A CHARACTERISTIC PROPERTY OF WHALE OILS CONCERNING THE ABSORPTION OF GASES II.

ON THE ABSORPTION OF NITROGEN BY WHALE OILS

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In a previous paper (Ishikawa, 1956), we have reported on the absorption of carbon dioxide by the oily substances, including whale oils, in which it has been established that the kinds of whale oils, especially the sperm oil from *spermaceti*, far exceed the vegetable oils, in the absorption velocity of carbon dioxide.

In this paper, tests were made with the absorption of nitrogen by several kinds of oily substances, not only on its solubility but also on the absorption velocity.

In connection with the present subject, reference may be made to a profound investigation pertaining to deep sea diving and aviation, in which Albert R. Behnke, JR. (1941-42) had found the solubility of various gases, including nitrogen, in olive oil and in water, at ordinary pressures and at 38°C. So that he had determined the oil-water solubility ratio of various gases. However, in his investigation, emphasis is laid upon the solubility of various gases, in a kind of oil. On the contrary, our present subject is to study the property of various kinds of oils, as to the absorption of nitrogen.

As a result of the present experiments, it was proved that the solubility of nitrogen in various materials, was rather small, compared to that of carbon dioxide. As for the absorption velocity, it has been suggested in the earlier report (Ishikawa, 1956) that a equation, $\Delta V_0 = A(1-e^{-\alpha t})$, will hold for the processes of this kind, if the process were subjected to constant pressure. In the case of carbon dioxide, however, the measurements were carried out not at constant pressure, but at constant volume. Furthermore the change of pressures caused by absorption was so great, owing to the great solubility of carbon dioxide, that the processes could not in any way, be regarded as such. Whereas, in the present experiments, they can be approximately regarded as at constant pressure, because of the small solubility of nitrogen. Consequently it seems fully probable that this equation may be valid for the processes, though they were carried out at constant volume, as well as in the previous work.

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Indeed, as a result, it was ascertained that this equation was valid, within the limits of experimental error, for any of the processes included. Details of analysis will be described later.

EXPERIMENTAL

Materials.—Three kinds of whale oils*, sperm oil from *spermaceti*, sperm whale body oil and blue whale oil were chosen. The first two are marked by containing of a large amount of wax. The other is one from a blue whale and the majority of it, is constituted from glycerides, as is clear from table 1. On the other hand, three kinds of vegetable oils, olive-, camellia- and castor oil were tested for the sake of comparison.

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF THE MATERIALS

Materials	Specific Gravity D_4^{35}	Index of Refraction n_D	Acid Value	Saponification Value	Iodine Value	Unsaponified Matter %
Water	0.994	—	—	—	—	—
Sperm Oil	0.858	1.4530 (35°)	0.65	147.8	54.9	34.2
Sperm Body Oil	0.865	1.4612 (35°)	1.23	138.5	72.8	31.8
Blue Whale Oil	0.907	1.4736 (35°)	0.52	195.7	101.8	0.36
Olive Oil	0.913	1.4631 (30°)	2.46	196.3	88.4	0.43
Camellia Oil	0.903	1.4692 (30°)	2.30	192.3	81.3	0.86
Castor Oil	0.967	1.4747 (25°)	2.16	188.7	87.4	0.46
Liquid Paraffin	0.874	—	—	—	—	—

Distilled water and liquid paraffin were also added as materials. The water which is the most important physiological matter, seems reasonable to be tested in comparison with oily substances. Liquid paraffin was chosen from another interest, for it is expected as a matter of poor absorption.

Physical and chemical properties of the materials used, were given in table 1.

Apparatus and Procedure.—Apparatus and procedure employed, have been fully described in the previous paper (Ishikawa, 1956), and only a brief description on essentials is given below.

In every measurement, 100 g. of a material was taken. With each material, the measurements were carried out under five pressure-lebels, i.e. under the pressure, near but a little higher than 1, 2 and 3 atmos. pressures respectively, and under every intermediate lebel.

Deaeration of the materials to be tested, was performed in the very same way as described in the earlier report (Ishikawa, 1956): Deaeration in boiling water bath, was followed by the deaeration in thermostat

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* Kindly supplied by the Taiyo Fisheries Co., Ltd.

of 35°C, until the temperature of the contents became constant. Nitrogen gas was then introduced from the gas-reservoir into the pressure-vessel, up to the desired pressures, for which operation 30 to 40 sec. elapsed.

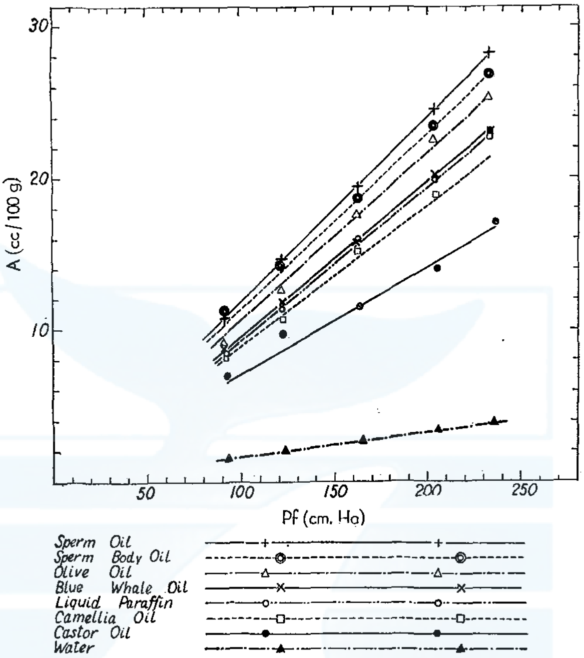

Fig. 1. Relation between probable solubility and pressure in various materials

The measurements were made at 35±0.05°C. The temperature was required to be closely constant, because the decrease in pressures caused by the absorption was relatively small, owing to the small solubility of nitrogen. On the other hand, with our apparatus, the temperature-gradient of pressure is 7.35 mmHg°C. This value is equivalent to about 5 cc/°C of the volume change. The fluctuation of the temperatures seems to be the largest error source.

Cooling effect which will occur on passing of the gas through the throttling cock, must be also a matter of consideration, on the same account. No preliminary test in this connection, has been done. But, granted that the process were entirely adiabatic, this effect can be estimated by the formula, $dT=\gamma\left(\frac{273}{T}\right)^{2}dP$, where dT is the decrease in temperatures which will occur when the difference of pressures between both sides, is dP, γ, a empirical constant, characteristic of the gas; it amounts to 0.3°C atmos. for nitrogen.

According to this, we have 0.2 to 0.4°C, for the decrease in temperatures, with our operations. However, considering that our processes are not adiabatic, but will occur rather isothermally, the net decrease in temperatures must be far smaller than the adiabatic one. Indeed our measurements were scarcely interfered by this effect, except that a slight irregularity of the decrease in pressures was recognized at the very earliest interval of the measurements (within 1 min. from outset).

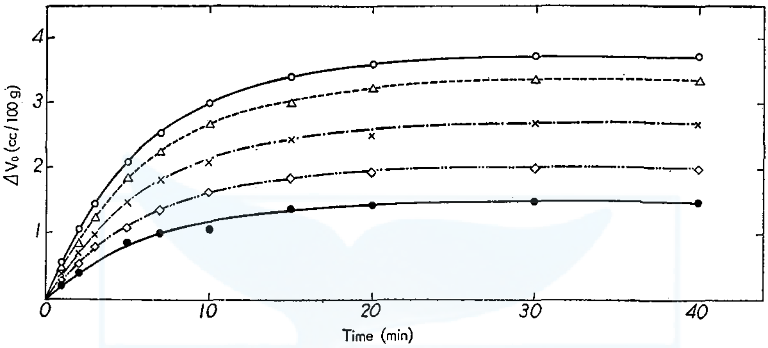

Fig. 2. Absorption curves for water under various pressure lebels.

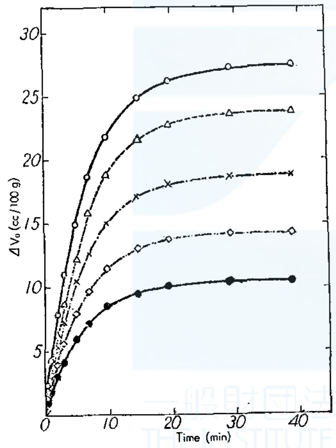

Fig. 3. Absorption curves for sperm oil under various pressure lebels.

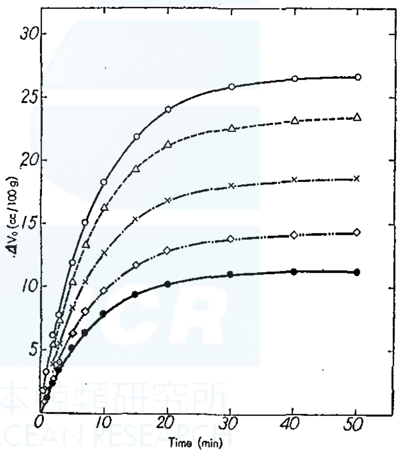

Fig. 4. Absorption curves for sperm body oil under various pressure lebels.

Mercury manometer employed, is of an open type, 2.2 m in height, graduated in mm interval, with a reading glass.

The mechanical conditions of the constant movement of the pressure-vessel and the other procedures were almost alike as those in the previous work (Ishikawa, 1956).

Obtaining of ΔV_0 from ΔP.—In the present work, as well as in the previous one, (Ishikawa, 1956) ΔP, the decrease in pressures caused by absorption, was punctually measured at constant volume. But, if supposed that the pressure were kept at initial constant value during the whole process, the decrease in volume will occur at this constant pressure and this decrease in volume at a initial definite P, must have been absorbed by the material, during the process.

This decrease in volume was obtained from ΔP, by the very same way as described in the earlier report (Ishikawa, 1956). The formula used, is

$$\Delta V_0 = \frac{T_0}{T} \frac{1}{P_0} V \cdot \Delta P \qquad (1)$$

where ΔV_0 is a decrease in volume (in cc) of a gas, reduced to standard state, $T_0=273°K$, $T=308°K$, $P_0=760$ mmHg, and V is the volume (684 cc) of the pressure-vessel less the volume of the material used. The formula (1) was deduced from the well known relation, $PV=\text{const.}$, for a given amount of a gas.

Thus, in the formula (1), $\frac{T_0}{T} \frac{1}{P_0}$ is a common constant disregarding the materials, and V is a constant regarding the capacity of the vessel and the amount of the material taken into the vessel. So we obtain ΔV_0 from ΔP, by multiplying ΔP with this constant factor, $\frac{T_0}{T} \frac{1}{P_0} V$, for a fixed amount of a material.

RESULTS

Solubility** of Nitrogen in Various Materials.—In figure 1, each curve gives the values of A's for each material, plotted against the final pressure, P_f. Symbol A, essentially represents the solubility of the gas in a material. It was obtained by some mathematical means, on the basis of $\Delta V_{0\,\max}$, the maximal volume of the gas absorbed. Upon the method, by which, A was obtained, we will describe in the next chapter. At any rate, there exists no great difference between A and $\Delta V_{0\,\max}$, for our experiments, where the measurements were made so long till the saturation was practically reached.

In figure 1, it is corollary that every curve must pass the origin, and therefore it takes a form reading

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** The solubility is expressed in terms of the volume (in cc.) of the gas per 100 g. of a material, when the latter has absorbed the former to a possible maximal extent. It must be also mentioned that the volume was measured indirectly from ΔP. So it may be quite possible that this volume differs from that of the real solubility, by the amount of the gas taken into the material, in some labile state, say, in the form of visible or invisible bubbles suspending. Though it is again questionable that the bubbles in a liquid, can effect a decrease in pressures, to what extent.

$$A=cP$$

The coefficient c may be a characteristic of the material. But there exists no remarkable difference between the values of c's for the various oily materials. So it seems impossible that they can be characterized by the magnitude of c. Although the closer examination of the figure 1, reveals that the value of c is greater for the wax-oils than for the glyceride-oils and the minimum for castor oil, which possesses hydroxy-acids in its molecules: The value of c is 0.12 cc/cmHg, for sperm oil and it is near but a little less than that for sperm body oil. For blue whale oil, is 0.098 and those for camellia oil and liquid paraffin stand

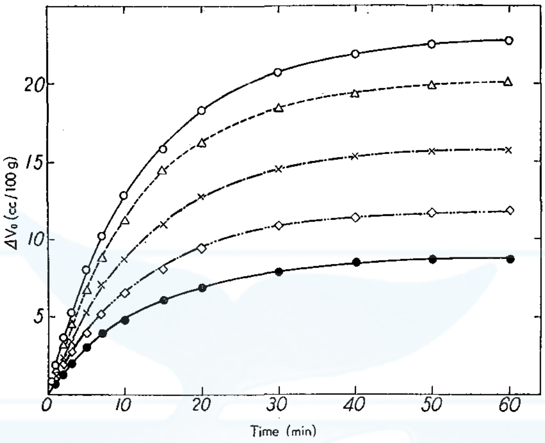

Fig. 5. Absorption curves for blue whale oil under various pressure lebels.

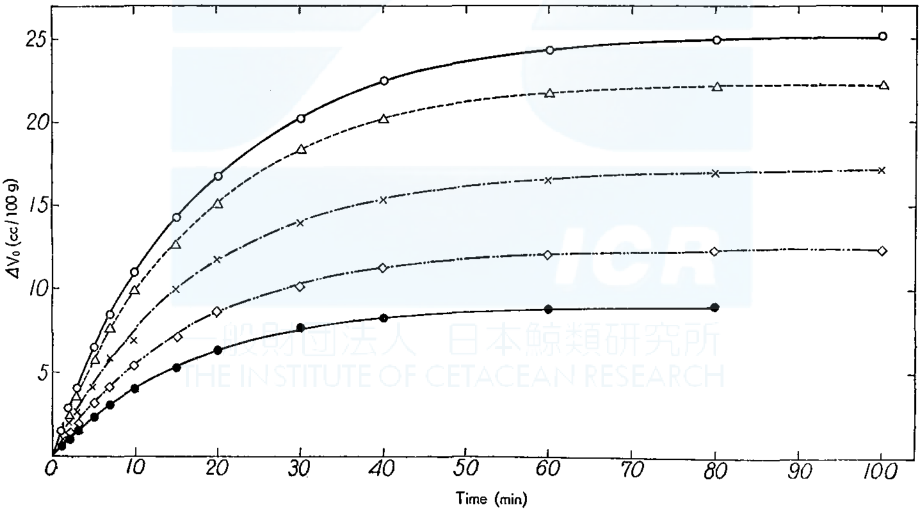

Fig. 6. Absorption curves for olive oil under various pressure lebels.

very close by that. For castor oil, c is 0.073.

On the other hand, it differs greatly therefrom and amounts to 0.016 cc/cmHg, for the water. Hence the coefficients for the oily materials (with the exception of caster oil), are 6 to 7.5 times as great as that for the water. In other words, the oily substances can absorb 6 to 7.5 times as much nitrogen as the water, at every pressure value. Even castor oil can absorb 4.5 times as much as the water.

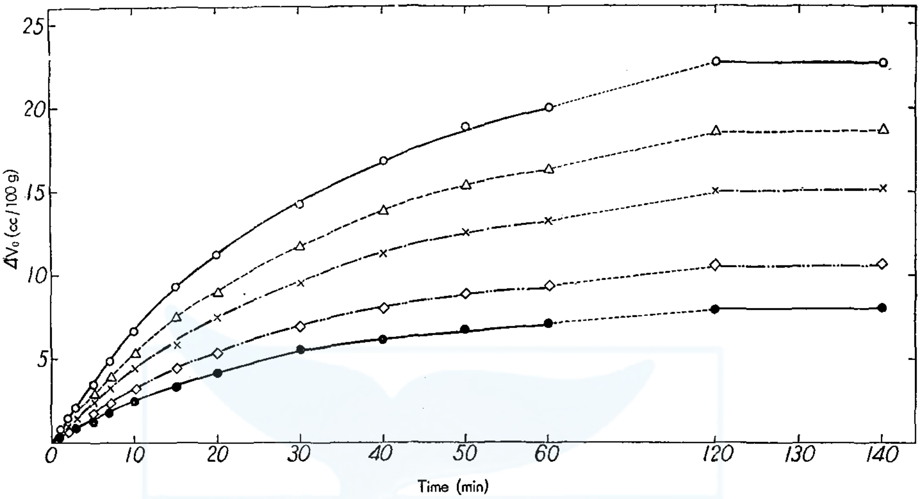

Fig. 7. Absorption curves for camellia oil under various pressure lebels.

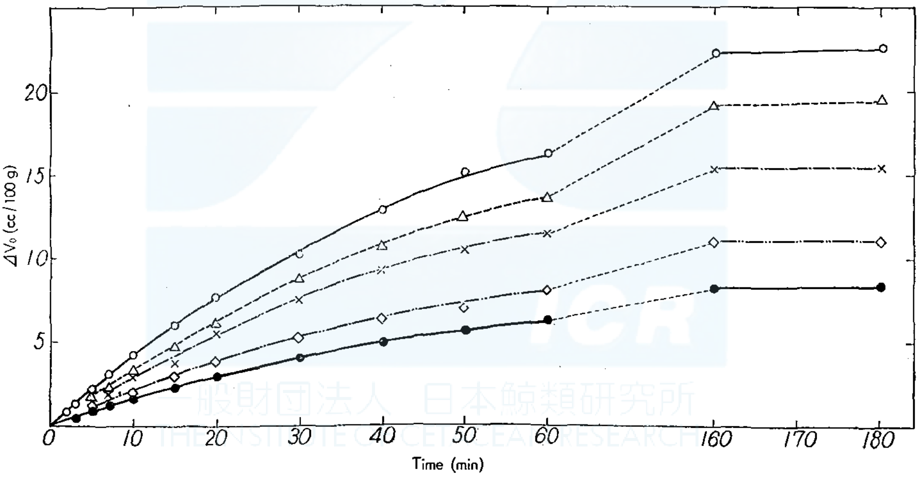

Fig. 8. Absorption curves for liquid paraffin under various pressure lebels.

In the case of carbon dioxide, it has been determined in the earlier paper, that c is 1.78 cc/cmHg, for sperm oil, and the values for the other oily substances, are of the magnitude close but less than that and the

c for water is 0.78 cc/cmHg. When compared within the oily materials, they can absorb nitrogen 1/10 or less, as much as carbon dioxide, at any pressure, and in the case of water, it can absorb nitrogen some 1/50 as much as carbon dioxide.

Absorption Curves.—In figure 2 to figure 9, each diagram shows absorption curves for each material respectively. Any of the diagrams consists of five curves, corresponding to five pressure lebels. Every curve was drawn based upon two or three times parallel experiments. In most of the cases, the discrepancy between the corresponding values of ΔV_0's, is less than 5%.

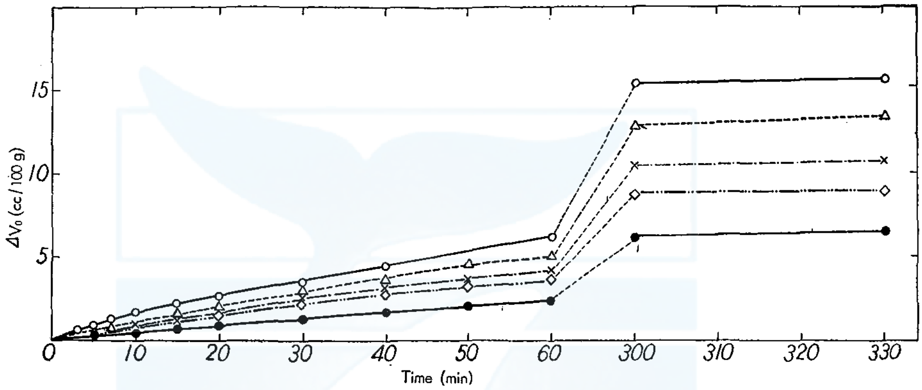

Fig. 9. Absorption curves for castor oil under various pressure lebels.

When comparing these 8 figures, there seems to exist a great difference in the absorption velocity of nitrogen, between the individual materials. But any quantitative evaluation about the velocity, can not be made without the analysis of the curves.

ANALYSIS

As noted in the foregoing chapter, it seems very probable that the equation

$$\Delta V_0 = A(1-e^{-\alpha t}) \qquad (2)$$

will be valid for any of the curves included. If it were true, $\log(A-\Delta V_0)$ must become linear against the time, t. Indeed, as illustrated in figure 10, it proved that in all of the cases, $\log(A-\Delta V_0)$ showed the strong linear regression to the time t. In equation (2), ΔV_0 is a decrease in volume caused by absorption, A, the solubility of the gas, and α, a velocity constant, as seen in its differentiated form

$$\frac{d}{dt}(\Delta V_0) = \alpha(A-\Delta V_0) \qquad (3)$$

Figure 10 was chosen altogether at random from 8 figures obtained for the 8 materials. Another 7 figures were given up to save space.

TABLE 2. THE VALUES OF A'S AND α FOR EACH MATERIAL

Materials	Pressure Lebels (mm. Hg) P_i	Pressure Lebels (mm. Hg) P_f	Period (min.)	A (cc.)	α (min^{-1})	r
Water	931.8*	929.5*	40	1.5	0.155	20.0
	1,238.7	1,235.7	〃	2.0^5		
	1,651.0	1,647.0	〃	2.7		
	2,060.0	2,055.0	〃	3.4		
	2,364.0	2,358.5	〃	3.8		
Sperm Oil	929.0	912.7	40	10.8	0.154	20.0
	1,241.0	1,219.0	〃	14.6^5		
	1,652.2	1,623.0	〃	19.4		
	2,061.3	2,025.0	〃	24.5		
	2,365.0	2,322.0	〃	28.3		
Sperm Body Oil	926.7	909.6	50	11.3^5	0.114	15.0
	1,238.2	1,216.7	〃	14.3		
	1,651.0	1,623.0	〃	18.7		
	2,060.5	2,025.3	〃	23.4^6		
	2,361.0	2,321.0	〃	26.8		
Blue Whale Oil	930.0	916.7	60	8.8	0.081	10.5
	1,241.5	1,224.0	〃	11.8^6		
	1,649.7	1,625.6	〃	15.8^5		
	2,063.3	2,035.0	〃	20.2		
	2,364.6	2,330.6	〃	22.9		
Olive Oil	929.8	916.2	80	9.2	0.056	7.5
	1,240.2	1,221.5	100	12.6		
	1,649.0	1,623.2	〃	17.3		
	2,059.0	2,027.3	〃	22.6		
	2,360.2	2,326.7	〃	25.3		
Camellia Oil	930.7	919.0	140	8.1	0.035	4.5
	1,240.3	1,225.0	〃	10.7		
	1,650.0	1,627.8	〃	15.2		
	2,061.0	2,033.0	〃	18.8		
	2,365.3	2,331.3	〃	22.8		
Liquid Paraffin	931.7	919.5	180	8.4^6	0.021	3.0
	1,241.0	1,224.3	〃	11.3^5		
	1,649.7	1,626.3	〃	15.9		
	2,060.4	2,031.0	〃	19.8		
	2,365.6	2,331.6	〃	23.0		
Caster Oil	930.4	920.8	330	7.0	0.0076	1.0
	1,240.0	1,226.7	〃	9.7		
	1,649.7	1,633.7	〃	11.5		
	2,060.5	2,040.7	〃	14.1		
	2,361.5	2,338.6	〃	17.0		

* These values in water, were obtained by substracting 42 mm. Hg, the saturated vapor pressure of dist. water at 35°C, from the total pressure.

Determination of A.—It may be essentially possible to determine two unknown factors, A and α, respectively, when the values of ΔV_0's and t's, more than two sets are given. However it is very difficult to solve such simultaneous equations as involving the exponential functions.

To avoid such difficulties, a graphical method is adopted: The first estimated value of A, is obtained from the $\Delta V_0 - t$ diagram, by extrapolating the curve to the infinite value of t. Then, using this value of A, the values of $\log(A-\Delta V_0)$'s are plotted against t. Thus, if the equation is valid, it will be sure that the $\log(A-\Delta V_0)$ becomes rather linear against t, in the interval, where t is relatively small. But, with increase of t, the curve will show a tendency to bend upwards or downwards, according as the estimated value of A is too great or too small. If the curve is bending downwards, some value is to be added to the first estimated value of A, to get a straight line. Then we have a second estimated value of A, and so forth, when $\log(A-\Delta V_0)$ becomes really linear against t, over the whole interval, the then value of A must be the value to be found.

Of course, individual points may fall rather scattering, up and down on the line, we must pay attention to the tendency. In the case of the materials with slow absorption, as castor oil and liquid paraffin, difference between A and $\Delta V_{0\,\max}$ becomes somewhat considerable, and in those with rapid absorption, as sperm oils and other whale oils, the difference is almost negligible.

Determination of α.—α was obtained by the *method of averages*, using the formula derived from the equation (2)

$$\alpha = 2.3026\frac{n\cdot\log A-\sum_{1}^{n}\log(A-\Delta V_0)}{\sum_{1}^{n} t}$$

Thus we have five different values of α, for each material. However, in all of the cases, the values of α's obtained within a given material, were found to be almost much the same, disregarding the pressure lebels. At least, we could not find any orderly relationship between the magnitude of α and pressure lebels. It seems likely that within such narrow range of pressures, α becomes approximately constant, though it is not a theoretical consequence. For this reason, by averaging the five values, a single value of α was given for each material, without regard to the pressure lebels.

As seen from table 2, the value of α is great in the decreasing order of water, sperm oil, sperm body oil, blue whale oil, olive oil, camellia oil, liquid paraffin and castor oil. This order proves to be consistent with that of the absorption velocity of carbon dioxide (cf. previous paper). Here again, the value of α is outstandingly greater for the whale oils than for the vegetable oils, and the greatest two are those for sperm oil and sperm body oil, both containing a large amount of wax.

In the table 2, the other descriptions were also given; in the second and third column, the pressure lebels, under which the measurements were carried out, in the fourth, the lapse of time, during which each measurement was made, in the fifth, the values of A, for each material, under various pressure lebels, and the last column headed by r, gives the ratio of α for each material to that for castor oil.

We shall now compare the absorption velocity of nitrogen with that of carbon dioxide, in various materials. Unfortunately, however, a general comparison is not possible, since another formulae are used in both cases: In the case of carbon dioxide, we have been obliged to use a experimental formula as

$$\frac{d}{dt}(\Delta V_0)=a'b\cdot t^{b-1} \qquad (4)$$

and in the present work, we can do with the equation (3). Therefore the absorption velocity of the both gases must be compared in a fixed condition, i.e. under a definite pressure lebel and at a definite time.

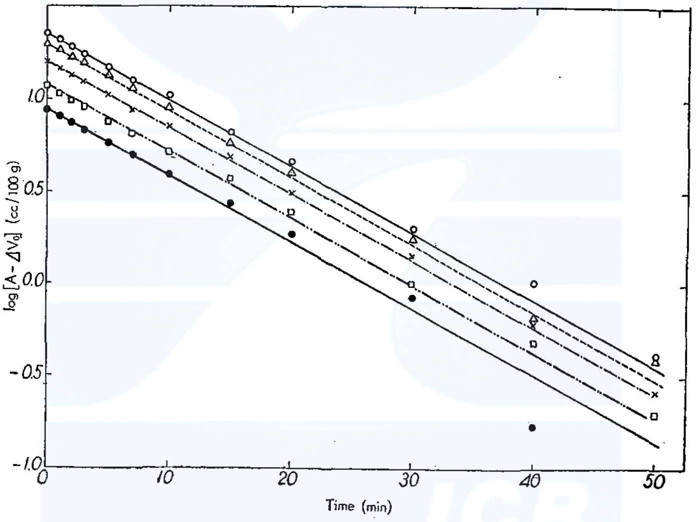

Fig. 10. Relation between log $(A-\Delta V_0)$ and t. (In the case of blue whale oil, as an illustration.)

Nevertheless, in the equation (4), $a'b$ shows the velocity at 1 sec after outset, that is approximately regarded as the initial velocity, whereas αA represents the initial velocity itself, in the equation (3). Thus we can make a rough comparison of the initial velocity of the both gases, by comparing $a'b$ with αA. For instance, in the case of sperm oil, the value of $a'b$ was 1.68 cc/sec (cf. p. 204 of the earlier paper), i.e. 100.8 cc/min, under the pressure lebel, whose initial pressure was 2,364 mmHg. While αA is 4.36 cc/min, under the pressure lebel, initial pressure of which is 2,365 mmHg. So, in the case of sperm oil, the initial absorption velocity of carbon dioxide, is some 23 times as great as that of nitrogen, at the same pressure.

Such ratio, $a'b/\alpha A$, at the same pressure, remains almost constant, within any of the materials used, disregarding the pressure lebels, but varies with the kind of material. It ranges from 20 to 30, in the oily materials, except castor oil, in which it comes to about 70. On the other hand, it amounts to some 200, in the case of the water.

SUMMARY

1. Asborption of nitrogen was studied with 8 kinds of substances, i.e. distilled water, sperm oil from *spermaceti*, sperm body oil, blue whale oil, olive oil, camellia oil, liquid paraffin and castor oil.

2. Decrease in pressures, ΔP, caused by absorption, was punctually measured with each material, at constant temperature ($35\pm 0.05^{\circ}$C) and at constant volume, under five different pressure lebels, i.e. under the pressure, near but a little higher than 1, 2 and 3 atmos. pressures respectively and under every intermediate lebel.

3. Decrease in volume, corresponding to ΔP, was reduced to standard state, and designated by ΔV_0, this volume of nitrogen must have been absorbed by a given material, during the process.

4. From the results obtained, following conclusions were drawn:

a. The value of A was found to be approximately proportional to the pressure, with each material, where A stood for the solubility of nitrogen in a material. Therefore the relation, $A=cP$, was postulated.

b. Within the oils and oily substances tested, the value of c does not differ so greatly from each other. So, we consider, they can not be characterized by this magnitude. On the contrary, there existed a great difference between c for water and those for oily substances, the latters are 6 to 7.5 times as great as the former.

c. As compared to the solubility of carbon dioxide, the solubility of nitrogen is of the magnitude about one-tenth of the former in the oily materials, and some 1/50, in the water.

d. The results of the analysis indicated that the equation (2) was valid in good approximation, for all the curves included.

e. The absorption velocity constant, α, was prominently characteristic of the material, its value was far greater for the oils from whale kinds, especially for the oils from sperm whale, which contain a large amount of wax, than for the vegetable oils.

f. The value of α was great in the order, named in section 1. of this summary.

g. In the order of magnitude, the absorption velocity of nitrogen is consistent with that of carbon dioxide, within the materials, used in common to both the works.

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