere with the light absorption of the solution. The absorbed light will be shared by both M and MQ, but it should be noted that MQ will not fluoresce whereas M^{+} will. The energy absorbed by MQ will probably be degraded into heat. Thus, the quencher will reduce the fluorescence of the solution according to the relation:

$$Fo/F - 1 = K_3(Q) \qquad (3)$$

It should be noted that the quenching constant is actually the equilibrium

constant and not the ratio of two constants as in equation (1).

We have only considered two cases: collisional and static quenching. In the case of static quenching, we have also assumed that the "compound" does not fluoresce. Should the forces causing the complex be quite strong, there is a possibility that absorption will take place, and as a result, the absorption spectrum of the solution will change. If this is the case, then we do not have a case of true quenching since the solution contains two different types of molecular structures. Because inter molecular forces are capable of fairly wide variation, no sharp line can be set between true quenching and complex formation. The problem is resolved by noting whether there is a pronounced change in the absorption spectrum of the solution or merely a small shift. There is also the possibility of the dependence of the quenching constant on the quencher concentration in strong collisional quenching agents[32]. This can be explained by assuming that both collisional and static quenching process occur. No attempt will be made to derive the relation; but that used by Bowen[17] will be given

$$\frac{Fo}{F} - 1 = (k \neq K_3)Q \neq kK_3(Q)^2 \qquad (4)$$

The quenching constant is now $(k \neq K_3) \neq kK_3(Q)$ and depends linearly on the quencher concentration[1]. It is thought that in such cases, the complex "compound" formed cannot be a very specific interaction.

We have thus outlined the three main types of quenching processes which are possible for luminescent solutions. In this investigation it was found that the simple Stern-Volmer mechanism would suffice to explain the quenching of fluorescence by oxygen gas. It is possible that should a different quencher be employed, the simple mechanism might fail. In this investigation, the most important aspect of the problem is that of O_2 quenching. The effects of other

gases on liquid scintillators will be discussed later on.

In a liquid, we suppose that quenching occurs when an excited molecule and a quenching molecule occupy neighbouring sites. Although the collision frequency between dissolved molecules in a liquid is approximately the same for the molecules occupying the same volume in the gaseous state, neighbouring molecules in liquids make many more repeated collisions with one another before separating by diffusion. These collisions are referred to as encounters[33]. If the number of repeated collisions in an encounter is large compared with the number of collisions which must take place before quenching occurs, then the value of K will be determined by the encounter frequency rather than the collision frequency. The encounter frequency, the rate at which molecules find new partners by diffusion, can be found by an approximate method[24] based on the Smoluchowski[34] diffusion equation. The maximum quenching constant K is then given by the following relation:

$$K = 4 \quad DRN \times 10^{-3} \qquad (5)$$

where   is the mean life of the fluorescent molecule, D - is the diffusional constant of fluorescent and quencher molecules, R - is the sum of the radii of fluorescent and quencher molecules and N is the Avogadro number. If we take the average values of these constants for organic solutions at ordinary temperatures, the following result is found:

$$K = \frac{T}{200} \qquad (6)$$

T is the absolute temperature and   the viscosity of the solution. For liquids of average viscosity, the value of K will be less than 300. Very efficient collisional quenching processes in solution have the peculiar property that the quenching constant K depends upon the viscosity of the solution.

A good example is the quenching of fluorescence by oxygen of liquid scintillator solutions. The theory may be verified readily by making liquid scintillator solutions of varying viscosities, and investigating the effect of the viscosity on the quenching constant K. In this investigation it was found that the quenching constant was quite large for xylene solutions (230) but drops almost to half the value in xylene solutions to which have been added measured amounts of viscous paraffin oil.

Using the encounter[30] theory, it is possible not only to predict the maximum value of the quenching constant K, but it is also possible to predict in the ideal case, the maximum value of K . As before, if the number of collisions in each encounter is large compared to the number required for collisional quenching, the limiting rate is set by the diffusion and K is given by the expression:

$$K_\phi = 8\pi NDr/1000\eta \; l. \quad sec.^{-1} \quad mole^{-1} \qquad (7)$$

D = diffusion coefficient, r molecular radius of solute. If we assume that Stokes' law is valid for the diffusion process of the solute molecules, the expression in (7) reduced to:

$$K_\phi = 8RT/3000\eta \; l. \quad sec.^{-1} \quad mole^{-1} \qquad (8)$$

where T is the absolute temperature and η is the viscosity of the solution. These K values will represent the theoretical maximum rates of bimolecular reactions in ideal solutions. Bowen[2] has calculated values for benzene, chloroform and kerosene solutions and the values are all of the order of 10^{10} at ordinary temperature. The investigations of this experiment have yielded values of 10^{10} for xylene and toluene as well. The good agreement between theory and experiment in view of the assumptions made can be attributed to

the fact that the assumptions regarding the kinetics of the process have been essentially correct.

Table II gives the data for all the solutions investigated. The primed values are those calculated using the slope K of equation (1) for each solution. The variation of luminescent output as a function of O_2 concentration is shown in Figures 3, 4, 5, 6 and 7. These figures show the magnitude of the oxygen quenching effect on a number of commonly employed liquid scintillator solutions. It is important to note that the curves are the theoretical curves obtained from equation (1) whereas the points are actual experimental values. In the majority of cases, the variations of the points about the curve is within experimental error. This represents extremely good agreement with the simple Stern-Volmer collisional process for the quenching reaction. In equation (1) the values of F_O were determined for the evacuated solutions. N_2 bubbling of these solutions in the same type of cells yielded values which were within one percent or less of the F_O values for the evacuated solutions.

Figures 8, 9, 10, 11 and 12 show plots of the relative luminescence efficiency $\frac{(F_O - F)}{F}$ vs O_2 concentration for the solutions investigated. As predicted by equation (1) a linear relationship is obtained and the variation of the points about the line is within experimental error. The slopes of these lines were used to evaluate the quenching constants K shown in Table III and for the calculation of the theoretical curves for Figures 3, 4, 5, 6 and 7. Assuming a value of 2×10^{-9} seconds as the decay time for the solutions, it is possible to calculate K_q from the relation $K_q = K/\tau$ for the systems. The values for K_q are tabulated in Table III.

TABLE II

xylene: 4 gm./l. terphenyl
         .1 gm./l. POPOP

O_2 Concentration Moles/liter $\times 10^4$	Relative Pulse Height	$F_0/F - 1$	O_2 Concentration' Moles/liter $\times 10^4$	Relative Pulse Height'
0	53.0		0	53.0
3.20	50.8	.04	10	43.8
7.60	47.5	.12	20	37.3
20.2	38.4	.37	30	32.5
28.0	35.0	.51	40	28.8
36.6	30.0	.76	50	25.8
49.2	25.4	1.08	60	23.4
59.2	23.8	1.22	70	21.4

xylene: 4 gm./l. terphenyl
         .1 gm./l. NPO

O_2 Concentration Moles/liter $\times 10^4$	Relative Pulse Height	$F_0/F - 1$	O_2 Concentration' Moles/liter $\times 10^4$	Relative Pulse Height'
0	50.2		0	50.2
3.80	47.4	.06	10	40.7
7.10	41.8	.20	20	34.4
17.9	36.3	.37	30	29.7
28.4	30.0	.67	40	26.1
35.5	26.6	.89	50	23.3
48.6	22.5	1.23	60	21.0
64.0	19.7	1.56	70	19.2
72.4	18.3	1.74	80	17.6

p-xylene: 4 gm./l. terphenyl

O_2 Concentration Moles/liter $\times 10^4$	Relative Pulse Height	$F_0/F - 1$	O_2 Concentration' Moles/liter $\times 10^4$	Relative Pulse Height'
0	36.8	0	0	
4.20	33.1	.11	5	33.2
9.10	31.6	.16	10	30.4
20.9	26.3	.40	20	25.8
35.6	21.0	.76	30	22.4
39.7	20.4	.80	40	20.0
47.6	19.3	.91	50	18.3
54.8	17.9	1.06	60	16.2
69.6	15.0	1.46	70	14.8
			80	13.6
			90	12.6

xylene: 4 gm./l. terphenyl
        .1 gm./l. DPO

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_o/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	29.5	0	0	29.5
2.60	28.0	.05	10	24.6
9.20	24.6	.20	20	21.2
16.5	23.0	.28	30	18.6
27.6	20.0	.47	40	16.5
34.4	17.5	.69	50	14.9
40.1	16.3	.84	60	13.6
56.0	13.9	1.12	70	12.5
66.0	12.5	1.36		

xylene: 4 gm./l. DPO
        .1 gm./l. POPOP

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_o/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	53.5	0	0	53.5
2.50	52.0	.03	10	45.5
7.30	49.0	.10	20	39.5
18.6	41.0	.30	30	35.0
25.0	37.0	.45	40	31.2
33.6	33.0	.62	50	28.3
39.0	29.4	.82	60	25.8
52.8	27.2	.97	70	23.8
60.0	24.6	1.18		

p-xylene: 4 gm./l. terphenyl
          .1 gm./l. POPOP

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_o/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	51.0	0	0	
2.20	49.5	.03	5	46.5
7.30	46.5	.10	10	42.0
18.9	38.0	.35	20	36.0
27.6	32.4	.57	30	31.4
40.0	27.8	.82	40	27.8
48.4	25.0	1.04	50	25.5
65.2	21.6	1.36	60	22.6
74.8	20.0	1.56	70	20.6
			80	19.0

xylene: 4 gm./l. terphenyl
         .1 gm./l. PBD

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_0/F - 1$	O_2 Concentration' Moles/liter x10^4	Relative Pulse Height'
0	48.5	0	0	48.5
3.60	47.0	.03	10	42.0
7.40	45.3	.07	20	37.0
17.0	38.5	.26	30	33.0
22.0	35.0	.39	40	30.0
31.6	32.0	.51	50	27.3
40.4	30.0	.65	60	25.0
56.0	25.0	.94	70	23.2
65.6	23.2	1.09		

xylene: 4 gm./l. PBD

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_0/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	56.0	0	0	
3.74	53.4	.05	5	
9.15	49.3	.14	10	49.5
20.5	44.0	.26	20	44.5
29.8	40.5	.38	30	40.0
33.2	39.5	.42	40	36.5
43.5	36.5	.53	50	34.0
51.5	34.0	.65	60	31.4
55.5	31.8	.76		

xylene: 4 gm./l. DPO

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_0/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	48.5	0	0	48.5
2.71	46.2	.05	10	41.3
8.36	43.0	.14	20	36.1
19.0	39.2	.24	30	32.0
28.2	33.0	.47	40	28.7
39.1	30.0	.62	50	26.0
44.5	28.0	.72	60	23.8
47.0	27.5	.76		
54.0	25.3	.92		

xylene: 5 gm./l. terphenyl

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_0/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	35.4	0	0	35.4
1.10	34.9	.02	10	30.8
7.70	32.0	.10	20	27.2
17.5	29.0	.22	30	24.4
24.0	26.5	.34	40	22.0
35.2	23.2	.52	50	20.2
43.3	21.0	.69	60	18.6
56.2	19.8	.79	70	17.3
60.2	18.6	.90		

xylene; 6 gm./l. terphenyl

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_0/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	36.4	0	0	36.4
2.34	35.4	.03	10	31.0
5.35	32.4	.12	20	27.0
16.3	28.0	.30	30	23.8
27.4	25.0	.45	40	21.4
34.4	22.6	.61	50	19.4
43.0	20.6	.77	60	18.1
50.7	19.6	.86	70	16.3
59.2	18.0	1.02		

toluene: 5 gm./l. terphenyl
        .1 gm./l. DPO

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_0/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	46.0	0	0	46.0
7.62	42.0	.11	10	40.4
14.7	37.8	.22	20	35.8
24.5	33.8	.36	30	32.4
29.8	32.2	.43	40	29.4
42.7	28.2	.63	50	26.9
52.0	27.2	.70	60	24.8
59.0	25.0	.84	70	23.0

toluene: 5 gm./l. terphenyl

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_o/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	33.4	0	0	33.4
6.5	30.8	.09	10	29.3
9.0	29.4	.14	20	26.0
25.2	24.6	.36	30	23.4
36.6	21.8	.53	40	20.3
44.0	20.5	.63	50	19.5
52.7	19.6	.71	60	18.0
67.2	17.0	.96	70	16.7

toluene: 5 gm./l. terphenyl
            .1 gm./l. POPOP

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_o/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	31.0	0	0	31.0
7.75	27.0	.15	10	27.5
17.1	25.2	.23	20	24.6
26.4	22.6	.37	30	22.3
34.4	20.2	.54	40	20.4
43.6	19.0	.63	50	18.8
53.5	18.0	.73	60	17.5
65.5	17.0	.82	70	16.3

toluene: 8 gm./l. PBD

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_o/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	51.3	0	0	51.3
7.72	48.8	.05	10	48.0
17.5	46.0	.11	20	45.0
29.8	42.8	.20	30	42.4
35.2	41.5	.25	40	40.3
40.7	40.0	.28	50	38.2
50.5	38.4	.33	60	36.2
57.0	36.0	.42	70	34.6

toluene: 8 gm./l. PBD
      .1 gm./l. POPOP

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_O/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	51.5	0	0	51.5
7.55	49.0	.05	10	48.0
16.7	46.5	.11	20	45.2
27.7	42.2	.22	30	42.5
35.8	40.3	.27	40	40.2
42.6	39.6	.30	50	38.0
49.6	39.0	.32	60	36.2
55.0	37.6	.37		

toluene: 4 gm./l. PBD

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_O/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	54.3	0	0	54.3
8.75	48.8	.11	10	48.3
15.8	45.0	.28	20	43.3
27.6	40.5	.38	30	39.4
39.2	36.2	.50	40	36.0
49.2	34.2	.59	50	33.2
61.0	31.4	.73	60	30.8
67.0	30.0	.81	70	28.8

toluene: 4 gm./l. PBD
      .1 gm./l. POPOP

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_O/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	53.5	0	0	53.5
7.75	48.6	.10	10	47.5
17.5	44.0	.22	20	42.5
25.4	40.0	.34	30	38.6
41.0	35.4	.51	40	35.4
48.5	34.0	.58	50	32.6
56.0	31.2	.72	60	30.2
65.5	28.5	.88	70	28.2

xylene: 4 gm./l. terphenyl
    .1 gm./l. POPOP
     2.5% by weight Mineral Oil

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_o/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
	47.4	0	0	47.4
7.9	43.5	.09	10	42.2
16.7	39.0	.21	20	38.0
26.4	35.2	.34	30	34.5
33.0	34.0	.39	40	31.6
40.7	31.3	.52	50	29.2
50.0	28.8	.65	60	27.0

xylene: 4 gm./l. terphenyl
    .1 gm./l. POPOP
     5.0% by weight Mineral Oil

O_2 Concentration Moles/liter x 10^4	Relative Pulse Height	$F_o/F - 1$	O_2 Concentration' Moles/liter x 10^4	Relative Pulse Height'
0	44.5	0	0	44.5
.30	44.0	.01	10	40.5
14.1	39.0	.14	20	36.8
21.5	36.2	.23	30	33.8
30.8	34.0	.31	40	31.4
36.6	32.4	.38	50	29.2
47.6	29.4	.51	60	27.3
55.0	28.0	.59		
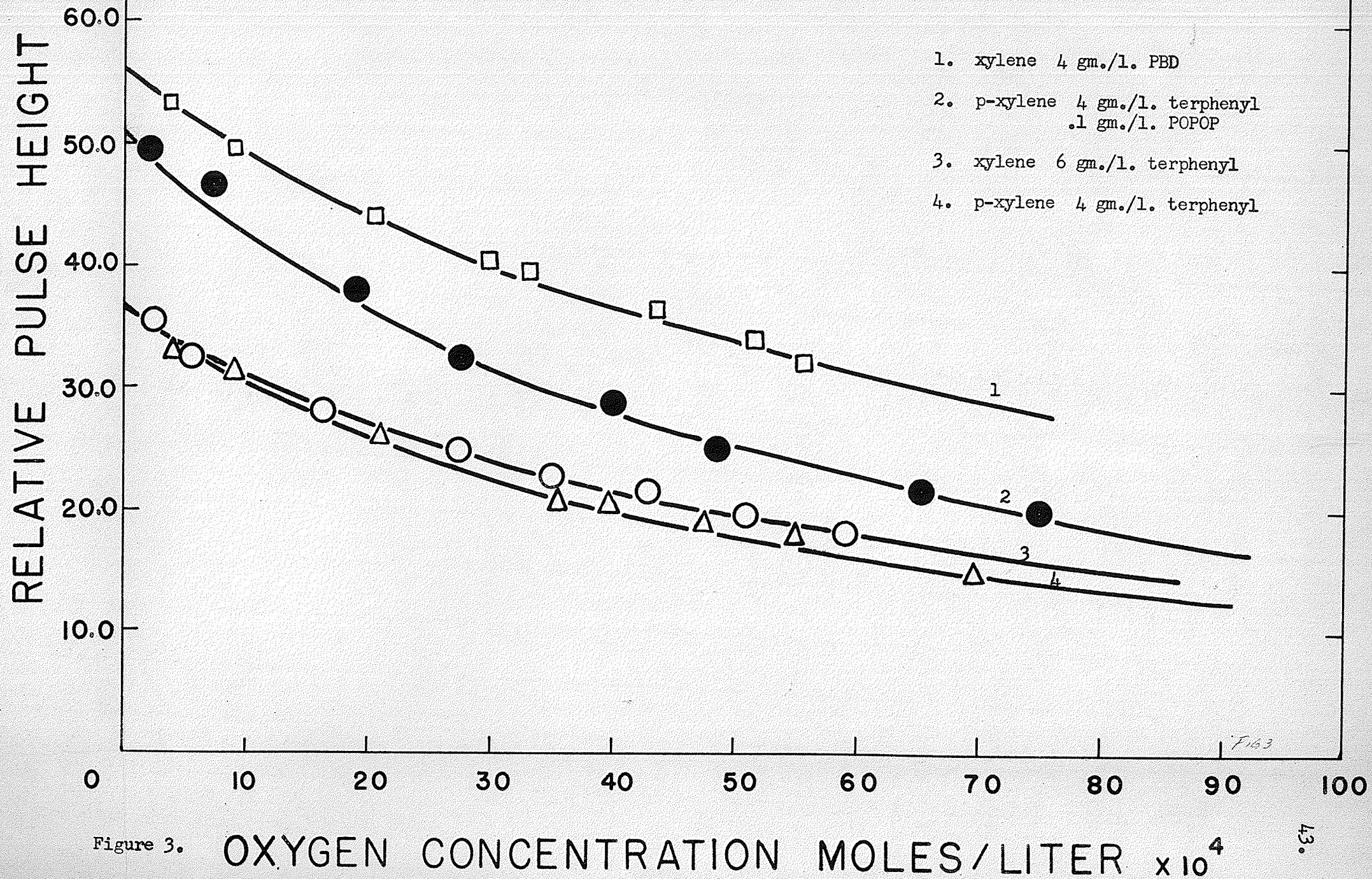
Figure 3. OXYGEN CONCENTRATION MOLES/LITER $\times 10^4$

1. xylene 4 gm./l. PBD
2. p-xylene 4 gm./l. terphenyl
       .1 gm./l. POPOP
3. xylene 6 gm./l. terphenyl
4. p-xylene 4 gm./l. terphenyl

43.

Figure 4. OXYGEN CONCENTRATION MOLES/LITER $\times 10^4$

1. toluene 8 gm./l. PBD
2. toluene 5 gm./l. terphenyl
3. toluene 4 gm./l. PBD
4. toluene 5 gm./l. terphenyl .1 gm./l. PPO
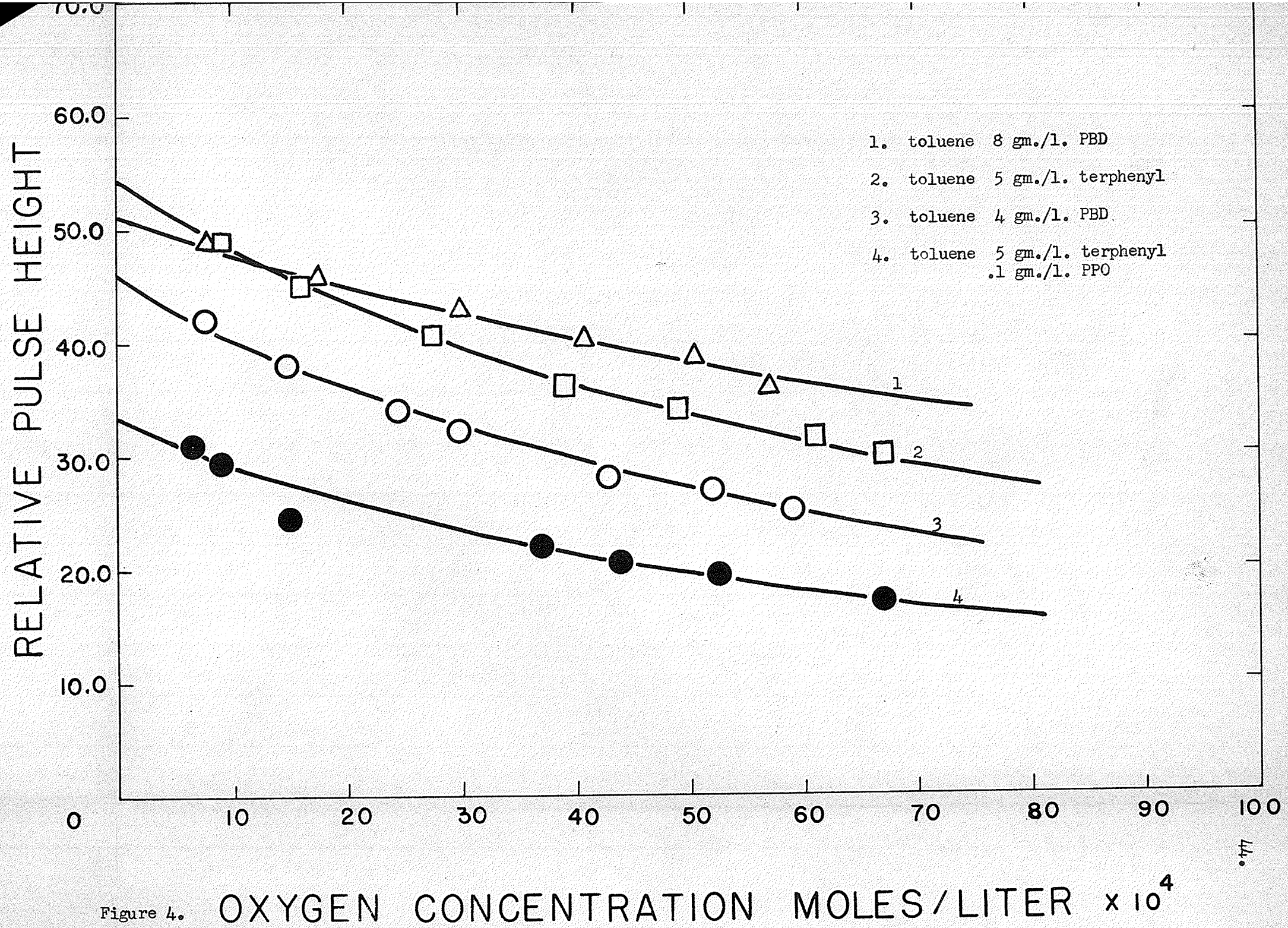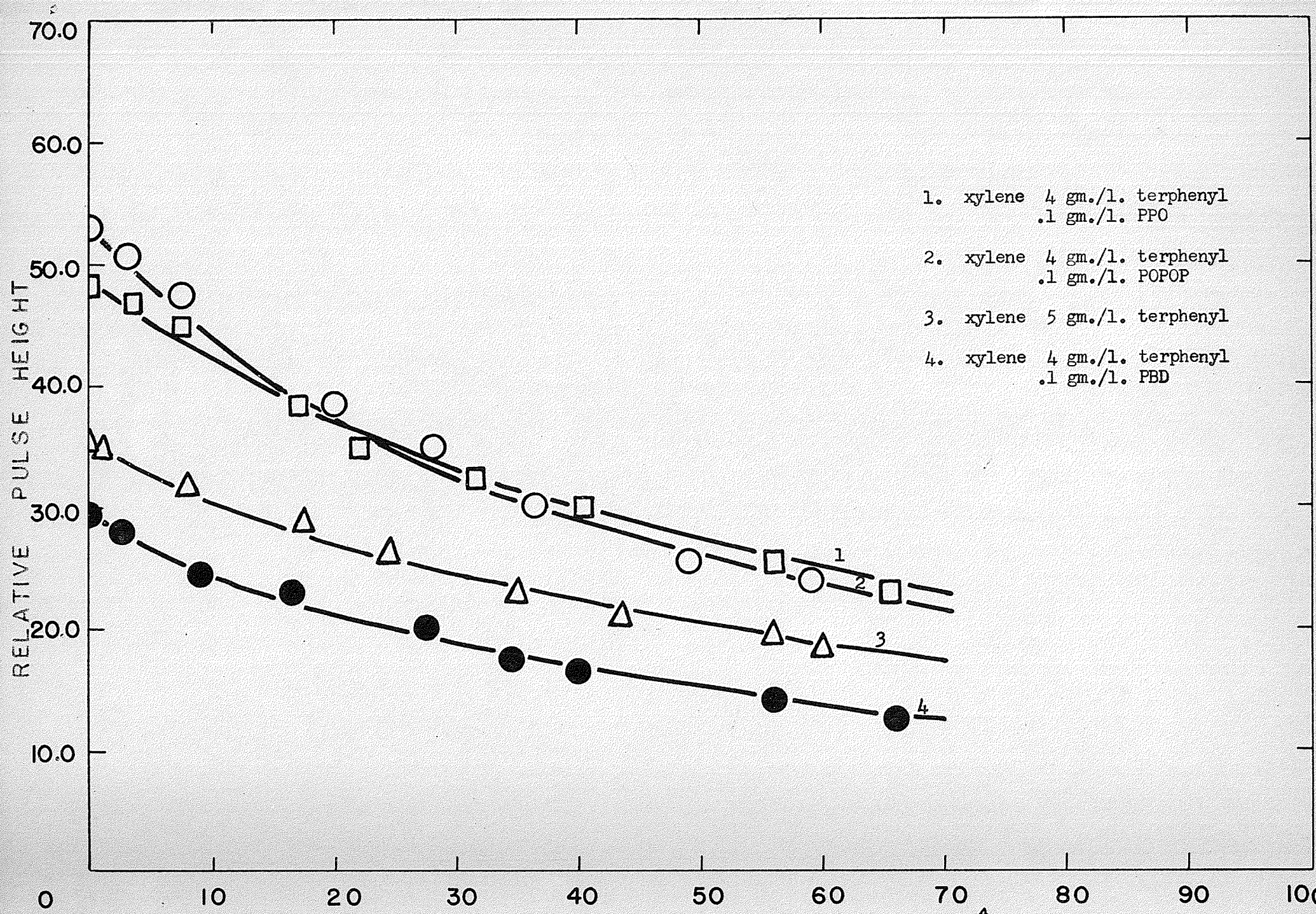
Figure 5.   OXYGEN CONCENTRATION MOLES / LITER X 10^4

Legend:

1. xylene 4 gm./l. terphenyl
           .1 gm./l. PPO

2. xylene 4 gm./l. terphenyl
           .1 gm./l. POPOP

3. xylene 5 gm./l. terphenyl

4. xylene 4 gm./l. terphenyl
           .1 gm./l. PBD

Figure 6.

Figure 7. OXYGEN CONCENTRATION MOLES/LITER X10

1. toluene   8 gm./l. PBD
              .1 gm./l. NPO

2. xylene   4 gm./l. terphenyl
              .1 gm./l. POPOP
   2.5% by weight Mineral Oil

3. xylene   4 gm./l. terphenyl
              .1 gm./l. POPOP
   5% by weight Mineral Oil

4. xylene   4 gm./l. terphenyl
              .1 gm./l. NPO

RELATIVE PULSE HEIGHT

Figure 8.   OXYGEN CONCENTRATION MOLES/LITER x 10^4

1. p-xylene   4 gm./l. terphenyl
                .1 gm./l. POPOP

2. xylene   6 gm./l. terphenyl

3. toluene   5 gm./l. terphenyl
                .1 gm./l. PPO

4. xylene   4 gm./l. PBD

Figure 9. OXYGEN CONCENTRATION MOLES/LITER × 10^4

$\dfrac{F_o}{F} - 1$

1. p-xylene 4 gm./l. terphenyl
2. toluene   5 gm./l. terphenyl
3. toluene   4 gm./l. PBD
4. toluene   8 gm./l. PBD
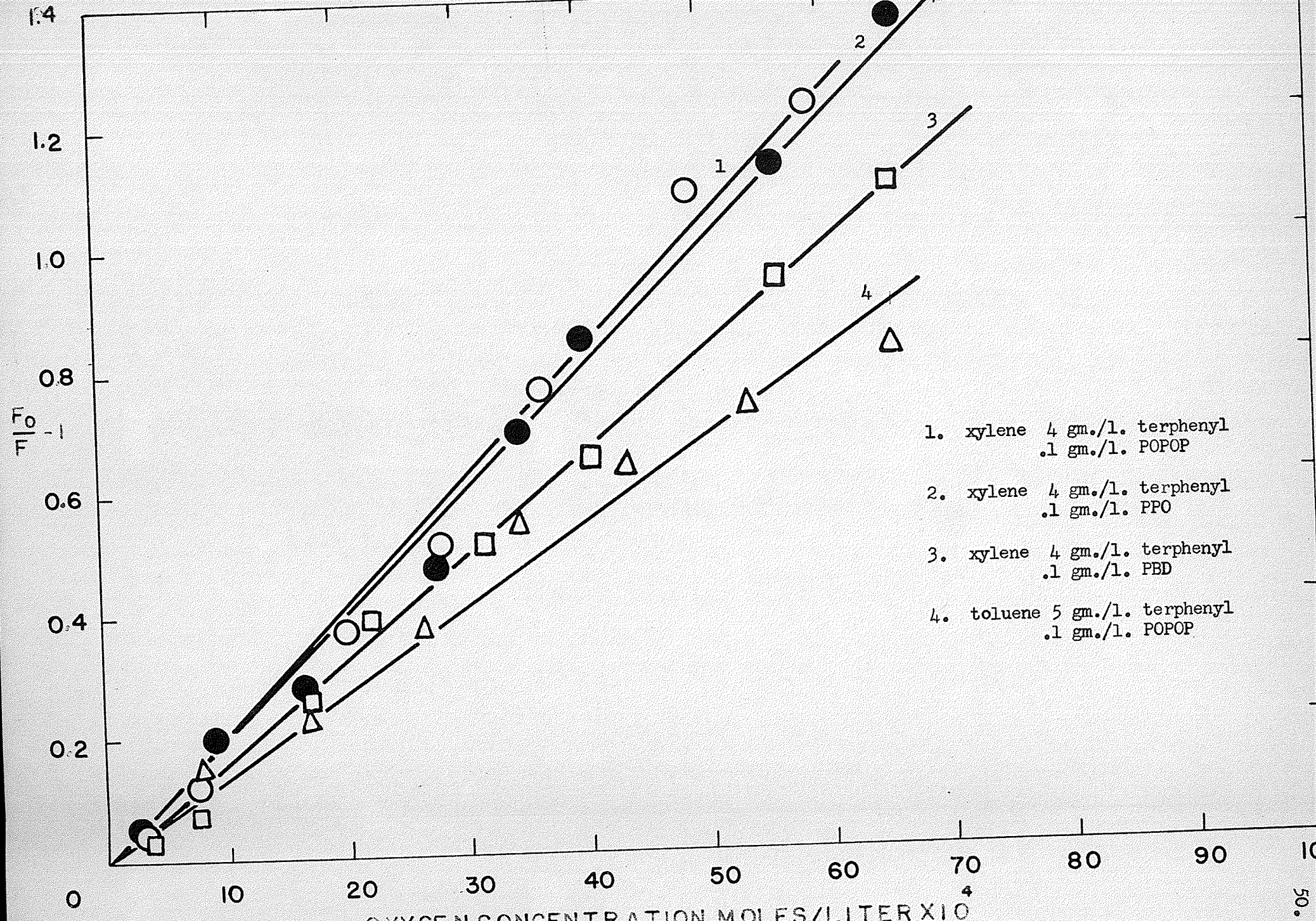
Figure 10.   OXYGEN CONCENTRATION MOLES/LITER X 10⁴

1. xylene 4 gm./l. terphenyl
   .1 gm./l. POPOP

2. xylene 4 gm./l. terphenyl
   .1 gm./l. PPO

3. xylene 4 gm./l. terphenyl
   .1 gm./l. PBD

4. toluene 5 gm./l. terphenyl
   .1 gm./l. POPOP

Figure 11. OXYGEN CONCENTRATION MOLES/LITER X10^4

1. xylene   4 gm./l. PPO

2. xylene   5 gm./l. terphenyl

3. xylene   4 gm./l. terphenyl
             .1 gm./l. POPOP
   2.5% by weight Mineral Oil

4. xylene   4 gm./l. terphenyl
             .1 gm./l. POPOP
   5% by weight Mineral Oil
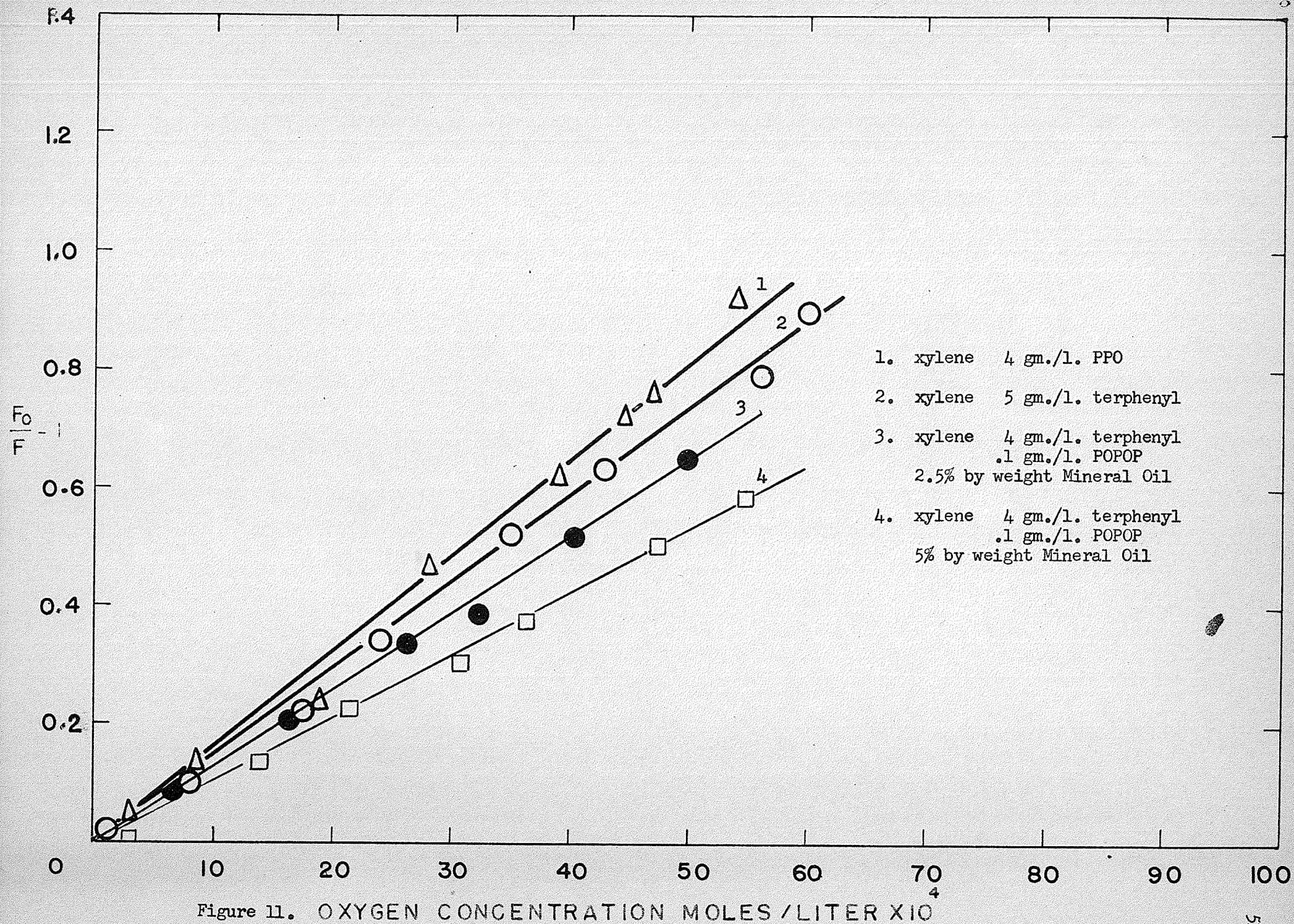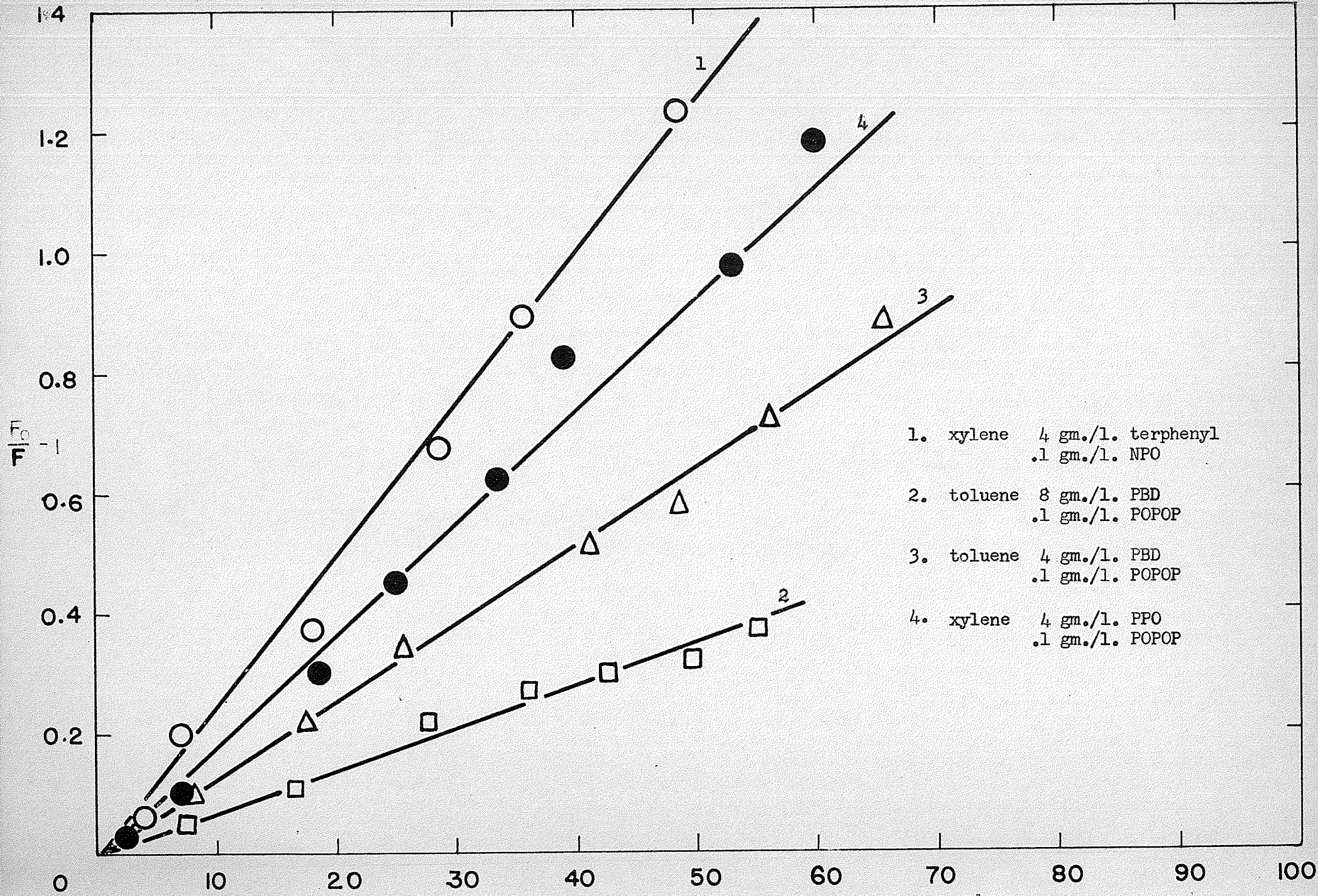
Figure 12. OXYGEN CONCENTRATION MOLES/LITER $\times 10^4$

1. xylene   4 gm./l. terphenyl
             .1 gm./l. NPO

2. toluene 8 gm./l. PBD
             .1 gm./l. POPOP

3. toluene 4 gm./l. PBD
             .1 gm./l. POPOP

4. xylene   4 gm./l. PPO
             .1 gm./l. POPOP

TABLE III

Solution	Quenching Constant $K = K_Q/K_F$	$K_Q = K/\tau$	Molar Conc. for 10% Quenching	Collisions /2 x 10^{-9} Seconds
xylene 4 gm./l. terphenyl .1 gm./l. POPOP	210	10.5×10^{10}	9.0×10^{-4}	.2
xylene 4 gm./l. terphenyl .1 gm./l. NPO	231	12.5×10^{10}	6×10^{-4}	.2
p-xylene 4 gm./l. terphenyl	213	10.7×10^{10}	5×10^{-4}	.2
xylene 4 gm./l. terphenyl .1 gm./l. PPO	195	9.8×10^{10}	7×10^{-4}	.2
xylene 4 gm./l. PPO .1 gm./l. POPOP	178	8.9×10^{10}	7×10^{-4}	.3
p-xylene 4 gm./l. terphenyl .1 gm./l. POPOP	210	10.5×10^{10}	5×10^{-4}	.2
xylene 4 gm./l. terphenyl .1 gm./l. PBD	155	7.8×10^{10}	8×10^{-4}	.2
xylene 4 gm./l. PBD	132	6.6×10^{10}	9×10^{-4}	.4
xylene 4 gm./l. PPO	173	8.7×10^{10}	7×10^{-4}	.3

Solution	Quenching Constant $K = K_Q/K_F$	$K_Q = K/\tau$	Molar. Conc. for 10% Quenching	Collisions $/2 \times 10^{-9}$ Seconds
xylene 5 gm./l. terphenyl	150	7.5×10^{10}	8×10^{-4}	.2
xylene 6 gm./l. terphenyl	175	8.8×10^{10}	6×10^{-4}	.1
toluene 5 gm./l. terphenyl .1 gm./l. PPO	143	7.1×10^{10}	8.5×10^{-4}	.2
toluene 5 gm./l. terphenyl	141	7.1×10^{10}	7×10^{-4}	.2
toluene 5 gm./l. terphenyl .1 gm./l. POPOP	130	6.5×10^{10}	6×10^{-4}	.2
toluene 8 gm./l. PBD	68	3.4×10^{10}	1.5×10^{-4}	.6
toluene 8 gm./l. PBD .1 gm./l. POPOP	70	3.5×10^{10}	9×10^{-4}	.4
toluene 4 gm./l. PBD	125	6.3×10^{10}	8×10^{-4}	.4
toluene 4 gm./l. PBD .1 gm./l. POPOP	128	6.4×10^{10}	15×10^{-4}	.7

One can obtain an insight into the mechanisms involved by calculating the effectiveness of the collisions between solute and quencher molecules. For such a comparison, one may select quite arbitrarily a molar concentration for ten percent quenching[24] and by means of kinetic theory, calculate the number of collisions between solute and quencher molecules within the lifetime of the fluorescent molecule. The kinetic theory expression for collisions between two unlike molecules is given by:

$$Z_{A,B} = \tfrac{1}{4} N_A N_B [\sigma_a + \sigma_b]^2 \left[8 \pi RT \; \frac{M_A + M_B}{M_A M_B} \right]^{\tfrac{1}{2}}$$

where N_A, N_B are the numbers of molecules of each species; σ_a, σ_b are the respective collisional diameters; M_A, M_B are the molecular weights, R is the gas constant and T the absolute temperature. The value of T used was 295°K. The collisional diameters used were: $O_2 \approx 2.0 \times 10^{-8}$ cm., p-terphenyl $\approx$ 5.0×10^{-8} cm., PBD $\approx 8.0 \times 10^{-8}$ cm., and PPO $\approx 6.0 \times 10^{-8}$ cm. These quantities are listed in columns 4 and 5 of Table III. For ten percent quenching, the data show that between .1 and .6 collisions occur between an activated solute molecule and an O_2 molecule within the lifetime of the former. For fifty percent quenching, the values are ten times as large; the same as predicted by Bowen[24].

These data show that the quenching process is characterised by an extremely rapid and efficient bimolecular collisional process. These data also show that the process may be explained by using a collisional mechanism identical to that of the Stern-Volmer mechanism whose final form is given by equation (1). It appears from the data that the quenching effect of O_2 on the solutions studied here may be explained by the use of a simple collisional process rather than a static one. The solutions studied obey

the Stern-Volmer equation and on the basis of simple kinetic theory, the
collisional process is found to be very efficient.

Self quenching effects have not been considered in this work and it can
be seen that the values of K vary with the concentration of primary solute.
At the higher concentration of primary solute, the value of K is seen to de-
crease. This is in accordance with theory since at higher concentrations,
self quenching will cause a decrease in the luminescent efficiency. Since
F_0 for the excess concentration is less than F_0 for the optimum value, K
will be smaller than for the case where the primary solute is used in the
optimum quantity. Although K does decrease according to theory, the actual
magnitude in some cases does not show too good an agreement. Studies of
self quenching for several primary solutes have been reported[12-13].

Up to now, we have only considered quenching due to oxygen gas. There
are other gases which quench fluorescence as well. In this investigation,
an attempt was made to use SO_2. However, the quenching effect of the gas is
so large that even with small amounts of gas in solution, the pulse height
dropped into the noise region of the apparatus so that no accurate measure-
ments could be made. Another difficulty encountered was the inability to
evacuate a solution that had absorbed SO_2. In most cases, the SO_2 combined
with the spectrum shifter to form a yellow-green solid which fell to the
bottom of the cell and prevented any measurement of the pulse height.
Studies were also made using N_2 and H_2 gases. In both cases, the addition
of gas had no effect. Thus the F_0 value was the same for an evacuated solu-
tion as for a solution containing measured amounts of either N_2 or H_2. The
results are shown in Table IV. Thus it appears that as long as the gas does
not quench the fluorescence, the pulse height will be the same for the
evacuated solution as for a solution containing some amount of non-quenching

gas like N_2 or H_2.

By using the encounter theory, one can find relations which will give both K and KQ as a function of the solution viscosity. In both cases, the constants are inversely proportional to the solution viscosity. Thus with an increase in the solution viscosity, there should be a corresponding decrease in the two constants. The effect of viscosity on the constants K and KQ was done in this investigation. The viscosity was changed by the addition of high purity Nujol mineral oil to the solutions in weighed amounts. When these solutions were subject to O_2 quenching, there was a definite drop in both K and KQ for these two solutions as compared to a pure xylene solution. One would expect a drop in K due to the fact that F_O for the more viscous solutions would decrease due to the diluting effect of the mineral oil. However, since the drop in the K values is of the order of fifty percent, one must conclude that the effect is due almost totally to the increased solution viscosity. Since the constant K decreases in value, one can conclude that quenching by O_2 is not so effective in the more viscous solutions since the collisional process will be arrested to some extent by the increased viscosity of the solution. The investigation of the two solutions of different viscosity shows that both K and KQ do decrease with an increase in viscosity of the solution as predicted by theory.

Another interesting point was to check the pulse height of a bubbled solution to which had been added some substance with a high viscosity. When poly-vinyl toluene was tried, there was a very noticeable drop in the pulse height. This could possibly be attributed to the inhibitor which was present in the liquid. However, when Dow "Styron" polymer was added to a solution, a noticeable increase in the pulse height occurred. The maximum occurred at a Styron concentration of between 0.5 - 1.0 percent by weight.

TABLE IV

Effect of H_2 and N_2 on Relative Pulse Height

xylene: 4 gm./l. terphenyl
    .1 gm./l. PPO

xylene: 4 gm./l. PPO
    .1 gm./l. POPOP

H_2 Concentration Moles/liter x 10^4	Rel.Pulse Height	N_2 Concentration Moles/liter x 10^4	Rel.Pulse Height	H_2 Concentration Moles/liter x 10^4	Rel.Pulse Height
0	30.4	0	30.0	0	53.7
1.1	30.7	2.4	29.5	1.4	53.0
3.2	30.4	6.4	29.8	5.2	53.0
7.2	30.8	10.4	30.0	10.4	53.0
12.8	30.4	17.2	30.2	14.0	53.8
15.6	30.8	32.0	29.5	19.6	53.0
22.4	30.2	37.2	30.3	21.6	53.0
24.0	30.0			22.8	53.0
25.6	30.4			25.2	52.8

TABLE V

Effect of Viscosity on Relative Pulse Height

Solution:	toluene: 5 gm./l. terphenyl .1 gm./l. PPO					
% by Weight Styron	0	1	2	3	4	5
Pulse Height of Bubbled Solution	61.5%	66.5	63.7	65.5	63.3	58.5

Solution:	xylene: 4 gm./l. terphenyl .1 gm./l. POPOP						
% by Weight Styron	0	.5	1.0	2.0	3.0	4.0	5.0
Pulse Height of Bubbled Solution	73.5%	75.5	77.0	67.0	66.5	64.5	63.5
% by Weight Poly-Vinyl Toluene	0	1	2	3	4		
Pulse Height of Bubbled Solution	73.1%	53.0	47.5	42.0	38.4		

Addition of further Styron caused a smooth decrease in pulse height. The results are listed in Table V. The increase in pulse height could be explained on the basis that the concentration quenching and solute quenching decrease due to the decrease in collisional processes. On the other hand, one would expect that the luminescence efficiency of a more viscous solution should drop slightly if the energy transfer occurs by means of the third mechanism given by Kallmann and Furst. It may be that this collisional mechanism is not the predominant one and concentration quenching is decreased to cause a rise in the luminescence output.

These data show that the quenching process is characterised by an extremely efficient collisional mechanism in which nearly every bimolecular collision is an effective quenching reaction. Although a number of mechanisms have been proposed - both static and collisional - the data show that the quenching of liquid scintillator solutions can be explained by applying the simple Stern-Volmer equation (1). Having verified this, calculations using kinetic theory have shown that the collisional process is extremely efficient at such low quencher concentrations. Kinetic studies of fluorescent solutions and vapors have yielded results which also prove that the Stern-Volmer mechanism is applicable in explaining the quenching process. The quenching constants for the vapors are of the same order of magnitude as predicted by kinetic theory for quenching on nearly every collision. Similarly, the constants for the solutions are comparable with the values predicted from calculations using the encounter theory. Thus the results obtained from studies of scintillator and fluorescent solutions are valuable since these measurements on strong quenchers could be used to extend and elaborate the general theory of encounters in the liquid state.

CONCLUSIONS

1. The O_2 quenching of the light emissive process of liquid scintil-
lators has been shown to be a collisional process explicable by
the Stern-Volmer mechanism.

2. Using the Kinetic Theory approximation, the number of effective
collisions between the activated solute and quencher molecules
can be calculated. For ten percent quenching, between .1 and .6
collisions occurred between the activated solute and quencher
molecules during the lifetime of the former.

3. The rate constants for the quenching process have been determined.
These results are in good agreement with those obtained by Bowen[24]
for fluorescent solutions.

4. An increase in the solution viscosity has been shown to cause a
decrease in the quenching constant of the solution. This is as
predicted by the encounter theory of liquids.

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