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Ottofuel II: Evaporation into Air and Diffusion into Sea Water

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NAVAL UNDERWATER SYSTEMS CENTER
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ADMINISTRATIVE INFORMATION

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The Technical Reviewer for this report was Dr. Robert S. Lazar (Code SB331).

REVIEWED AND APPROVED: 14 June 1973

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ABSTRACT

The factor which controls the buildup of Ottofuel vapor in the atmosphere of any environment in which Ottofuel is spilled is the rate of evaporation of material from the spill. In order to obtain more information on the quantitative aspects of the problem, the evaporation rate of Ottofuel II at 25-27°C was determined by weight loss measurements in a nitrogen atmosphere. After an initial period of 3-4 hours, the evaporation rate was found to be 0.18 $g/hr/ft^2$ of the spill. An initially higher weight loss is attributed in part to water that was dissolved in the ottofuel and in part to the presence of a volatile impurity that could not be removed by drying the liquid with calcium sulfate.

The observed evaporation rate was in good agreement with the rate of 0.52 $g/hr/ft^2$ reported for propylene glycol dinitrate (PGDN) at 35°C, and with the rate of 0.135 $g/hr/ft^2$ calculated for PGDN at 25°C using Langmuir's method of calculating the evaporation rate of liquids into a stagnant atmosphere. (PGDN is the main ingredient of Ottofuel — 76 percent by weight.)

A new technique, based on differential pulse polarography, was developed for the quantitation of PGDN in sea water. This technique was used to follow the diffusion of Ottofuel through a stagnant layer of sea water. After 250 hours, the transport rate of Ottofuel through sea water was found to be 7.8×10^{-5} $g/hr/ft^2$. The saturation value for PGDN was found to be 0.123 percent by weight in sea water at 22°C. The agreement between the observed transport rate and the calculated evaporation rate from a saturated solution is good.

Under favorable circumstances (i.e., complete coverage), the covering of an Ottofuel spill with sea water reduces the evaporation rate by a factor of 10^{-4}. Values between 2.4×10^{-5} $g/hr/ft^2$ and 0.18 $g/hr/ft^2$ at 25°C will be observed if the Ottofuel is not completely covered, but floats on top of the water as it sometimes does despite its great density.

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INTRODUCTION

OBJECTIVES

The purpose of this study was to obtain quantitative information on one of the problems that arises when Ottofuel II is spilled aboard a submarine, namely, whether evaporation of the fuel can cause a rapid rise in the concentration of Ottofuel in the air of the submarine. Furthermore, it was desired to know what delay in the evaporation of Ottofuel might take place if the spill were covered with sea water. The latter question could, however, not be investigated until there was available a method by which the change in the concentration of Ottofuel in sea water could be followed without using large samples of sea water. This obstacle was overcome with the development of an electroanalytical method for the quantitation of propylene glycol dinitrate (PGDN) in sea water, PGDN being the main ingredient (see table 1) of Ottofuel II. The technique, based on differential pulse polarography, is discussed in appendix A.

The study is divided into two parts: Part I deals with the experiments on the evaporation of Ottofuel into air; Part II covers the diffusion of Ottofuel in sea water.

BACKGROUND

The atmosphere of a submarine, if contaminated with Ottofuel vapors, would cause inconvenience to personnel and have a deleterious effect on life support systems. The experiments discussed in this report were conducted to obtain information on the possible level of contamination that would occur in the event of accidental spills of Ottofuel in service. Before discussing these experiments it would be useful to first describe several conditions under which a liquid may be evaporating. These are:

1. The liquid is evaporating into a vacuum;
2. The liquid is evaporating into stagnant air;
3. The liquid is evaporating into air which is moving at several feet per second;
4. The liquid is diffusing into another liquid.

The latter three cases could occur aboard a submarine. The first case, evaporation into a vacuum, does not specifically apply to the submarine situation, but is included here to enhance the general picture of the evaporation process of liquids.

Case 1. The Liquid Evaporates into a Vacuum

It was generally believed that this situation could be described completely in terms of the basic postulates of the kinetic theory. One of these is that when there is no longer an increase in pressure due to the evaporation of the liquid, a state of equilibrium has been reached in which, by definition, as many molecules are evaporating into the space above the liquid as are condensing into the surface of the liquid. The pressure in the container is then the vapor pressure of the substance at that particular temperature. At all the internal surfaces of the container, molecules are exchanging momentum with the walls of the container and the surface of the liquid at the same rate. This is another way of saying that the pressure is uniform on all of the surfaces. Therefore, the number of molecules that are bouncing back from a unit area of the walls is the same as the number of molecules that are leaving a unit area of the surface of the liquid.

But in actual experiments with the evaporation of many pure liquids into a vacuum, the rate predicted by the kinetic theory has to be multiplied by a factor — often much less than 1.0 — called the "evaporation coefficient" to make it agree with the actual rate. The significance and the nature of evaporation coefficients has been the subject of much discussion. Some believe that it has no meaning, but signifies only that the surface of the liquid was dirty. Others think that because evaporation requires a flow of heat, the temperature of the surface during an evaporation is lower than the bulk temperature; but Heideger and Boudard[1] took special precautions with the liquid they investigated (glycerol) to ensure a clean surface and a uniform temperature through stirring. Boudard suggested that the evaporation coefficient (0.051) is the ratio of partition functions for rotation of the substance in the liquid state to that in the gas state. He showed that it can be calculated from the thermodynamic and physical properties of the substance without recourse to experiment.

Case 2. The Liquid Evaporates into Stagnant Air

This is a diffusion-controlled process which generally follows Fick's laws. Fick's first law, in its simplest form, is expressed as (see appendix B for elaboration):

$$J = -D\frac{dc}{dx}.$$

In this form it is especially easy to see that the process operates because of a concentration differential between two points. The diffusion coefficient (D) is not only a property of the substance that is diffusing, but also of the medium into which the diffusion takes place. Diffusion coefficients for the same substance differ by less than a factor of 10 with the concentration and the temperature. But they differ generally by a factor of 10^5 depending on whether the substance is diffusing into air or into water.

The evaporation of liquids from spherical surfaces has been investigated by Langmuir.[2] This process follows a form of the diffusion law given in appendix B.

Case 3. The Liquid Evaporates into Moving Air

In this situation, the resulting mass transfer is no longer solely a function of the molecular properties of the substances which participate in the transfer. The velocity of the air enters into the calculation via the Reynolds number. But the driving force of the reaction is still the difference in the partial pressure of the material at the surface and in the stream of air. (Eckert and Drake[3] treat the evaporation process of water into air in some detail.)

Case 4. The Liquid Diffuses into Another Liquid

This process is also subject to Fick's laws. Because diffusion in the absence of other forms of mass transfer takes place so slowly in liquids, it is necessary to take certain shortcuts in performing experiments. In the work reported on here, a steady state of diffusion was considered to have been reached after observing the concentration of PGDN in a column of sea water, either 14 inches high or 6 inches high, for about 300 hours. Since for a long time before the end of the experiment a uniform concentration gradient had been observed, the transport rate of the PGDN through the water column was calculated from this gradient.

PART I. EVAPORATION OF OTTOFUEL II INTO AIR

EXPERIMENTAL METHODS

Figure 1 shows the apparatus used in the evaporation experiments. Two drying towers (not shown) filled with calcium sulfate were used to bring the nitrogen to the same humidity as the Ottofuel that had been dried with calcium sulfate. The Mettler balance shown in figure 1 has the accuracy (±0.02 mg) required for measurement of the weight loss when the surface area exposed is small. The measurements were made with about 20 grams of Ottofuel (see table 1) in a petri dish. The liquid formed a layer which was several millimeters thick. During the first hour, readings were taken at 5-minute intervals.

Table 1. Composition of Ottofuel II

Constituent	Weight Percent	Mole Fraction
Propylene glycol dinitrate	76	0.856
Di-n-butyl sebacate	22.5	0.131
2-Nitrodiphenylamine	1.5	0.013
Water	up to 0.31% at 77°F	
Propylene glycol dinitrate: Mwt — 167; boiling point — 92.6°C (10 mm); vapor pressure — see figure 4		
Di-n-butyl sebacate: Mwt — 314.5; boiling point — 344-345°C (760 mm); vapor pressure — 0.001 mm at 75°C		
2-Nitrodiphenylamine: Mwt — 214.2; melting point — 75°C		

NOTE: See Reitlinger.[7]

EXPERIMENTAL RESULTS

Table 2 and figure 2 show the results of following the weight loss of a sample of Ottofuel at 25-27°C. The data refer to the average of five determinations. In some experiments a stream of nitrogen was blown over the surface of the liquid. Even at the highest rate (0.3260 ft^3/hour), which caused the atmosphere inside the balance case to change once every hour, there was no noticeable increase in the rate of evaporation over that found at lower nitrogen flow rates.

Table 2. Weight Loss of Ottofuel from a 3-1/2-Inch-Diameter Petri Dish (Sample Used as Received)

Elapsed Time (min)	Observed Loss (grams)	Evaporation Rate (g/hr/ft^2)
0-5	0.055	--
5-10	0.035	--
10-15	0.026	--
15-20	0.021	--
20-25	0.018	--
25-30	0.015	--
30-60	0.060	--
0-60	0.230	3.45
60-120	0.050	0.76
120-180	0.023	0.34
180-240	0.012	0.18
240-	0.001 g/5 min	0.18

NOTES: Temp: 25-27°C; weight losses are averages of five determinations; the samples used weighed about 22 grams.

From table 2 it is seen that a much higher average rate of evaporation was observed during the first hour (3.45 g/hr/ft^2) than in the hours thereafter. At the end of 4 hours the evaporation rate with a sample as received and undried, weighing 22 grams, was 0.18 g/hr/ft^2. Meticulous drying over calcium sulfate reduced the evaporation rate to an initial 1.53 g/hr/ft^2 (at 29.5°C) for a 16.2-gram sample; but thereafter the rate also approached 0.18 g/hr/ft^2 (see table 3 and figure 3). Since the dried sample had lost about 0.3 percent of its weight in the first 20 minutes, this was taken to mean that there was present after drying an impurity of 0.3 percent which boils at a lower point than the other constituents of Ottofuel. It would have been interesting to determine the evaporation rate of a sample of pure PGDN, fractionated over a narrow boiling range, but none was available.

Table 3. Weight Loss of Dried Ottofuel II from a 3-1/2-Inch-Diameter Petri Dish (Sample Dried Over Drierite)

Elapsed Time (min)	Observed Loss (grams)	Evaporation Rate ($g/hr/ft^2$)
0-5	0.0202	--
5-10	0.0200	--
10-15	0.0126	--
15-20	0.0110	--
20-25	0.0077	--
25-30	0.0075	--
30-35	0.0065	--
40-45	0.0060	--
50-55	0.0055	--
55-60	0.0050	--
0-60	0.102 (total)	1.50
60-65	0.0045	--
65-70	0.0045	--
70-75	0.0040	--
75-80	0.0035	--
80-85	0.0035	--
85-90	0.0032	--
90-95	0.0030	--
95-100	0.0030	--
105-110	0.0026	--
110-115	0.0030	--
115-120	0.0027	--
120-180	0.0016 avg/5 min	0.27

NOTES: Temp: 29°C; nitrogen gas dried over Drierite; flow rate: 0.05 ft^3/hr; weight of sample: 16.2 grams.

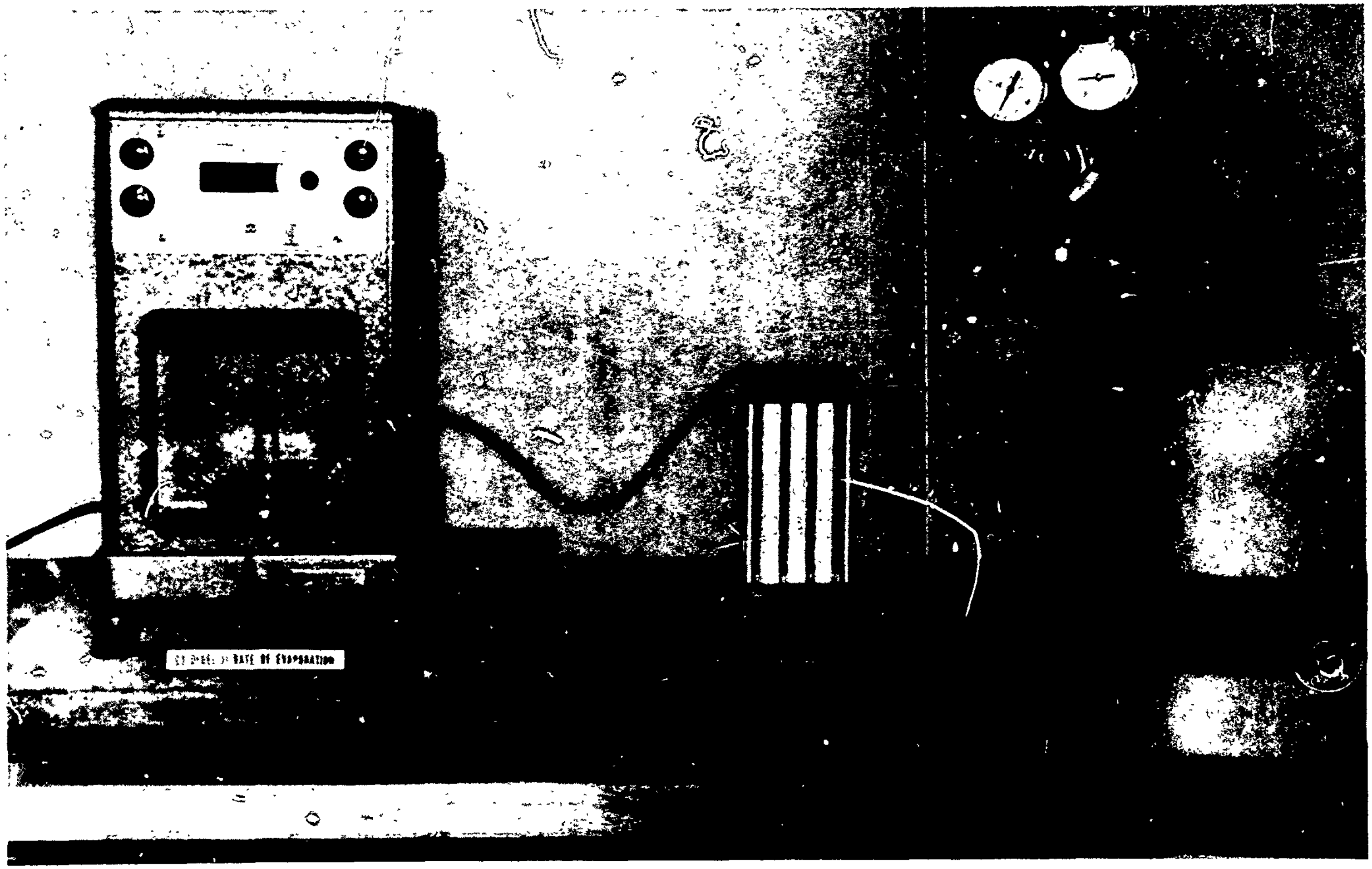

Figure 1. Apparatus Used in Evaporation Experiments.

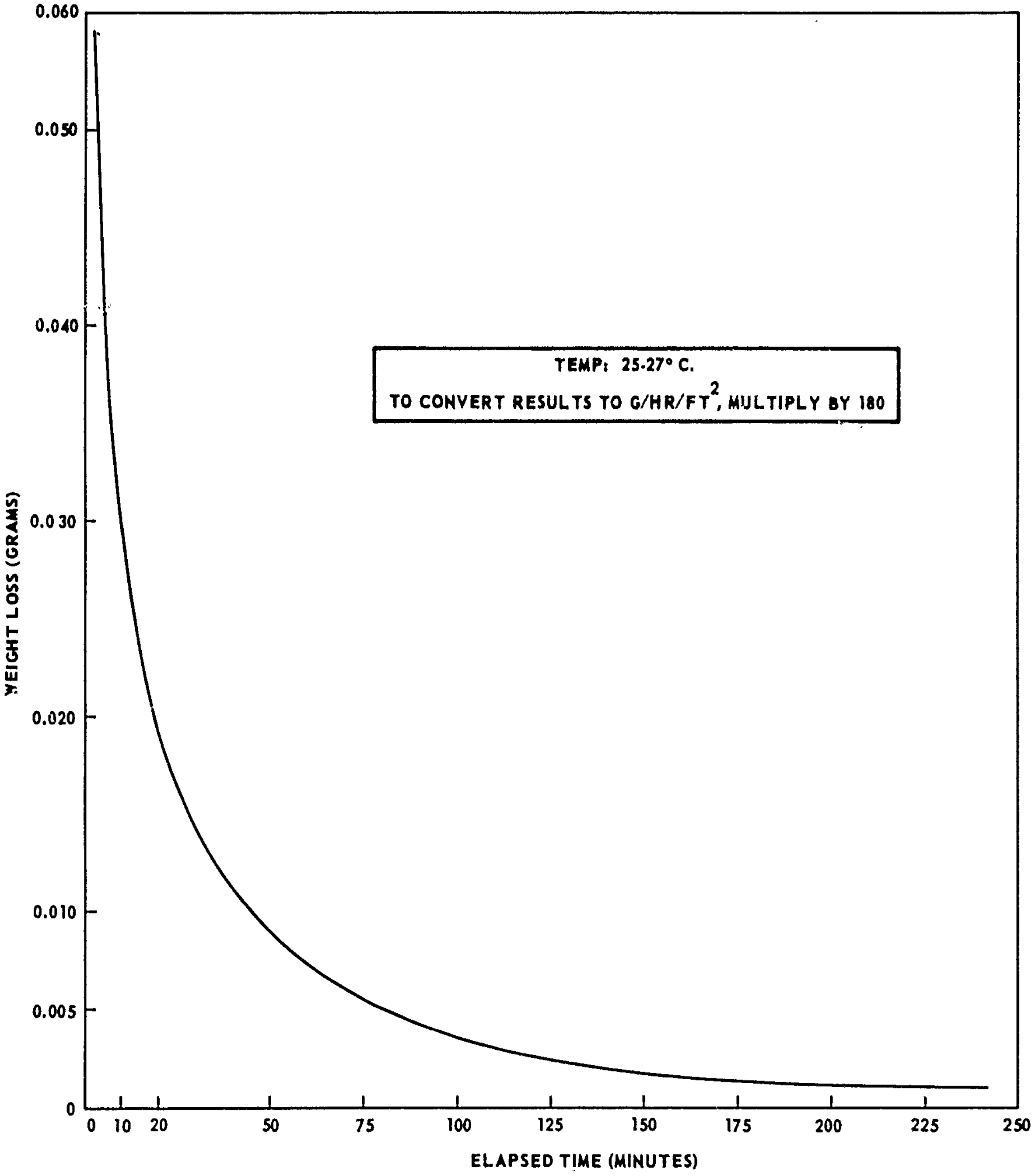

Figure 2. Weight Loss of Ottofuel II from a 3-1/2-Inch Petri Dish.

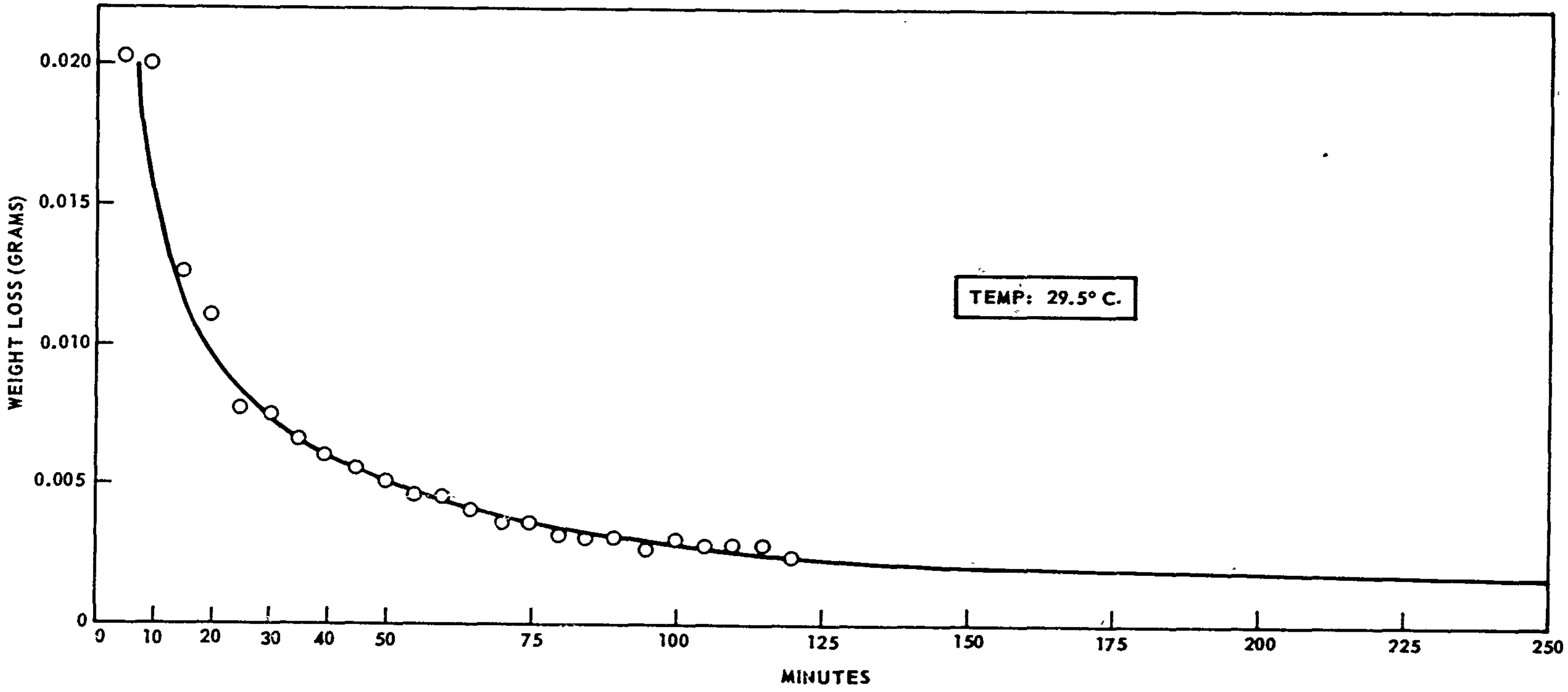

Figure 3. Weight Loss of Dried Ottofuel II from a 3-1/2-Inch Petri Dish.

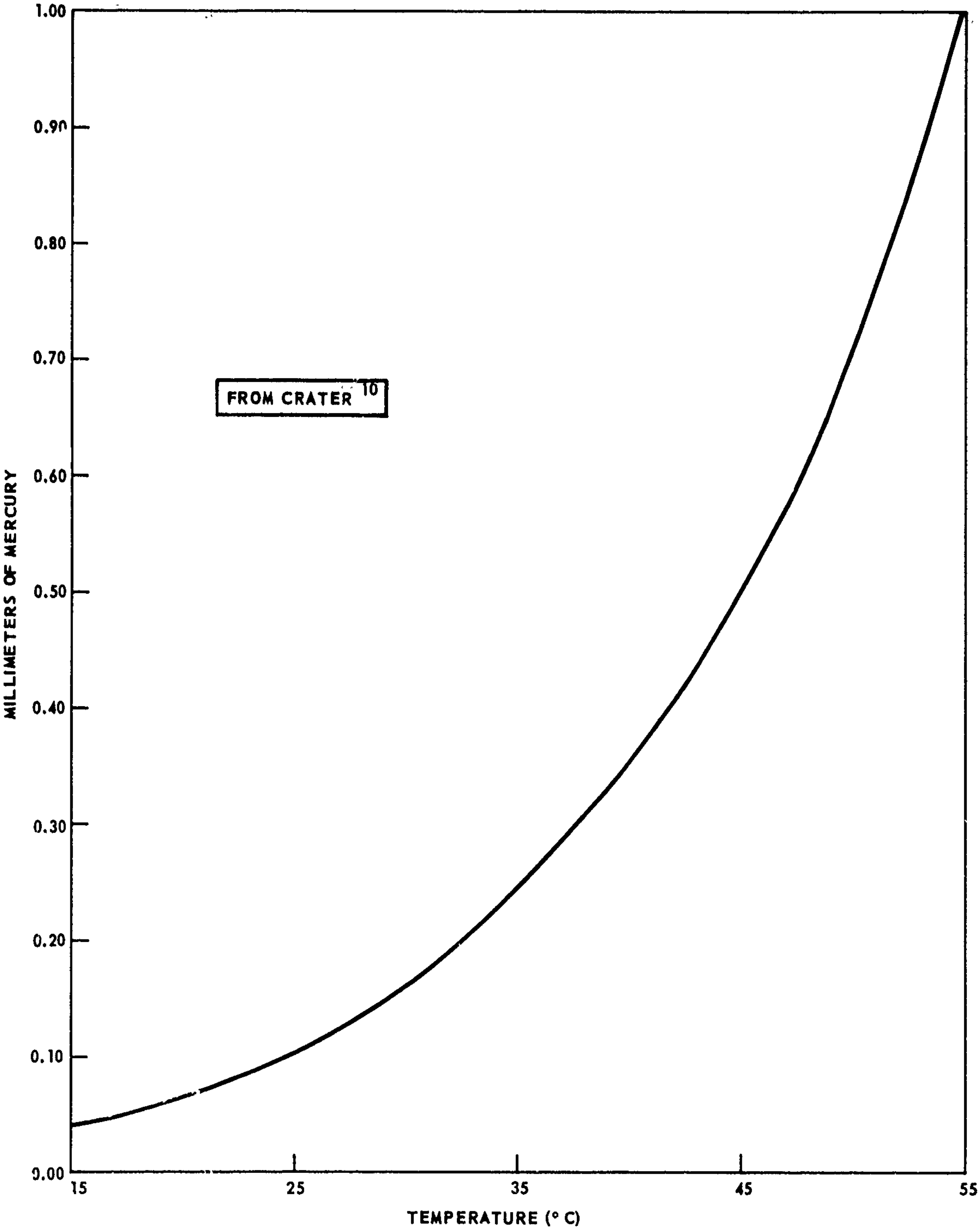

Figure 4. Vapor Pressure of PGDN.

DISCUSSION OF RESULTS

The rate of evaporation of a pure liquid into air can be determined experimentally by carefully measuring the weight loss of a sample over a period of time when it is exposed to an atmosphere of constant humidity and constant temperature. Naoum[4] reported results of such weight change measurements made experimentally in which propylene glycol dinitrate (PGDN) evaporated from a dish into air. An evaporation rate of 0.52 g/hr/ft^2 at 35°C was observed over a period of 24 hours.

Calculations can also be made to predict rates of evaporation of liquids into still air without recourse to experiments. The rate of evaporation of many liquids into air has been calculated using Langmuir's formula of mass transfer from a sphere placed into a stagnant fluid.[2] The evaporation is a diffusion-controlled process, and the formula for calculating it is a form of Fick's law (see appendix B for meaning of symbols):

$$N_A = \frac{2D_V\,(p_i - p)}{DRT} \text{ lb-moles/hr/ft}^2$$

Using this formula the evaporation rate of pure PGDN into air was calculated to be 0.135 g/hr/ft^2 at 25°C. The calculation was made using D_V, a diffusion coefficient obtained from Klotz and Miller,[5] where D is the diameter of a sphere equal in area to that of the petri dish used in the NUSC experiments with Ottofuel.

As shown in table 4, the agreement among the reported evaporation rate for PGDN,[4] the calculated evaporation rate for pure PGDN, and the observed evaporation rate for Ottofuel II is good if one disregards the high evaporation rate obtained during the first few hours. The high rate (3.45 g/hr/ft^2) for the first hour means that more than 1 percent by weight of the sample was evaporating. Since water is soluble in Ottofuel II only to the extent of 0.31 percent at 77°F,[6] there was some uncertainty as to whether the higher weight loss during the first hour took place because there was more water present than 0.3 percent, or whether there was also present a small amount of a lower boiling impurity as was later shown to be the case. The presence in Ottofuel of a small amount of an impurity more volatile than PGDN was also observed when an atmosphere which contained Ottofuel was analyzed by means of gas chromatography in connection with a different problem.[8] Moreover, Urbanski[9] indicated that the initial weight loss in heating nitrocellulose esters consisted of moisture and residual solvent.

Evaporation is not a sequential process; PGDN also begins to evaporate as soon as Ottofuel is exposed to the air. There is, in fact, no reason to believe that the evaporation rate of PGDN is seriously influenced by the presence of a small amount of lower-boiling material.

Table 4. Calculated and Observed Evaporation Rates of Ottofuel II and PGDN

Chemical	Method	Evaporation Rate (g/hr/ft^2)	Temperature (°C)	Remarks
PGDN	Calc'd	0.135	25	See appendix B
PGDN	Calc'd	0.33	35	
PGDN	Obs'd	0.52	35	See Note 1
Ottofuel II	Obs'd	3.45	25-27	During first hour (see NOTE 2)
Ottofuel II	Obs'd	1.53	29	During first hour - 16.2 grams of dried Ottofuel II
Ottofuel II	Obs'd	0.18	25-27	During fourth hour and later (see NOTE 2)
Ottofuel II	Obs'd	0.27	29	During fourth hour - 16.2 grams dried Ottofuel II

NOTES: 1. Naoum[4] compares the loss in weight of PGDN and trimethylene glycol dinitrate. For PGDN, the loss in weight at 35°C from dishes 60 mm in diameter is given as 3.8 percent of a 10-gram sample in 24 hours.

2. Rates obtained using Ottofuel as received in a 3-1/2-inch-diameter petri dish which contained on the average 22 grams of Ottofuel. During first hour observed weight loss was 0.230 gram which is 1 percent of the amount that was present. During fourth hour, observed weight loss was only 0.012 gram which gives an evaporation rate of 0.18 g/hr/ft^2.

The good agreement of the observed evaporation rate of Ottofuel II after a period of 3-4 hours with that reported in the literature by Naoum and that calculated by the use of Langmuir's formula suggests that the initially higher evaporation rates for undried and dried Ottofuel can be disregarded as far as the importance to concentration buildup of PGDN in submarine atmospheres is concerned. The initially higher evaporation rate can be disregarded for the following reason: evaporation rates are usually reported on the basis of weight loss per unit of area per unit of time; such a method does not take into account the thickness of the layer of spill. When there is a low boiling constituent present, the time within which a steady rate of evaporation is obtained is a function of the thickness of the layer of spill, since the thickness determines the absolute quantity of low boiling material that evaporates during the initial period. It seems quite possible that a thinner layer of material (the layer present in the subject tests was several millimeters thick) would have given an initial rate of evaporation which might not have differed appreciably from the final rate. This low initial rate would be due to the rapid exhaustion of the small quantity of low boiling constituent present in the thin Ottofuel film. (This point was difficult to prove experimentally because of the limitations in the sensitivity of the weighing device.)

Factually, after as little as an hour after a spill the concentration of PGDN itself in, for example, a 100-cubic meter compartment is 0.26 ppm, which is about as much as the recommended limit (0.2 ppm) if it is distributed homogeneously throughout the compartment. This calculation has been made assuming an evaporation rate of 0.18 g/hr/ft^2 for PGDN.

The question is thus raised as to the identity of the material that evaporates at the beginning from a dried sample of Ottofuel. This was not investigated, but it is not all PGDN. Very little experimental work has been done to identify the lower boiling impurity and there is even some doubt that it is present in all batches of Ottofuel that have been manufactured.

The presence of Ottofuel can fortunately be detected by its odor at low concentrations and measures for the control of the evaporation can be taken. One of these, the covering of Ottofuel with a layer of sea water is discussed in Part II.

PART II. DIFFUSION OF OTTOFUEL II INTO SEA WATER

EXPERIMENTAL METHODS

Diffusion experiments give meaningful results only if the interface between the two components remains free of convective or mechanical transport of material. Special care was taken in introducing Ottofuel into the bottom of the sea water-filled tube using the method described by Jost.[11] The Ottofuel was introduced by means of a 6-mm glass tube attached to a separatory funnel which reached through the sea water to the bottom of the 2-inch-diameter diffusion tube (see figure 5). It is not difficult to obtain a rather sharp interface by allowing the Ottofuel to flow through the 6-mm tube and settle at the bottom of the sea water column. None of the Ottofuel was allowed to float on top of the water as it often does despite its great density. The apparatus was kept in a thermostatted room during the experiments. Small samples of the sea water were withdrawn periodically with a syringe through the ports of the tube and their PGDN content was determined as described in appendix A.

The depths of the columns of sea water (see table 5 for composition) that were examined were 14-3/8, 10, and 3-3/4 inches. The first two columns covered two or three ports of the tube; the third column covered only one port. Consequently, the concentration of Ottofuel could be measured simultaneously at two different points with only the two deeper columns.

Table 5. Composition of Synthetic Sea Water

The sea water used in the experiments was a synthetically prepared solution containing 41.953 grams of SEA-SALT per 1000 ml of solution. SEA-SALT is a simulated sea salt mixture containing those elements found in natural sea salt in quantities greater than 0.004 percent. The formula mixture contains U.S.P., N.F., and high-grade commercial salts in the following proportions (ASTM D-1141-52):

Component	Percent
NaCl	58.490
$MgCl_2 \cdot 6H_2O$	26.460
Na_2SO_4	9.750
KCl	1.645
$NaHCO_3$	0.477
KBr	0.238
H_3BO_3	0.071
$SrCl_2 \cdot 6H_2O$	0.095
NaF	0.007

The SEA-SALT was obtained from Lake Products Co., Inc., St. Louis, Missouri.

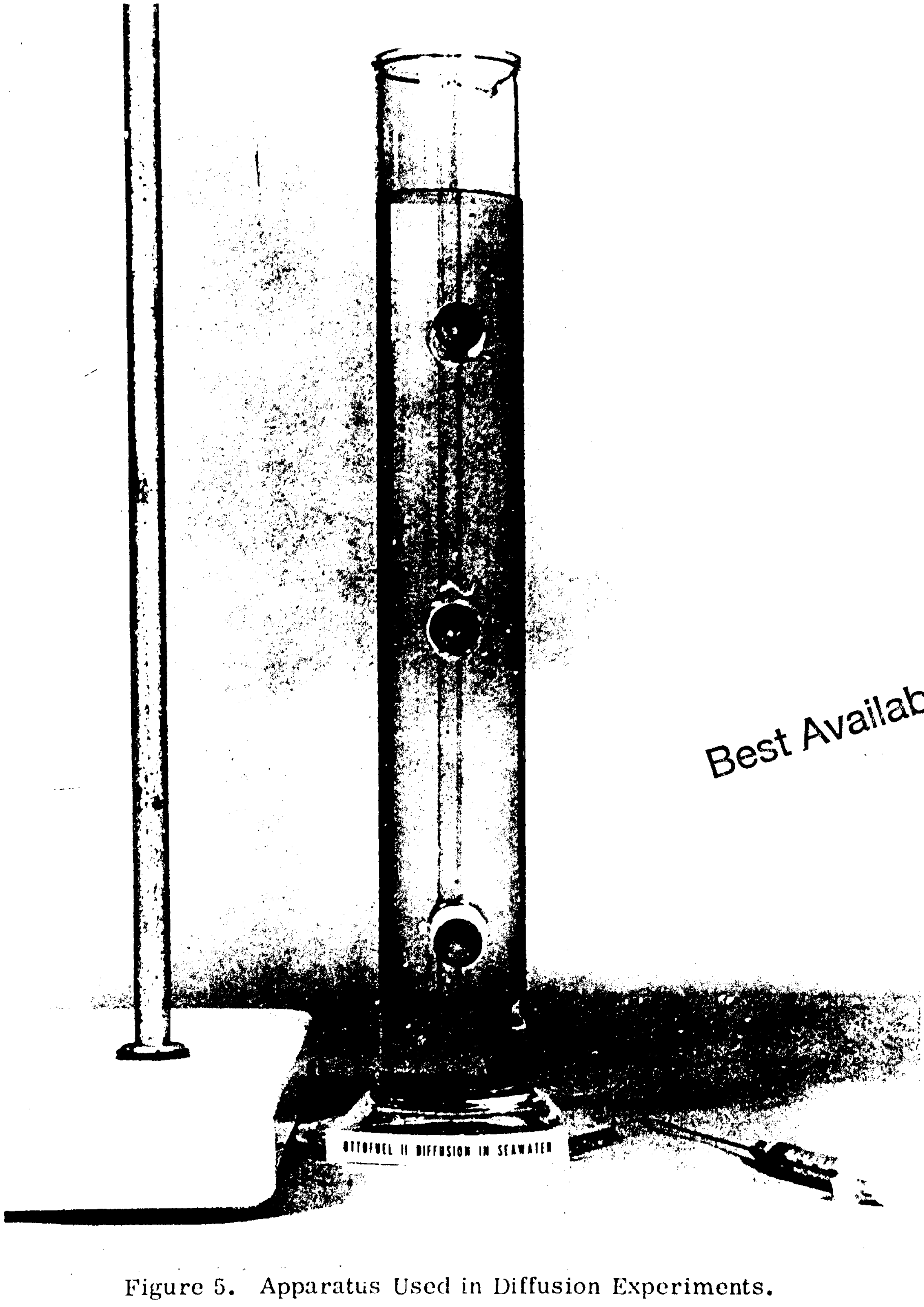

Figure 5. Apparatus Used in Diffusion Experiments.

EXPERIMENTAL RESULTS

Figures 6, 7, and 8 show the change in concentration of PGDN with time in the three different columns of sea water. The curves are characterized by a steep rise in concentration at the beginning and a more gradual rise for many hours thereafter. The curves (drawn free-hand) also show that the shortest of the columns (figure 8) contained, after 250 hours, about 500 mg/liter of PGDN at a point 2 inches above the surface of the Ottofuel. This was the highest concentration of PGDN observed. In the 14-3/8-inch column and the 10-inch column, the concentrations of PGDN at a point 6-1/8 inches above the surface of the Ottofuel were about 200 mg/liter and 300 mg/liter, respectively. The experiment thus gave the expected result that the shorter the column of water, the larger will be the concentration of PGDN after the same number of hours has elapsed. No real steady state of diffusion was reached even after 200 hours, but this was not considered necessary.

From the concentrations measured after 250 hours at the two ports on the diffusion column (which contained a layer of sea water 14-3/8 inches thick), the transport rate of the PGDN through the solution was calculated. It was assumed that after 250 hours the Ottofuel/PGDN would be evaporating out of the top about as fast as it was being transported up the column. The rate obtained was 7.8×10^{-5} g/hr/ft^2 at 22°C. (See appendix C for calculations.)

The changes in the concentration of PGDN were followed at several levels of the diffusion tube when it was filled with columns of sea water of different depths. The results obtained were plausible in terms of a diffusion-controlled experiment. But it was realized that conditions aboard a submarine might not be so ideal and that the sea water might soon become saturated with PGDN. Therefore, the concentration of PGDN in sea water that was saturated with it was also determined. This was found to be 1230 mg of PGDN per liter of sea water.

The determination of small amounts of nitroesters in water poses a problem if it requires that several cubic centimeters of water be withdrawn from a solution into which diffusion continues to take place. Moreover, the results of an electrochemical analysis are sometimes non-linear with respect to the concentration of the nitroester. The electrochemical behavior of simple nitroesters[12-16] and polynitroesters[17] has been investigated and methods for their determination have been developed.[18-24] However, only Gogis and Hamrick[24] dealt directly with PGDN. Their method had to be modified (as described in appendix A) so that the volume of the withdrawn samples of sea water needed to be only 0.25 to 2 ml.

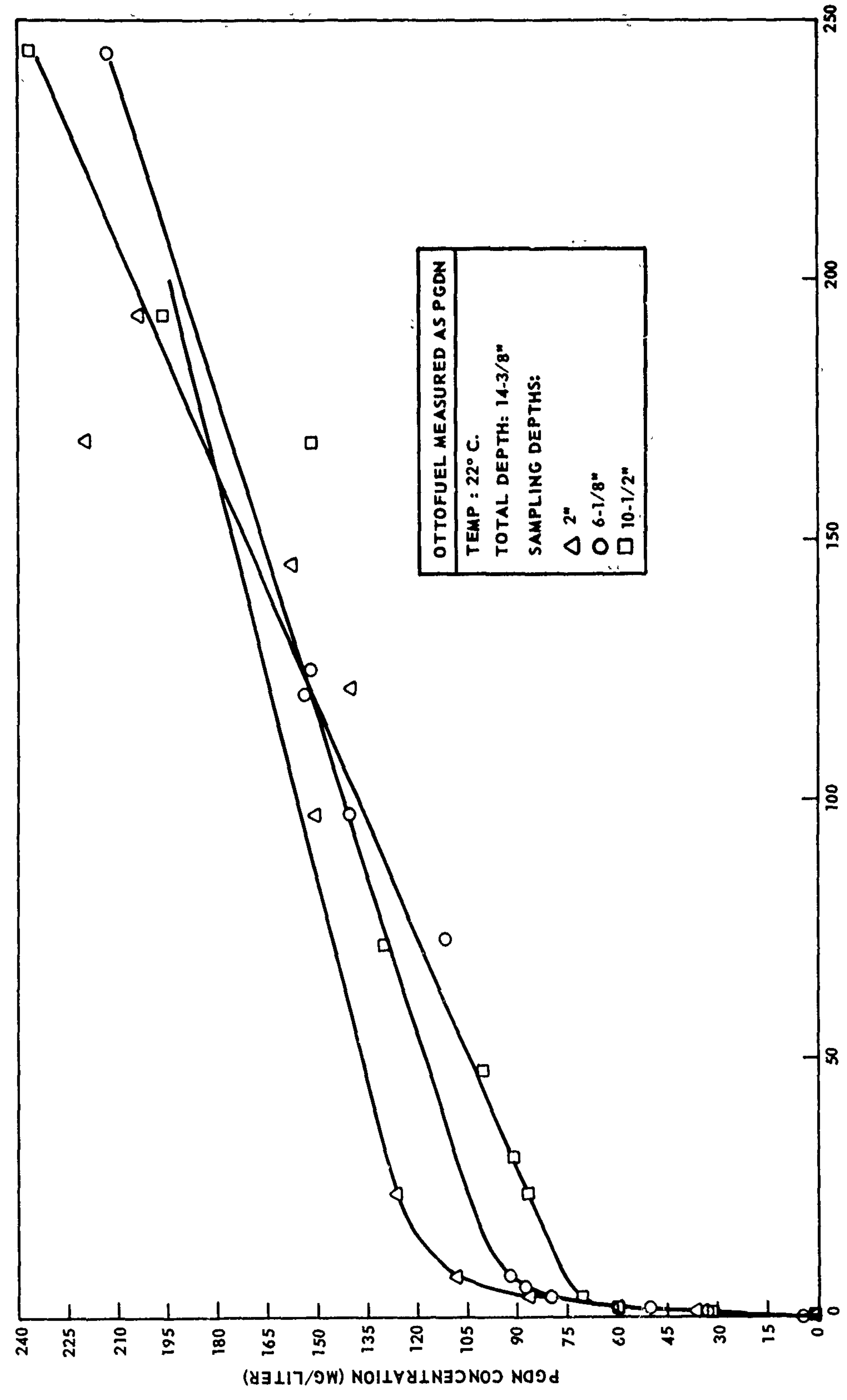

Figure 6. Diffusion of Ottofuel into Sea Water (Total Depth: 14-3/8- Inches).

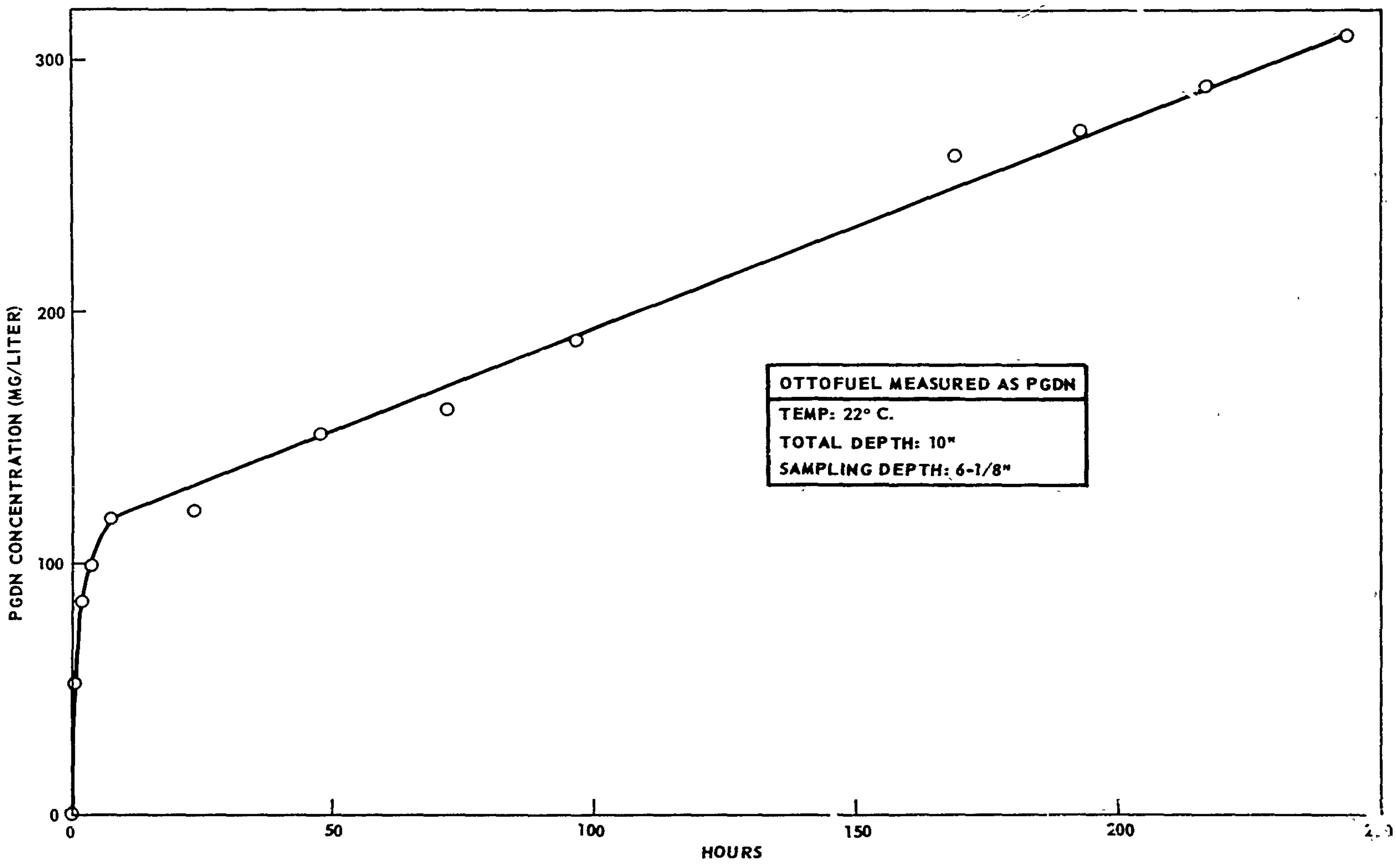

Figure 7. Diffusion of Ottofuel into Sea Water (Total Depth: 10 Inches).

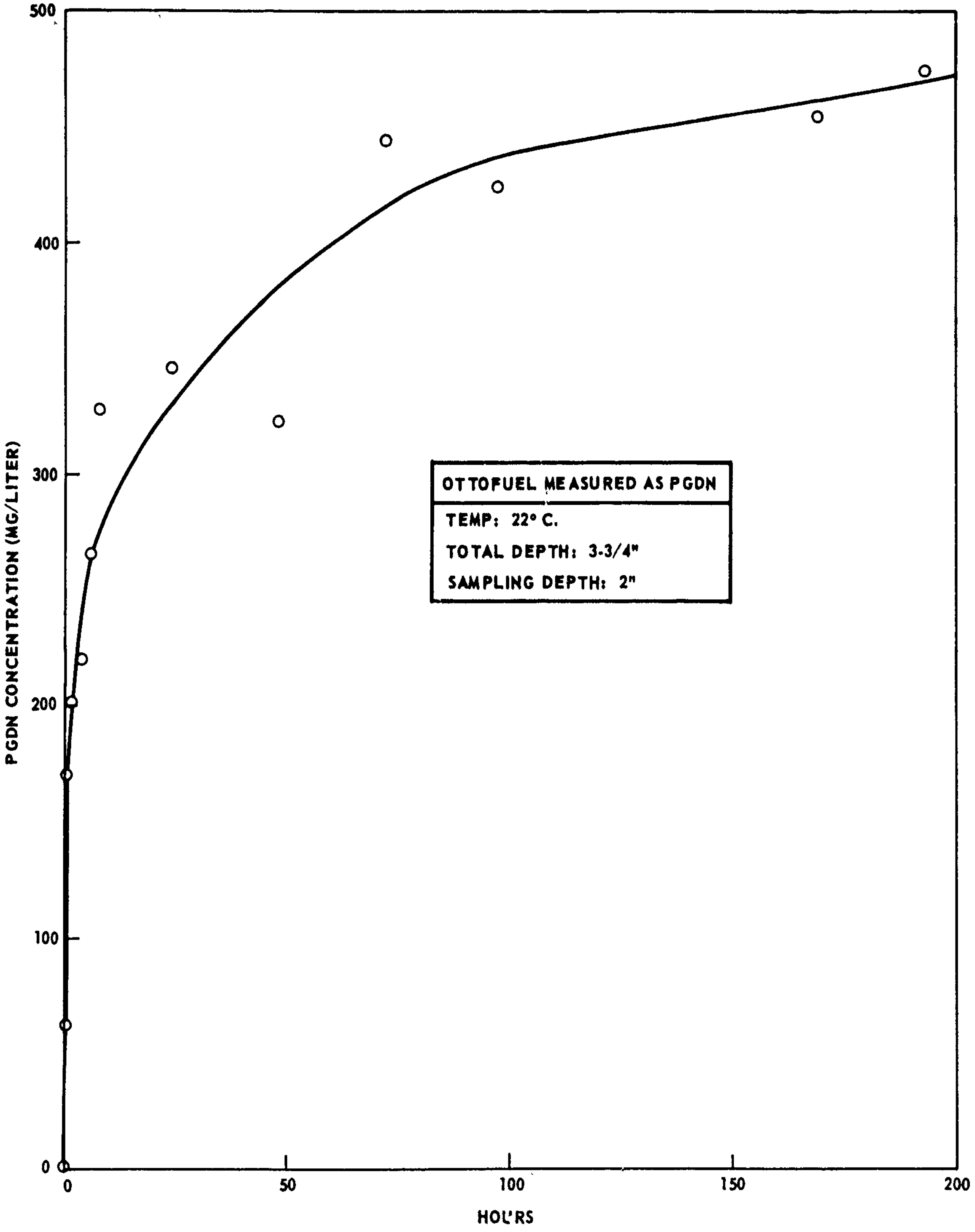

Figure 8. Diffusion of Ottofuel into Sea Water (Total Depth: 3-3/4 Inches).

DISCUSSION OF RESULTS

The diffusion of a liquid into water is a much slower process than its diffusion into air, and it takes a much longer time to establish a steady state of diffusion. In considering the diffusion process, the following assumptions were made: (1) at the beginning all of the Ottofuel is covered by sea water, i.e., none of it floats on top; (2) material transport is controlled only by diffusion; (3) sea water that is saturated with PGDN (0.123 percent by weight at 22-25°C) forms an ideal solution. These assumptions mean that the vapor pressure of PGDN at the interface with air would be the product of the mole fraction of PGDN in the solution and its vapor pressure in the pure state.

The last assumption leads to the conclusion that since the mole fraction of PGDN at 0.123 percent by weight is 1.32×10^{-4}, the evaporation rate is diminished by a factor of 1.32×10^{-4} relative to that of pure PGDN which, of course, has a mole fraction of 1.0. This conclusion is also based on the assumption that PGDN evaporates from a solution according to its vapor pressure and its diffusion coefficient.

The foregoing leads to a calculated evaporation rate for PGDN of about 2.4×1^{-5} g/hr/ft^2 at 25° from a spill that is covered with water. The situation changes of course, if the PGDN does not form a homogeneous solution, but floats on top of the water covering a part or all of it. In this case it would probably evaporate as fast as it does when it is not covered with water at all. Under especially unfavorable circumstances, it might evaporate even faster if, when it is spread out on top of the water, its surface is larger than it would have been had it remained uncovered. By and large, however, the covering of Ottofuel with sea water is believed to be beneficial.

The agreement between the observed transport rate of PGDN through sea water (7.8×10^{-5} g/hr/ft^2 at 22°C after 250 hours) and the calculated evaporation rate for a solution which contains 0.123 percent PGDN by weight (2.4×10^{-5} g/hr/ft^2 at 25°C) is remarkably good considering the uncertainties that existed with respect to the state of equilibrium and diffusion conditions. (The slightly higher rate of diffusion measured experimentally may be due to a small amount of convective transport.) If, however, the diffusion-controlled transport of material through the column had been seriously disturbed, the transport rate would have been considerably different.

CONCLUSIONS AND RECOMMENDATIONS

A steady-state evaporation rate of 0.18 g/hr/ft^2 at 25°C should be adopted for Ottofuel II and an evaporation rate of 0.52 g/hr/ft^2 should be used for calculations referenced to a temperature of 35°C. These values agree well with calculated and observed evaporation rates for PGDN, if the initial high rate of evaporation of Ottofuel II is disregarded.

Ottofuel II contains, in addition to a trace of water, another unidentified impurity estimated at less than 1 percent by weight. This impurity is more volatile than the other constituents of Ottofuel II, and causes the evaporation rate of the fuel to be higher during the first several hours than after a period of 4 hours. This initially higher rate was observed both in samples used as received and in samples dried over Drierite.

Ottofuel II, when shaken up with sea water until the sea water is saturated with it, forms a solution that contains 0.123 percent by weight of PGDN at 22-25°C. Because PGDN evaporates out of sea water faster than it diffuses into it, stagnant sea water never becomes saturated with Ottofuel. Any layer of sea water, regardless of its depth, will slow down the Ottofuel/PGDN evaporation rate by a factor of 1.32×10^{-4} at 22°C compared to the rate for Ottofuel/PGDN as a dry liquid. The diffusion rate of Ottofuel through a stagnant layer of sea water has been observed to be 7.8×10^{-5} g/hr/ft^2 at 22°C. This is in good agreement with a rate calculated by taking the observed weight loss into air (at 25°C) and multiplying it by the factor 1.32×10^{-4}, which yields 2.8×10^{-5} g/hr/ft^2.

A 1-square-foot spill of Ottofuel at 25°, covered completely with sea water and enclosed in 1 cubic meter of air, causes that cubic meter to contain about 0.004 ppm of Ottofuel after 1 hour if the vapor is distributed homogeneously. Similarly, that cubic meter of air over a 1-square-foot spill of Ottofuel not covered with sea water would contain 26 ppm of Ottofuel after 1 hour. This reduction of the concentration by a factor of 1.32×10^{-4} should be of great assistance in lessening the effects of an Ottofuel spill.

Evaporation rates that have been calculated or observed experimentally should not be used by themselves to calculate the ventilation rates of spills that have been covered with sea water. The evaporation rate of such spills is governed by the effective concentration of Ottofuel at the water/air interface, and will be small only if no undissolved Ottofuel floats on the surface.

The addition of a detergent to the sea water used in covering an Ottofuel spill may be beneficial, although this was not experimented with. A non-foaming detergent would probably be better for this purpose than a foaming one, since the former would sink the Ottofuel by reducing the surface tension of the water while possibly not concentrating Ottofuel in the bubbles.

It is realized that this report may generate interest in a "total analysis" of Ottofuel. It may be desirable to have this done, but only if the future of Ottofuel as a torpedo propellant warrants the effort.

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APPENDIX A

AN ELECTROANALYTICAL METHOD FOR THE QUANTITATION OF PROPYLENE GLYCOL DINITRATE IN SEA WATER*

Polarographic techniques have not been used routinely for organic analysis, primarily because the classical dc polarographic method is insensitive to trace amounts, and because most analysts are unaware of the potential and scope of the relatively new pulse polarographic techniques. Many organic compounds contain groupings which are amenable to direct polarographic analysis. The nitrate ester PGDN falls into this class and the use of differential pulse polarography (DPP) offers an accurate and convenient route for its analysis.

Studies of the reduction of simple nitrate esters[12, 13] at the Dropping Mercury Electrode (DME) have revealed a two-electron reduction wave for mononitrate esters. Examination of polynitrate esters[17] is in agreement with this and shows a two-electron transfer per nitrate ester group. All investigators have reported the reduction to be diffusion-controlled and that the diffusion current and half-wave potential are independent of pH (between pH 3 to 13 in ref. 12 and pH 4 to 11 in ref. 17). Gogis and Hamrick[24] have developed a polarographic determination for trace amounts of PGDN.

Small concentrations of propylene glycol dinitrate in sea water can be determined directly by means of DPP. The method described in NUSC TM No. SB322-4546-72 is rapid; and experience has shown that the analysis can be performed without having to resort to lengthy extraction procedures to remove the nitrate ester from the sea water. Concentrations as small as 0.118 ppm (7.1×10^{-7} moles/liter) have been measured. The method works best within a pH range of 6.50 to 10.08. The concentration of the nitrate ester should, if necessary, be adjusted by dilution to be no higher than 80 ppm. The DPP technique yields data which are easy to quantitate and can also be used for qualitative identification (the half-wave potential is unique for a given species in a given system).

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* A full treatment of the method is available in NUSC TM No. SB322-4546-72 of 1 December 1972 by Walter G. Cox.

APPENDIX B

CALCULATION OF THE EVAPORATION RATE OF PGDN*

Fick's first law:

$$J = -D \frac{dc}{dx}$$

where J is the transport rate ($g/cm^2/sec$), D is the diffusion coefficient (cm^2/sec), dc is the change in concentration (g/cm^3), and dx is the distance (cm) between points where concentrations are measured.

The formula (based on Fick's law) for mass transfer from a sphere into a stagnant fluid is:

$$N_A = \frac{2D_V\ (p_i - p)}{DRT},$$

where N_A is expressed in lb-moles/hr/ft^2 (the evaporation rate (E_A) = $N_A \times 454 \times 167$ g/hr/ft^2),
D_V is the molecular diffusivity in air (ft^2/hr),
p_i is the vapor pressure of diffusing gas at the boundary (atmospheres),
p is the partial pressure of diffusing gas in the main stream,
D is the diameter of the sphere (ft) — the sphere has the same area as the petri dish used in the NUSC experiments,
R = 0.728 ft^3 atm/lb-mole/°R, and
T = °R (°R = °F + 460).

For pure PGDN:
Mol. weight = 167
p_i = 0.098 mm at 25°C
D_V = 0.403 ft^2/hr at 25°C (calculated from collision diameter of molecules of similar molecular weight)
D = 0.148 ft

$$E_A = \frac{2 \times 0.403\ (0.098-0) \times 454 \times 167}{0.728 \times 0.148 \times 537 \times 760} = \frac{0.135g}{hr/ft^2}.$$

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* From Langmuir[2].

APPENDIX C

CALCULATION OF THE TRANSPORT RATE OF PGDN THROUGH SEA WATER (AT 22°C AFTER 250 HOURS)

Fick's first law:

$$J = -D \frac{dc}{dx} ,$$

where J is the transport rate (g/cm^2/sec), D is the diffusion coefficient* (6×10^{-6} cm^2/sec) of PGDN in sea water, dc is the change in concentration (g/cm^3), and dx is the distance (cm) between sampling points. Thus:

$$J = \frac{40.7 \times 10^{-6}\ \text{g} \times 6 \times 10^{-6}\ \text{cm}^2}{\text{cm}^3 \times 10.48\ \text{cm} \times \text{sec}} = \frac{2.33 \times 10^{-11}\ \text{g}}{\text{cm}^2 \times \text{sec}}$$

$$= \frac{2.33 \times 10^{-11} \times 3600\ \text{sec} \times 930\ \text{cm}^2}{\text{cm}^2 \times \text{sec} \times \text{hour} \times \text{ft}^2} = \frac{7.8 \times 10^{-5}\ \text{g}}{\text{hr/ft}^2} .$$

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* From Whitnack et al.[17]

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13. ABSTRACT

The factor which controls the buildup of Ottofuel vapor in the atmosphere of any environment in which Ottofuel is spilled is the rate of evaporation of material from the spill. In order to obtain more information on the quantitative aspects of the problem, the evaporation rate of Ottofuel II at 25–27°C was determined by weight loss measurements in a nitrogen atmosphere. After an initial period of 3–4 hours, the evaporation rate was found to be 0.18 $g/hr/ft^2$ of the spill. An initially higher weight loss is attributed in part to water that was dissolved in the Ottofuel and in part to the presence of a volatile impurity that could not be removed by drying the liquid with calcium sulfate.

The observed evaporation rate was in good agreement with the rate of 0.52 $g/hr/ft^2$ reported for propylene glycol dinitrate (PGDN) at 35°C, and with the rate of 0.135 $g/hr/ft^2$ calculated for PGDN at 25°C using Langmuir's method of calculating the evaporation rate of liquids into a stagnant atmosphere. (PGDN is the main ingredient of Ottofuel – 76 percent by weight.)

A new technique, based on differential pulse polarography, was developed for the quantitation of PGDN in sea water. This technique was used to follow the diffusion of Ottofuel through a stagnant layer of sea water. After 250 hours, the transport rate of Ottofuel through sea water was found to be 7.8×10^{-5} $g/hr/ft^2$. The saturation value of PGDN was found to be 0.123 percent by weight in sea water at 22°C. The agreement between the observed transport rate and the calculated evaporation rate from a saturated solution is good.

Under favorable circumstance (i.e., complete coverage), the covering of an Ottofuel spill with sea water reduces the evaporation rate by a factor of 10^{-4}. Values between 2.4×10^{-5} $g/hr/ft^2$ and 0.18 $g/hr/ft^2$ at 25°C will be observed if the Ottofuel is not completely covered, but floats on top of the water as it sometimes does despite its great density.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Diffusion-Controlled Processes						
Ottofuel Composition						
Propylene Glycol Dinitrate						
Polarography						