# A Characteristic Property of Whale Oils Concerning the Absorption of Gases III 

On the Absorption of Oxygen by Whale Oils

Yasutaro ISHIKAWA<br>Department of Fisheries, Faculty of Fisheries and Animal Husbandry, Hiroshima University, Fukuyama<br>(Text-figs. 1-9; Tables 1-4)

## INTRODUCTION

In recent publications ${ }^{1,2)}$, ISHIKAWA has reported on the absorption of carbon dioxide and of nitrogen by a variety of oils and oily substances, including sperm waxes and vegetable oils. In these papers, it has been indicated that oils and oily matters can absorb greater amount of the gases than water does: oils and oily matters absorb some twice as much carbon dioxide, and 5 to 7 times as much nitrogen as the water, at the same pressure and temperature. As for the absorption rate, it has been pointed out that the earliest absorption rate for carbon dioxide is generally smaller in oils than in water, but some waxes show the earliest absorption rate to be comparable with that in water. With the absorption of nitrogen, the majority of the oily materials investigated surpasses water in the absorption rate at early stages. The most remarkable is the fact that whale waxes are greatly superior in this property, compared with vegetable oils and other materials.

These findings have led me to some speculation, which is related to the respiration of animals. Oily substances (especially sperm waxes), which are capable of absorbing carbon dioxide and nitrogen in greater amount and, in some cases, at quicker rates as compared with water, might be playing a role in the respiratory economy of some animals-whether in the transport of the gases between tissues, or in the gas-exchange through body surface. As already has been suggested in the earlier paper, ${ }^{1)}$ adequate explanation has not been given to the presence of a large amount of wax only in sperm whale, which is known to be able to stay submerged much longer than other whales.

The present paper is concerned with the absorption of oxygen by various oily materials and water, and offers the results of measurements on solubility and absorption rate at constant temperature of $35^{\circ} \mathrm{C}$. and at variable pressures.

Since the classical study of HENRY who was followed by BUNSEN and OSTwALD, the solubility of various gases in liquid solvents has been studied by numerous investigators. However, the measurements have been made chiefly with water as a solvent. Works with organic solvents are rather wanting. J. HORIUCHI ${ }^{3}$ ) studied the solubility of hydrogen, nitrogen and 11 other gases in numbers of organic solvents of relatively low molecular weights.

As far as my deficient knowledge is concerned, works on the solubility of gases in
oils, particularly those regarding the absorption rates in gas-liquid systems, are scarce. A. R. BEHNKE ${ }^{4}$, however, studied the solubility of several gases in olive oil, for the medical purpose. According to his paper, olive oil can dissolve 4.9 times as much oxygen as the water does at $38^{\circ} \mathrm{C}$. and ordinary pressures. P. S. SChAFFER and H. S. HALLER ${ }^{5}$ ) also investigated the solubility of hydrogen, oxygen, air, nitrogen and carbon dioxide in butter oil, cottonseed oil and lard.

## EXPERIMENTAL

Material. - The materials for the present study were the same as those used in the previous work ${ }^{2)}$ of this series: namely, sperm oil from spermaceti, sperm whale body oil, blue whale oil, olive oil, camellia oil, castor oil, liquid paraffin and distilled water. The first two are characterized by containing a large quantity of wax, but the other oils have no such peculiarity and consist of usual glycerides as seen from Table 1.

Table 1. Physical and chemical properties of the materials.

| Material | Specific gravity $\left(D_{4}^{35}\right)$ | $\begin{aligned} & \text { Refractive } \\ & \text { index } \\ & \left(n_{D}^{20}\right) \\ & \hline \end{aligned}$ | $\begin{gathered} \text { Acid value } \\ \text { (mg. } \mathrm{KOH} / \mathrm{g} . \text { oil) } \end{gathered}$ | $\begin{gathered} \text { Saponifn. } \\ \text { value } \\ \text { (mg. } \mathrm{KOH} / \mathrm{g} . \text { oil } \text { ) } \end{gathered}$ |  | Unsaponifd. matter <br> (\%) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Sperm oil | 0.865 | 1.4526 ( $n_{D}^{40}$ ) | 1.10 | 147.4 | 59.7 | 37.5 |
| Sperm whl. body oil | 0.866 | 1.4567 (/1) | 0.25 | 138.5 | 80.3 | 31.8 |
| Blue whl. oil | 0.906 | 1.4730 | 0.83 | 196. 1 | 112.9 | 0.52 |
| Olive oil | 0.908 | 1.4713 | 0.052 | 195.3 | 94.3 | 0.52 |
| Camellia oil | 0.903 | 1.4684 | 1.32 | 193.0 | 75.3 | 0.28 |
| Castor oil | 0.951 | 1.4790 | 0.70 | 188.7 | 77.3 | 0.35 |
| Liquid paraffin | 0.873 | 1. 4813 | - | - | - | - |
| Dist. water | 0.994 | 1.3330 | - | - | - | - |

The three kinds of whale oils were kindly supplied by the Taiyo Whaling Co., Ltd.; the camellia oil was extracted from the seeds of camellia (Camellia japonica L.) in our laboratory; the other oils and liquid paraffin were commercial preparations of Japan Pharmacopoia grade. Before and during the experiment, sufficient care was taken for preserving the materials: they were filled with nitrogen gas and kept in the cold storage. Physical and chemical properties of the materials are given in Table 1.

Apparatus and Procedure. - The apparatus and procedure employed were thoroughly detailed in one ${ }^{1)}$ of the preceding reports, and only brief description is given below. Throughout the present study, every measurement was carried out with 100 g . of the materials at constant temperature of $35 \pm 0.05^{\circ} \mathrm{C}$. (checked with an electric resistance thermometer). The temperature control had to be very rigid, because of the great sensitivity of volume change of the gas to changing temperatures. This was accomplished by means of a thermo-regulator connected with an electronic tube relay. With every material, measurements were made at three pressure-levels, starting with pressures a little higher than 1,2 and 3 atm . respectively. The deaeration preceding every absorption test was performed in the same way as was described in the earlier paper ${ }^{1)}$. That is, the major part of the deaeration took place in a boiling water bath at a reduced
pressure below $1 \mathrm{~mm} . \mathrm{Hg}$ during a period more than twice as long as it took in the subsequent absorption test. Following this, the material in a pressure-bottle was left standing at the same reduced pressure in a large thermostat (ca. 70 1.) at $35 \pm 0.05^{\circ} \mathrm{C}$. for an hour, for the purposes of permitting the thermal equilibrium between the inside and the outside of the bottle and effecting further deaeration. Oxygen gas was then introduced into the pressure-bottle from a gas reservoir, which had been maintained at $35 \pm 0.05^{\circ}$, until a desired reading of the mercury manometer was obtained. The manometer employed was of an open type, 2.2 m . in height, graduated at mm . intervals and equipped with a magnifying lens.


Text-fig. 1. Relation of solubility of oxygen to pressure.- From top to bottom:
(T) sperm oil ; $\square$ sperm whale body oil; $\triangle$ liquid paraffin; olive oil; $\times$ blue whale oil ; $\square$ camellia oil ; $\mathbf{\Delta}$ castor oil; $\bigcirc$ distilled water.

The mechanical arrangements to effect the constant movement of the pressure-bottle and other experimental conditions were already described in the previous paper. ${ }^{1)}$ The absorption velocity and other data reported in this paper are therefore completely comparable with those in the earlier works. ${ }^{1), 2)}$

Computation of the Absorbed Volume of the Gas. - In the present study as well as in the earlier papers, ${ }^{1,2)} \Delta P$, the decrease in pressures caused by absorption, was punctually measured at constant volume and constant temperature. So the absorbed
volume of the gas was not directly known from the experiment. This volume was computed from the value of $\Delta P$ in the following manner.

Suppose that the pressure be kept at


Text-fig. 2. Plot of $\Delta V_{0}$ and $\log \left(A-\Delta V_{0}\right)$ against $t$ (Distilled water). - Pressure levels (in $\mathrm{mm} . \mathrm{Hg}$ ) from top to bottom: $2364.9 \sim$ 2354.2 (circles), $1650.1 \sim 1642.2$ (triangles), 929.2~924.9 (squares). an initial constant value throughout the whole process of an absorption test by some device. Then the decrease in volume will occur at this constant pressure, instead of the decrease in pressure at constant volume. This assumptive decrease in volume of the gas phase should represent the volume of the gas absorbed by a liquid material.

If we write $P$ and $(P-\Delta P)$ for the pressure at time 0 and $t$ respectively, and $V$, for the efficient volume of the gas phase, $(P-\Delta P) V$ must be equal to $P(V-\Delta V)$ from the well-known relation as $P V=$ const. for a given amount of a gas, where $\Delta V$ represents the decrease in volume of the gas at pressure $P$. Thus we have

$$
\Delta V=\frac{V}{P} \Delta P .
$$

Furthermore we can write

$$
\Delta V_{0}=\frac{T_{0}}{T} \frac{1}{P_{0}} V \cdot \Delta P,
$$

where $\Delta V_{0}$ is the decrease in volume of the gas phase (i. e., the absorbed volume of the gas) reduced to standard state, $T_{0}=273^{\circ} \mathrm{K} ., T=308^{\circ} \mathrm{K} .\left(35^{\circ} \mathrm{C}.\right), P_{0}=760 \mathrm{~mm} . \mathrm{Hg}$ and $V$ is the real volume of the gas phase, that is, the whole internal capacity of the pressure-bottle (estimated at $684 \pm 0.5 \mathrm{cc}$., including the inner space of rubber and glass tubings) minus the volume* of the liquid material taken into the bottle.

In the last formula, $\frac{T_{0}}{T} \frac{1}{P_{0}}$ is the common constant independent of the materials, and $V$ is definite for a fixed amount of a given material. Thus we have $\Delta V_{0}$ by multiplying $\Delta P$ by these constant factors, for a given amount of a material.

## RESULTS

Solubility of Oxygen. - Figure 1 gives the solubility of oxygen plotted against

[^0]pressure (final pressure) for various materials. The solubility is expressed in terms of the volume (in cc.) of the gas per 100 g . of a solvent. Each solubility value was determined from an absorption curve (cf. Figures 2-9), which was traced experimentally till the saturation was nearly reached, by extrapolating the curve to the infinite value of time and by applying further such graphical operations as will be later noted. It is clear from Figure 1 that the solubility is the linear function of pressure in every material, i.e., it obeys Henry's law on the diluted solution of gas. So, in the present experiments, the relationship can be stated by $A=c P$, where $A$ is solubility, $P$, pressure and $c$, the pressure-gradient of solubility.


Text-fig. 3.(left) Plot of $\Delta V_{0}$ and $\log \left(A-\Delta V_{0}\right)$ against $t$ (Sperm oil).-Pressure levels (in $\mathrm{mm} . \mathrm{Hg}$ ) from top to bottom: $2365.7 \sim 2301.5$ (circles), 1649.3~1603.7 (triangles), 931.9~906.5 (squares).
Text-fig. 4.(right) Plot of $\Delta V_{0}$ and $\log \left(A-\Delta V_{0}\right)$ against $t$ (Sperm whale body oil).-Pressure levels (in $\mathrm{mm} . \mathrm{Hg}$ ) from top to bottom: $2365.0 \sim 2302.5$ (circles), $1653.3 \sim 1609.5$ (triangles), $932.9 \sim 907.3$ (squares).

For gases of smaller solubilities such as oxygen and nitrogen, the linear relationship between solubility and pressure is likely to hold upto fairly high pressures. As for the case at very high pressures, J. BASSET and M. DODE ${ }^{6)}$ reported the existence of a maximum in the solubility-pressure curve, in studying the absorption of nitrogen in water at ultrahigh pressures from 500 to $4,500 \mathrm{~kg} / \mathrm{cm}^{2}$. They were followed by I. R. Krichevsky, ${ }^{7}$ ) who also ascertained the presence of a solubility maximum in his investigation.

Table 2. Solubility of oxygen in various materials

| Material | $A / P(\mathrm{cc} . / 100 \mathrm{~g} ., \mathrm{cm} . \mathrm{Hg})$ |  |  |
| :--- | :---: | :---: | :---: |
|  | $\mathrm{O}_{2}$ | $\mathrm{~N}_{2}{ }^{*}$ | $\mathrm{CO}_{2}{ }^{*}$ |
| Sperm oil | 0.190 | 0.121 | 1.76 |
| Sperm whale body oil | 0.192 | 0.117 | 1.59 |
| Blue whale oil | 0.171 | 0.098 | 1.53 |
| Olive oil | 0.175 |  | (Fin whale oil) |
| Camellia oil | 0.167 | 0.110 | 1.60 |
| Castor oil | 0.116 | 0.093 | 1.53 |
| Liquid paraffin | 0.179 | 0.098 | 1.40 |
| Distilled water | 0.0315 | 0.0175 | 1.10 |

Table 2 shows the values of $A / P$ for oxygen in comparison with those for nitrogen and carbon dioxide. It will be seen from both Figure 1 and Table 2, that no remarkable difference exists between the solubilities of oxygen in various oily materials including liquid paraffin, and that the solubility in water, however, differs greatly therefrom.


Text-fig. 5. Plot of $\Delta V_{0}$ and $\log \left(A-\Delta V_{0}\right)$ against $t$ (Blue whale oil).——Pressure levels (in $\mathrm{mm} . \mathrm{Hg}$ ) from top to bottom: 2365.7~2307.7 (circles), 1643.9~1604.3 (triangles), 933.9~911.3 (squares).

[^1]The value of $A / P$ ranges from 0.17 to $0.19 \mathrm{cc} . / 100 \mathrm{~g} ., \mathrm{cm} . \mathrm{Hg}$ in the oily materials except castor oil (the value in which is 0.116 ), wihle the value is $0.0315 \mathrm{cc} . / 100 \mathrm{~g} ., \mathrm{cm}$. Hg in water. Namely, the oily materials in general can absorb, at every tension and at $35^{\circ}, 5.5$ to 6 times as much oxygen as the water does.

Some comparison may be made here. From Table 2, nitrogen gas is 5.5 to 7 times as soluble in the oily substances as in water, with the exception of castor oil. The oilwater solubility ratio of nitrogen is therefore slightly greater than that of oxygen in all the cases. On the other hand, the solubilities of carbon dioxide in oily substances, taking the solubility of the gas in water as unity, are far smaller, ranging from 1.7 to 2.0 .

Another comparison can be made transversely in Table 2. The values of the solubility ratio of the three gases $\left(\mathrm{CO}_{2}: \mathrm{O}_{2}: \mathrm{N}_{2}\right)$ in various oily materials are as follows: sperm oil ( $14.5: 1.57: 1$ ); sperm whale body oil (13.6: 1.64: 1); blue whale oil ( $15.6: 1.74$ : 1) ; olive oil (14.5: $1.59: 1$ ); camellia oil ( $16.5: 1.80: 1$ ); castor oil (19.4:1.61: 1); and liquid paraffin (11.2: $1.83: 1$ ). It may be said that the ratio averages 15: 1.7:1 in the oily materials, excluding castor oil and liquid paraffin. Whereas the solubility ratio of the three gases is $45: 1.8: 1$, in water.

In summary, the following points have been clarified on the solubility of gases: (1) In every material examined, the solubility of oxygen is directly proportional to the pres-


Text- fig. 6. Plot of $\Delta V_{0}$ and $\log \left(A-\Delta V_{0}\right)$ against $t$ (Olive oil).——Pressure levels (in mm. Hg ) from top to bottom: 2357.8~2299.5 (circles), 1653.0~1610.7 (triangles), 927.2~903.7 (squares).
sure, at such pressures as were dealt with in this work. And this is also the case with nitrogen and carbon dioxide. (2) The oil-water solubility ratio of oxygen is slightly smaller than that of nitrogen in all the materials studied. (3) The solubility ratio of the three gases in the one oily material is conserved almost invariably in the other oily materials, in accordance with the classical view of JUST ${ }^{8)}$. (4) The value of this ratio is greatly varied in water, chiefly in the point of the solubility of carbon dioxide.

The extraordinary great relative solubility of carbon dioxide in water may be ascribed to the fact that carbon dioxide can easily undergo hydration and the hydrated form is readily soluble in water.

Table 3. Values of $\alpha$ and $\alpha A / P$ for oxygen in various materials

| Material | $\begin{aligned} & \text { Pressure-level } \\ & \quad(\mathrm{mm} . \mathrm{Hg}) \end{aligned}$ | $\begin{gathered} \alpha \\ \left(\min ^{-1}\right) \end{gathered}$ | $\begin{gathered} \alpha A / P \\ (\mathrm{cc} . / 100 \mathrm{~g} ., \mathrm{cm} . \\ \mathrm{Hg}, \text { min. }) \end{gathered}$ | $\alpha A / P$ for $\mathrm{N}_{2}{ }^{* *}$ (cc./100 g., cm. $\mathrm{Hg}, \mathrm{min}$.) | $a^{\prime} b / P$ for $\mathrm{CO}_{2}{ }^{* *}$ (cc./100 g., cm. Hg. min.) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Water | $\begin{gathered} 2364.9 \sim 2354.2^{*} \\ 1650.1 \sim 1642.2^{2} \\ 929.2 \sim 924.9 \end{gathered}$ | 0.083 | $2.61 \times 10^{-3}$ | $2.65 \times 10^{-3}$ | $540 \times 10^{-3}$ |
| Sperm oil | $\begin{gathered} 2365.7 \sim 2301.5 \\ 1649.3 \sim 1603.7 \\ 931.9 \sim 906.5 \end{gathered}$ | 0.097 | 18.4 " | 18.6 " | 540 /" |
| Sperm wh. body oil | $\begin{gathered} 2365.0 \sim 2302.5 \\ 1653.3 \sim 1609.5 \\ 932.9 \sim 907.3 \end{gathered}$ | 0.082 | 15.7 / | 13.3 /" | 440 " |
| Blue whale oil | $\begin{gathered} 2365.7 \sim 2307.7 \\ 1643.9 \sim 1604.3 \\ 933.9 \sim 911.3 \end{gathered}$ | 0.038 | 6.50 ॥ | 7.94 / | 300 " (Fin whale oil) |
| Olive oil | $\begin{gathered} 2357.8 \sim 2299.5 \\ 1653.0 \sim 1610.7 \\ 927.2 \sim 903.7 \end{gathered}$ | 0.041 | 7.18 /" | 6.16 /" | 140 / |
| Camellia oil | $\begin{gathered} 2365.0 \sim 2309.7 \\ 1652.3 \sim 1612.3 \\ 932.2 \sim 908.6 \end{gathered}$ | 0.036 | 6.01 /" | 3.26 /" | 100 / |
| Castor oil | $\begin{gathered} 2366.0 \sim 2327.5 \\ 1642.3 \sim 1615.0 \\ 977.4 \sim 960.8 \end{gathered}$ | 0.010 | 1.16 /" | 0.55 " | 45 " |
| Liquid paraffin | $\begin{gathered} 2363.8 \sim 2301.7 \\ 1650.8 \sim 1608.2 \\ 933.4 \sim 910.0 \end{gathered}$ | 0.019 | 3.40 " | 2.06 / | 76 " |

Absorption Velocity of Oxygen. - Figures 2 to 9 give the oxygen absorption curves in various materials at different pressure levels. Every diagram comprises not only $\Delta V_{0}-t$ curves but also $\log \left(A-\Delta V_{0}\right)-t$ curves. In every Figure, each equivalent pair of $\Delta V_{0}$ and $\log \left(A-\Delta V_{0}\right)$ is represented by hollow and solid symbols similar in shape. Here $A$ denotes the solubility of the gas in a liquid material. The value of $A$ was determined as follows (cf. previous paper ${ }^{2}$ ). The first estimated value of $A$ was obtained from a $\Delta V_{0}-t$ curve (which was determined as far as the saturation was almost reached). However, if this value were taken too small, the curve of $\log \left(A-\Delta V_{0}\right)$ obtained will show

[^2]a tendency to bend downwards more and more with increase of $t$, and vice versa. By utilizing this tendency, one could find the proper value of $A$. The values of $A$ which already appeared in the preceding section were so determined.

It will be seen from Figures 2 to 9 that the following equation holds for every series of measurements:

$$
\begin{equation*}
\Delta V_{0}=A\left(1-e^{-\alpha t}\right) . \tag{1}
\end{equation*}
$$

The value of $\alpha$ was computed for each curve by the method of averages, using the formula derived from Equation (1),

$$
\begin{equation*}
\alpha=2.303 \frac{n \log A-\sum_{1}^{n} \log \left(A-\Delta V_{0}\right)}{\sum_{1}^{n} t} . \tag{2}
\end{equation*}
$$

Thus we had three different values of $\alpha$ for each material, corresponding to the three pressure levels. However, the three values of $\alpha$ obtained within a given material were found almost much the same, irrespective of the pressure levles. At least, we did not find any correlation between the magnitude of $\alpha$ and pressure level. For this reason, a single value of $\alpha$ was shown for each material in Table 3.


Text-fig. 7. Plot of $\Delta V_{0}$ and $\log \left(A-\Delta V_{0}\right)$ against $t$ (Camellia oil).——Pressure levels (in mm. Hg ) from top to bottom: $2365.0 \sim 2309.7$ (circles), $1652.3 \sim 1612.3$ (triangles), $932.2 \sim 908.6$ (squares).

Differentiation of Equation (1) gives

$$
\begin{equation*}
\frac{d}{d t}\left(\Delta V_{0}\right)=\alpha\left(A-\Delta V_{0}\right) . \tag{3}
\end{equation*}
$$

It states that the absorption velocity is proportional to $\alpha$, as well as to the solubility $A$ (which is characteristic of a given combination of solute and solvent at a given pressure and temperature) minus the volume of the gas absorbed up to the time $t$.

Therefore, the value of $\alpha A / P$ is of importance in broad comparison of the early absorption rate in various liquid materials. As a matter of fact, it represents the initial absorption velocity itself. With progress of time, the discrepancy between this value and true absorption rate becomes greater. However, we are particularly interested in the absorption rate at the early stages, when we inquire into whether the oily matters in animal tissues can possibly be linked into the system of gas exchange. In Table 3, the values of $\alpha$ and $\alpha A / P$ for oxygen are given in comparison with those of $\alpha A / P$ for nitrogen and $a^{\prime} b / P$ (to be explained later) for carbon dioxide.

In preceding section, it has been pointed out that the solubility of oxygen does not differ so greatly in different oils and oily matters, though it is markedly smaller in water. On the contrary, it can be seen from Table 3 that the rate of oxygen absorption differs greatly among the oily substances. $\alpha$ is great in the decreasing order of sperm oil, water, sperm whale body oil, olive oil, blue whale oil, camellia oil, liquid paraffin and castor oil. This orderly relationship holds good with regard to $\alpha A / P$ as well, except that water falls in its rank from the second to the last but one. $\alpha A / P$ for sperm oil (the greatest) is some 16 times as great as that for castor oil (the smallest), and about 7 times as great as that for water.

The aforementioned order regarding the initial absorption rate $(\alpha A / P)$ for oxygen coincides with the order concerning the $\alpha A / P$ for nitrogen, except that the ranks of blue whale oil and olive oil are reversed. $\alpha A / P$ for oxygen is $6.50 \times 10^{-3}$ in blue whale oil and $7.18 \times 10^{-3}$ in olive oil, whereas $\alpha A / P$ for nitrogen is $7.94 \times 10^{-3}$ and $6.16 \times 10^{-3}$, respectively in the two oils. However, it seems that further investigations are necessary in order to determine whether this inversion is characteristic of the two oils in question.

With carbon dioxide, the earliest absorption rate $\left(a^{\prime} b / P\right)$ is great in the order of water, sperm oil, sperm whale body oil, fin whale oil, olive oil, camellia oil, liquid paraffin and castor oil. This order is in agreement with that of $\alpha A / P$ for nitrogen, except that water ranks first instead of sixth (cf. Table 3). In the case of carbon dioxide, we have used the following formula in lieu of Equation (3),

$$
\begin{equation*}
\frac{d}{d t}\left(\Delta V_{0}\right)=a^{\prime} b t^{b-1} \tag{4}
\end{equation*}
$$

Consequently, it is not possible to compare the initial absorption rates of the three gases in terms of $\alpha A / P$. However, in Formula (4) $a^{\prime} b$ represents the absorption rate when $t=1$; that is, it represents the absorption rate one second after the outset, if the second is used as the unit of time. So that, broad comparison can be made between the values of $a^{\prime} b / P$ and $\alpha A / P$, although the former is of course somewhat smaller than the latter.


Text-fig. 8. Plot of $\Delta V_{0}$ and $\log \left(A-\Delta V_{0}\right)$ aginst $t$ (Castor oil). - Pressure levels (in $\mathrm{mm} . \mathrm{Hg}$ ) from top to bottom: $2366.0 \sim 2327.5$ (circles), 1642.3~1615.0 (triangles), $977.4 \sim 960.8$ (squares).

Finally, if we call for the present, both $\alpha A / P$ and $a^{\prime} b / P$ "early absorption rate", neglecting a minute difference between them, the following important conclusions are obtained from Table 3: (1) early absorption rate for oxygen nearly agrees with that for nitrogen in size in most of the materials, and (2) early absorption rate for carbon dioxide is of a very different order: it is 20 to 30 times as great as that for oxygen or nitrogen in most of the oily matters, and 200 times as great, in water.

Occurrence of Oxidation - It is interesting to know whether the oils were oxidized in the course of the absorption tests. The absorption tests reported in this paper were carried out under such conditions that the oil was exposed to the oxygen atmosphere of $1-3 \mathrm{~atm}$. at $35^{\circ}$ for a certain period of time (liquid paraffin, 240 min .; castor oil, 360 min .; and the others, 80 to 180 min .). Throughout the period of exposure, the oils were subjected to constant shaking.

Table 4. Change of acid value and peroxide value of the oily materials

| Material | Acid value <br> (mg. $\mathrm{KOH} / \mathrm{g}$. oil) |  | Peroxide value <br> (mg. mol O$/ 1000 \mathrm{~g}$. oil) |  |
| :--- | :---: | :---: | :---: | :---: |
|  | Before exposure | After exposure |  | Before exposure |
| After exposure |  |  |  |  |
| Sperm oil | 1.10 | 0.93 | 12.03 | 12.58 |
| Sperm whl. body oil | 0.25 | 0.27 | 12.24 | 12.36 |
| Blue whale oil | 0.83 | 1.02 | 6.30 | 8.20 |
| Olive oil | 0.052 | 0.15 | 10.40 | 11.25 |
| Camellia oil | 1.32 | 1.50 | 6.47 | 7.20 |
| Castor oil | 0.70 | 0.81 | 3.80 | 4.75 |



Text-fig. 9. Plot of $\Delta V_{0}$ and $\log \left(A-\Delta V_{0}\right)$ against $t$ (Liquid paraffin).——Pressure levels (in $\mathrm{mm} . \mathrm{Hg}$ ) from top to bottom: $2363.8 \sim 2301.7$ (circles), $1650.8 \sim 1608.2$ (triangles), $933.4 \sim 910.0$ (squares).

The oxidation experiments were made as follows: A hundred grams of the material in the pressure-bottle were exposed to oxygen atmosphere of $236-237 \mathrm{~cm} . \mathrm{Hg}$, for three hours (in castor oil, 6 hrs.) at $35^{\circ}$, with the bottle constantly shaken. These conditions are almost identical with those of the absorption tests, taking the upper limits of the pressure and period. Before and after the exposure determination of the acid value and peroxide value was made with each material. Prior to the measurement of peroxide value, deaeration was undertaken at room temperature, until bubbles of gases were not appreciable.

It will be seen from Table 4 that acid value was scarcely changed in any of the materials. As for peroxide value, a considerable increase occurred in the blue whale oil; a little increase in olive oil, camellia oil and castor oil; and scarce increase in sperm oil and sperm whale body oil. From these results, it is inferred that oxidation may have taken place to some extent in our absorption tests. However, there is left much to be learnt in order to draw any definite conclusion on this problem.

## SUMMARY

1) Absorption of oxygen was studied with eight kinds of materials, i.e., distilled water, sperm oil, sperm whale body oil, blue whale oil, olive oil, camellia oil, castor oil and liquid paraffin.
2) Decrease in pressure, $\Delta P$, caused by absorption was measured punctually with lapse of time at constant volume and constant temperature of $35 \pm 0.05^{\circ} \mathrm{C}$. at variable pressure levels up to about 3 atm .
3) Decrease in volume was computed from $\Delta P$. It was reduced to standard state and designated by $\Delta V_{0}$, which represents the amount of oxygen absorbed by the liquid materials.
4) The solubility of oxygen was found to be directly proportional to pressure, namely, the relation $A=c P$, holds in every of the materials studied, where $A$ is solubility, $P$, pressure and $c$, the proportional constant.
5) The solubilities of oxygen in various materials were compared in terms of $A / P$. Within the oils and oily substances, the values of $A / P$ do not differ so greatly from each other and are 5.5 to 6 times as great as $A / P$ in water.
6) Some comparison was made between the value of $A / P$ for oxygen and that for nitrogen or carbon dioxide. The ratio of solubility of the three gases $\left(\mathrm{CO}_{2}: \mathrm{O}_{2}: \mathrm{N}_{2}\right)$ averages 15:1.7:1 in the oily materials, and is $45: 1.8: 1$ in water.
7) As for the absorption rate, the relation, $\Delta V_{0}=A\left(1-e^{-a t}\right)$, holds for the absorption of oxygen by each liquid material.
8) The initial absorption rate for oxygen was compared in terms of $\alpha A / P$. It is greater in waxes than in glycerides or in water. $\alpha A / P$ in sperm oil (the greatest) is 16 times as great as that in castor oil (the smallest) and some 7 times as great as that in water.
9) Comparison was made between the "early absorption rate" for oxygen and that for nitrogen or carbon dioxide. The early absorption rate for oxygen agrees with that for nitrogen in size in every material, but early absorption rate for carbon dioxide is of a very different order. It is 20 to 30 times as great as that for oxygen or nitrogen in the oily matters, and 200 times as great in water.
10) Experiments were made to ascertain whether oxidation of oils took place in the absorption tests.

## REFERENCES

1) Ishikawa, Y. 1956. Sci. Rep. Whale Res. Inst., No. 11: 191-213, June 1956.
2) Ishikawa, Y. 1958. Sci. Rep. Whale Res. Inst., No. 13: 309-21, Sept. 1958.
3) Horiuchi, J. 1931. Sci. Papers Inst. Phys. Chem. Res., 17: 125-256, 1931.
4) Behnke, A. R. Jr. 1941-42. Harvey Lectures, Ser. 37: 198-226, (1941-42).
5) Schaffer, P. S. and Haller, H. S. 1943. Oil and Soap, 20: 161-2, 1943.
6) Basset, J. and Dodé, M. 1936. Comp. rend. hebd. Séances Acad. Sci., 203: 775-7, 1936, (cited from Chem. Centr., 108: I, 511, 1937).
7) Krichevsky, I. R. 1937. J. Am. Ch. Soc., 59, 596, 1937.
8) Just, G. 1901. Z. phys. Chem., 37: 342-367, 1901.

[^0]:    * It must be considered that some volume expansion (dilatation) of the liquid phase will occur upon absorption of the gas. However, its quantity is probably so small as to be neglected in the calculations mentioned above.

[^1]:    * Computed from the earlier papers ${ }^{1)}$, 2).

[^2]:    * In the case of water, the values of pressures indicated here, are of the partial pressures of oxygen, namely, the saturated vapor pressure of dist. water at $35^{\circ}(42 \mathrm{~mm} . \mathrm{Hg})$ was subtracted from total pressure.
    ** Calculated from the earlier reports ${ }^{1 / 2)}$.

