The Solubility of Air in Fats, and its Relation to Caisson Disease.

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As is now well known, the very varied symptoms produced by rapid decompression from high atmospheric pressures, and popularly known as "caisson disease" or "diver's palsy," are due to liberation of bubbles of gas—chiefly nitrogen—in the blood and tissues. In the course of a recently published investigation, I found that air is much more soluble in certain oils than in water. Dr. J. S. Haldane pointed out to me the interest of this fact in connection with the causation of caisson disease, and at his suggestion I have repeated and extended my observations.

The fats experimented with were olive oil, cod liver oil and lard. In the case of the first two, the solubility was measured at 15° and at 37° C., whilst for lard it was determined at 45° C. In the observations made at room temperature, the oil was shaken violently with air in a bottle for several minutes, and was allowed to stand for 1 to 1½ hours till all the air bubbles had risen to the surface. It was then weighed, and about 40 to 50 grammes of it were sucked up into the vacuous flask of a Geissler's mercury pump. This flask contained 70 to 100 c.c. of 0·5 per cent. sulphuric acid which had previously been well boiled for an hour so as to get rid of all traces of air. The mixture of oil and water was now boiled for half an hour, the oil breaking up into a very fine emulsion and giving up practically all of its gas in the first few minutes. This gas was pumped off and analysed with Haldane's* gas analysis apparatus. The oil was boiled with dilute acid instead of water, so as to obtain the whole of the carbon dioxide present, both combined and in solution. In determining the solubility at 37°, the oil, previously saturated at room temperature, was warmed to about 38° to 39°, and was shaken vigorously with air for about two minutes. At the end of this time its temperature had fallen to about 36°·5. It was warmed up a second time and the shaking repeated, and was then kept in a water bath at 37° for about half an hour in the case of the cod liver oil, and an hour in the case of the olive oil, these being the times required for all the bubbles of air to rise to the surface. The gaseous content of a weighed amount of the oil was then determined as before. The results obtained are given in the tables. They

* Haldane, 'Journ. Physiol.,' vol. 22, p. 465, 1898.

represent the volumes of gas, reduced to 0° and 760 mm., contained in 100 c.c. of the oil at the temperature recorded, when saturated with air at a pressure of 760 mm. To calculate these values, it was assumed that the specific gravity of olive oil at 15° is 0·917, and at 37°, 0·902.* The specific gravity of cod liver oil, compared with that of water at 15°, was found by direct experiment to be 0·928 at 15°, and 0·914 at 37°.

100 c.c. of olive oil contain—								
	At 15° C.			Mean.	At 37° C.			Mean.
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Oxygen	2·20	2·23	2·42	2·28	2·33	2·36	2·30	2·33
Nitrogen	5·23	5·30	5·27	5·26	5·19	5·23	5·15	5·19
CO_2	0·19	0·24	0·16	0·20	0·17	0·13	0·18	0·16

100 c.c. of cod liver oil contain—								
	At 15° C.			Mean.	At 37° C.			Mean.
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Oxygen	2·34	2·31	2·22	2·29	2·21	2·22	2·22	2·22
Nitrogen	4·95	5·15	5·07	5·06	5·05	5·10	5·08	5·08
CO_2	0·19	0·25	0·19	0·21	0·18	0·24	0·20	0·21

Considering only the mean values, we see that in the case of each oil the solubility at 37° is within the limits of experimental error the same as its solubility at 15° C. A similar constancy was found by Bunsen for the solubility of oxygen in alcohol at temperatures from 0° to 24°, though Timofjew† has since found that the solubility does slightly diminish with the temperature. In any case the diminution is small (6·8 per cent. diminution for oxygen and 5·2 per cent. diminution for nitrogen between 0° and 24°) and if it exists at all in the case of these oils, it must be smaller still. A simple proof of the slight effect of temperature on solubility is obtained by saturating the oil at room temperature, and heating it gradually in a water bath. Not a trace of gas is observed to come off if the temperature be kept at 97°, but at 100° it bubbles off in very small quantities.

The observations on lard were carried out at one temperature only. Lard melts at 36° to 48°, and solidifies at 27° to 30°, but if melted and shaken with

* See Lewkowitsch, "Chemical Analysis of Oils, Fats and Waxes," London, 1898, p. 454.

† Timofjew, 'Zeit. Phys. Chem.,' vol. 6, p. 151.

air at 37° it is too viscid to allow the air bubbles to rise to the surface in a reasonable time. Hence the solubility was determined at 45°. The lard was heated to about 48°, and then shaken violently for a minute with air, its temperature at the end of this time having fallen slightly below 45°. The process was repeated, and after keeping the lard in a water bath at 45° for about 35 minutes the gases were boiled off in the usual way. They came oft quite as readily as from the olive and cod liver oils. The data obtained are given in the table, they being calculated on the supposition that the specific gravity of lard at 45°, as compared with water at 15°, is 0·895.* If the mean values be compared with the mean values for the other fats, it will be seen that the solubility of oxygen is practically constant throughout. That of nitrogen varies slightly, it being 5·23 c.c. for olive oil (an average of the values at 15° and at 37°), 5·11 c.c. for lard, and 5·07 c.c. for cod liver oil. Still these differences are almost within the limits of experimental error. In the case of the lard, it is possible that the two minutes' shaking with air was not quite sufficient for complete saturation, but more thorough shaking was not possible, as it brought down a slight precipitate which prevented the rapid clearing of the air bubbles.

	100 c.c. of lard at 45° C. contain—			Mean.
	c.c.	c.c.	c.c.	c.c.
Oxygen	2·23	2·40	2·35	2·33
Nitrogen	5·05	5·09	5·18	5·11
CO_2	0·12	0·12	0·15	0·13

In that fats of such very different composition as the three experimented with dissolve practically the same amounts of oxygen and nitrogen, we are fully justified in assuming that human fat would behave similarly. From the physical and chemical constants collected in the accompanying table,† we see that the melting point of human fat lies between those of cod liver oil and lard, whilst its iodine value is 61·5 per cent., or about the same as that of lard. In that cod liver oil has an iodine value of about 145 per cent., and

	Cod liver oil.	Olive oil.	Lard.	Human fat.
Solidifying point	0° to −10°	−6° (?)	27° to 30°	15°
Melting point ...	—	—	36° to 48°	17·5°
Specific gravity	0·928 at 15°/15°	0·917 at 15°/15°	0·895 at 45°/15°	0·903 at 25°/25°
Iodine value......	123 to 168 per cent.	79 to 88 per cent.	50 to 70 per cent.	61·5 per cent.

* Lewkowitsch, *loc. cit.*, p. 564.

† Lewkowitsch, *loc. cit.*, pp. 454, 477, 562 and 564.

olive oil one of about 83 per cent., it follows that the proportion of unsaturated acids present in a fat has little or no influence upon its solvent powers for oxygen and nitrogen.

From the absorption coefficients for oxygen and nitrogen given by Bohr and Bock* it is calculated that 100 c.c. of water saturated with air at 15° absorb 0·733 c.c. of oxygen and 1·411 c.c. of nitrogen. Taking a mean of all the values obtained with cod liver oil and olive oil at 15°, the solubility of oxygen is found to be 3·1 times greater than in water, and of nitrogen 3·7 times greater. At 37° Bohr and Bock's values show that 100 c.c. of water absorb 0·507 c.c. of oxygen, and 0·975 c.c. of nitrogen. Taking a mean of all the values obtained with cod liver oil and olive oil at 37°, and with lard at 45° (for doubtless the solubility at this temperature is practically the same as at 37°), the solubility of oxygen is found to be 4·5 times greater than in water, and that of nitrogen 5·3 times greater. It has been found by Bohr,† that blood plasma dissolves 2·5 per cent. less nitrogen than an equal volume of water, whilst blood dissolves slightly less still; hence we may conclude that *at body temperature the fat of mammals dissolves at least five times as much nitrogen as water or as blood and blood plasma.*

The solubility of oxygen in fats, though apparently less than that of nitrogen, may in reality be as great. It is well known that oils are able to absorb and combine with oxygen, and the rate of this absorption is by no means inconsiderable. For instance, a sample of olive oil was saturated with air at 15°, and was kept for 23 hours at 18° in a stoppered bottle filled to the brim. It then yielded only 0·49 c.c. of oxygen per 100 c.c., whilst some of the sample from which the air was boiled off an hour after saturation yielded 2·40 c.c. Owing to its richness in unsaturated acids, cod liver oil absorbs oxygen more quickly still, and a sample saturated with air at 15°, and kept 23 hours at 18° in a stoppered bottle, gave only 0·05 c.c. of oxygen per 100 c.c. Undoubtedly, therefore, there must have been some absorption of dissolved oxygen during the half to one and a-half hours the air-saturated oils were kept before analysis.

It might be thought that the solubilities determined by the above described method are invalidated, or liable to be invalidated, by leakage of air into the vacuum pump. This is not the case if due precautions are taken. The pump must be in such good order that no appreciable leakage occurs when it is left vacuous for several days, and it must be kept vacuous for a week or more before use, for if air be left in it a small amount attaches itself to the glass walls of the apparatus, and only escapes slowly when the pump is

* Bohr and Bock, 'Wied. Ann.,' vol. 14, p. 318, 1891.

† Bohr, 'Nagel's Handb. d. Physiol.,' vol. 1, p. 62, 1905.

made vacuous again. Air likewise attaches itself to the walls of the boiling flask, but it is got rid of by the preliminary boiling of the dilute acid previous to the introduction of the oil. In all analyses of gases, whether in oil, water, or salt solutions, such a preliminary boiling was invariably adopted, and by taking these precautions many hundreds of analyses have been made without invalidation of results by leakage of air. I have elsewhere* recorded nearly a hundred analyses of the gases in sea water, and the mean nitrogen values then obtained are almost identical with the nitrogen absorption values determined by Dittmar.

The bearing of the above recorded results upon many phases of caisson disease is probably a direct one. The commonest symptoms observed in caissoniers consist of joint and muscular pains, and in paralysis, the latter being the result of injury to the spinal cord. Thus in autopsies of caissoniers, Bert observed softening of some inches of the spinal cord in the dorsal region. v. Leyden, in a case of death 15 days after decompression, observed signs of myelitis, and small irregular fissures in the mid-dorsal cord, probably produced by the escape of gas. Autopsies of divers have shown necrobiosis and hæmorrhages in the spinal cord,† and distention of the blood vessels by air bubbles.‡

Chemical analysis shows that spinal cord and peripheral nerves contain nearly 20 per cent. of fat and fat-like substances. Adipose tissue contains about 83 per cent. of fat, and yellow bone marrow (as distinct from red marrow, which is poor in fat) contains no less than 96 per cent. of fat (Gorup-Besanez). If these tissues were saturated with nitrogen at, for instance, four atmospheres of atmospheric pressure, 100 c.c. of them would contain, instead of the $0{\cdot}975 \times 4 = 3{\cdot}90$ c.c. of dissolved nitrogen present in an equal volume of water, about 7 c.c. in the case of the spinal cord and nerve, and 20 c.c. in the case of yellow bone marrow. On sudden decompression, therefore, the volume of nitrogen bubbling off in a gaseous form might be two to six times as much as that from the non-fatty fluids and tissues of the body.

It has been found that the severity of the symptoms developed by caissoniers is influenced greatly by the time of exposure to increased pressure. In sinking the foundations of a bridge at St. Louis, a pressure reaching at a maximum to 50 lbs. above normal was used, and a large proportion of the workers were affected. As the depth of the caissons increased, the shifts were shortened from four hours to one hour, with the result that the serious

* Vernon, 'Journ. Physiol.,' vol. 19, p. 68, 1895.

† Cited by Hill and Macleod, 'Journ. Hygiene,' vol. 3, pp. 408 and 409, 1903.

‡ See Hill's "Recent Advances in Physiology," p. 250, 1906.

accidents were reduced to *nil.** Presumably, therefore, the body tissues were not so fully saturated with nitrogen in the shorter as in the longer period. On the other hand, Hill and Greenwood† found that on exposing themselves to a pressure of 30 to 45 lbs., their urine became saturated with the theoretical amount of nitrogen in 10 to 15 minutes. This quicker saturation must be due to the blood-flow through the kidney being much more rapid than that through the spinal cord, and very much more rapid than that through adipose tissues. Even if it were as rapid through fat-containing tissues as through the kidney, the fats, in virtue of their greater solvent power, would take longer to become fully saturated than the fluids of non-fatty tissues.

Conclusion.

At body temperature, fats dissolve more than five times as much nitrogen as an equal volume of water or blood plasma.

The special tendency of the fat-containing tissues (such as subcutaneous tissues, spinal cord and peripheral nerves) of caisson workers and divers to suffer injury from the liberation of gas bubbles after rapid decompression is dependent on this great solubility.

* See Paul Bert's "La Pression Barométrique," Paris, 1878, p. 404.

† Hill and Greenwood, 'Roy. Soc. Proc.,' B, vol. 79, p. 21, 1907.