

LX.—*The Supposed Relation between the Solubility of a Gas and the Viscosity of its Solvent.*

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IN the *Zeit. physik. Chem*, 9, 171, 1892, appeared a short communication by L. W. Winkler, in which he traced an empirical connection between the diminution which is brought about by rise in temperature in the absorption coefficient of a gas and the corresponding diminution in the viscosity coefficient of the solvent. His conclusions

were based upon his own determinations of the solubilities of hydrogen, oxygen, nitrogen, nitric oxide, and carbon monoxide in water, and the relative numbers given by Graetz for the viscosity coefficients. It seemed to us to be of interest to ascertain how far Winkler's conclusions were in accord with our own observations on the viscosity coefficients of water (*Phil. Trans.*, 1894).

The relationship given by Winkler, which also involves a connection between the diminution in solubility and the molecular weight of the gas, may be expressed as follows:—If  $\beta_t$  and  $\beta_{t'}$  be the absorption coefficients at the temperatures  $t$  and  $t'$ , if  $\eta_t$  and  $\eta_{t'}$  be the viscosity coefficients of water at the same temperatures; if, further,  $m$  be the molecular weight of the gas and  $K$  a constant, then

$$\frac{\beta_t - \beta_{t'}}{\beta_t} = \frac{\sqrt[3]{m}}{K} \frac{\eta_t - \eta_{t'}}{\eta_t} \quad (1.)$$

For the same gas,  $\sqrt[3]{m}/K$ , which we will deal with at a later stage, is a constant which we may write as  $N$ , hence for the same gas

$$\frac{\beta_t - \beta_{t'}}{\beta_t} = N \frac{\eta_t - \eta_{t'}}{\eta_t}. \quad (2.)$$

It follows, therefore, from (2) that for the same temperature interval the percentage diminution in solubility should be proportional to the percentage diminution in viscosity. By mere inspection, it was evident that for  $t = 40^\circ$  and  $t' = 50^\circ$  the value of  $(\eta_t - \eta_{t'})/\eta_t$ , as obtained from Graetz's numbers, would differ by about 4 per cent. from the value derived from our own determinations of viscosity. We therefore calculated the values of  $N$  for intervals of  $10^\circ$  between  $0^\circ$  and  $50^\circ$ ,  $50^\circ$  being taken as the upper limit since, at higher temperatures, determinations of the absorption coefficient with an accuracy sufficient for the comparison are almost impossible with present experimental appliances. The calculation led to the surprising result that  $N$  gave no indication whatever of being constant for any of the gases. This point is made clear in the following table, the data being taken from Winkler's measurements of solubility and our own measurements of viscosity.

$t.$	$N = \frac{\beta_t - \beta_{t+10}}{\beta_t} \bigg/ \frac{\eta_t - \eta_{t+10}}{\eta_t}$		
	Oxygen.	Nitrogen.	Hydrogen.
$0^\circ$	0.832	0.782	0.336
10	0.795	0.734	0.301
20	0.770	0.643	0.324
30	0.657	0.649	0.179
40	0.578	0.500	0.135

In all cases  $N$  steadily diminishes as the temperature rises, the diminution being always greater than 30 per cent. on passing from  $0^\circ$  to  $40^\circ$ . It was thus definitely proved that equation (2) was incorrect, and this conclusion was the more perplexing as Winkler gives a considerable amount of evidence to show that (2) satisfactorily represents the facts. The equation may be written as

$$\beta_{t'} = \beta_t \left( 1 - N \frac{\eta_t - \eta_{t'}}{\eta_t} \right). * \quad (3.)$$

and he establishes the validity of the equation by showing that the values of  $\beta_{t'}$  calculated by means of (3), knowing the quantities on the right-hand side of the expression, closely approximate to those actually observed. On further examination, the reason for this agreement was found to depend on the fact that, in using his equation, Winkler always employs the values obtained at  $t = 0^\circ$  for  $\beta_t$  and  $\eta_t$ . His results consequently show that

$$\frac{\beta_0 - \beta_{t'}}{\beta_0} = N \frac{\eta_0 - \eta_{t'}}{\eta_0},$$

which, since  $\beta_0$  and  $\eta_0$  are constants, we may write as

$$\beta_0 - \beta_{t'} = N^1 (\eta_0 - \eta_{t'}), \quad (4.)$$

where  $N^1$  is a new constant equal to  $N\beta_0/\eta_0$ . The accord between the observed and calculated values of  $\beta_{t'}$  does not show, therefore, that for any temperature interval the percentage diminution of solubility is proportional to the percentage diminution in viscosity, but that the actual diminutions themselves are proportional.†

To ascertain how closely this proportionality remained constant at different temperatures, we calculated for oxygen, hydrogen, and nitrogen, the values of  $N^1$  for successive intervals of  $10^\circ$  between  $0^\circ$  and  $50^\circ$ . The results are collected in the following table. In the

\* Owing probably to a typographical error the formulæ  $\beta_1 = \beta - \frac{\mu - \mu_1}{\mu} \sqrt[3]{\frac{m}{M}}$ , and

and  $\beta_1 = \beta - \frac{\mu - \mu_1}{\mu} \sqrt[3]{\frac{m}{M}}$  are given instead of  $\beta_1 = \beta \left( 1 - \frac{\mu - \mu_1}{\mu} \sqrt[3]{\frac{m}{M}} \right)$ ,

and  $\beta_1 = \beta \left( 1 - \frac{\mu - \mu_1}{\mu} \sqrt[3]{\frac{m}{M}} \right)$ , on p. 172 in Winkler's paper.

† From Winkler's equation it would follow that  $\frac{1}{\beta} \frac{d\beta}{dt}$  is proportional to  $\frac{1}{\eta} \frac{d\eta}{dt}$ , or, on integrating, that the difference between the natural logarithms of the absorption coefficients at any two temperatures is proportional to the difference between the natural logarithms of the viscosity coefficients. The real relationship appears to be that  $\frac{d\beta}{dt}$  is proportional to  $\frac{d\eta}{dt}$ , and, therefore, that the difference between the absorption coefficients is proportional to the difference between the corresponding viscosity coefficients.

column "W," we give for each gas the values of  $N^1$ , obtained by using Winkler's numbers for the absorption coefficients. We also thought it worth while to find if any appreciable alteration took place in the values of  $N^1$  on employing the mean of all the trustworthy observations on absorption coefficients which we could find. The results thus obtained are given in the column headed "Mean." The observers whose results have been used are:—

*Oxygen* : Dittmar, Bohr and Bock, and Winkler.\*

*Nitrogen* : Dittmar, Bohr and Bock, Hamberg and Winkler.

*Hydrogen* : Dittmar, Timoféeff, and Winkler.

As before, we use our own values for the viscosity coefficients.

<i>t.</i>	$N^1 = (\beta_t - \beta_{t+10}) / (\eta_t - \eta_{t+10})$ .					
	Oxygen.		Nitrogen.		Hydrogen.	
	W.	Mean.	W.	Mean.	W.	Mean.
0°	2·29	2·26	1·03	1·01	0·41	0·35
10	2·32	2·36	1·05	1·06	0·45	0·45
20	2·38	2·42	0·99	1·12	0·59	0·71
30	2·15	2·38	1·09	1·21	0·38	0·57
40	2·04	2·05	0·91	1·14	0·34	0·45
Mean....	2·24	2·29	1·01	1·11	0·43	0·51

In the case of hydrogen, the experimental errors in determining the solubility are evidently too large to admit of any very definite conclusion being drawn; in the case of oxygen and nitrogen, however, the values of  $N^1$  are, roughly speaking, constant, although in general they increase, reach a maximum, and then diminish as the temperature increases. It is this approximate constancy in the value of  $N^1$  which is the real temperature relationship involved in Winkler's equation.

It has already been pointed out that equation (1) besides involving a relationship between solubility and viscosity, also embodies a connection between solubility and the chemical nature of the gas; the latter relationship was based on the fact that between 0° and 20°, D, the percentage diminution in the solubility, was apparently proportional to the cube root of the molecular weight of the gas. The following table makes it evident that the values of the absorption

\* From the observations of Roscoe and Lunt on the amount of oxygen dissolved by water out of atmospheric air, absorption coefficients may be calculated. We have confined ourselves, however, to absorption coefficients determined by the ordinary methods.

coefficients for hydrogen alone decide that the cube root shall be the particular function of the molecular weight employed. It will be seen that for all the substances with the exception of hydrogen, the ratios of  $D$  to the square root of the molecular weight, or even to the molecular weight itself, are practically as nearly constant as when the cube root of the molecular weight is used.

Gas.	$m$ .	$D = \frac{\beta_0 - \beta_{30}}{\beta_0} \times 100$ .	$D/\sqrt[3]{m}$ .	$D/\sqrt{m}$ .	$D/m$ .
H <sub>2</sub>	2	15.32	12.17	10.83	7.66
N <sub>2</sub>	28	34.33	11.30	6.49	1.226
CO	28	34.44	11.34	6.51	1.229
NO	30	36.24	11.66	6.62	1.208
O <sub>2</sub>	32	36.50	11.51	6.46	1.142

The molecular weights and the values of  $D$  for all the gases other than hydrogen differ so little from one another that they give no indication as to what function of  $m$  is the most suitable. Now, since the observations on hydrogen are the least satisfactory on account of the small temperature alteration in the absorption coefficient, and the difficulties involved in working with this gas, the above relationship did not seem to be very well grounded. It was therefore thought advisable to see how  $D/\sqrt[3]{m}$  varied with the temperature, as there is considerable uncertainty in trusting to the numbers obtained for a single temperature interval arbitrarily chosen. The following table gives for 10° intervals the ratios of  $D$  and  $\sqrt[3]{m}$  for oxygen, nitrogen, and hydrogen, using Winkler's values for the absorption coefficients.

$t$ .	$\frac{\beta_t - \beta_{t+10}}{\beta_t} / \sqrt[3]{m} = D/\sqrt[3]{m}$ .		
	Oxygen.	Nitrogen.	Hydrogen.
0°	7.01	6.89	9.0
10	5.80	5.59	7.0
20	4.94	4.31	6.6
30	3.73	3.86	3.2
40	2.95	2.67	2.2

For all the gases, the values of the ratio rapidly diminish as the temperature rises. For the same interval, those of oxygen and nitrogen are not very different from one another, but differ widely from those of hydrogen. The fact, therefore, that the ratio for hydrogen given by Winkler agrees within moderate limits with those

for the other gases, is mainly dependent on the particular temperature interval for which he happened to make the comparison.

The data are obviously insufficient to decide in what way  $D$  is related to  $m$ . But even although  $D/\sqrt[3]{m}$  for the same temperature interval had been found to be proportional to the percentage diminution in solubility, its introduction into a general equation connecting solubility and viscosity would not be justified. The assumptions made by Winkler in (1) are (a) that for the same gas the percentage diminution in solubility for any temperature interval is proportional to the percentage diminution in viscosity, and (b) that for any gas the percentage diminution in solubility is also proportional to the cube root of the molecular weight; (a) has been proved to be invalid, the diminutions themselves are really proportional, and it is obviously erroneous to introduce into the factor of proportionality a relationship like (b) which depends on the *percentage* diminution of solubility.

For this reason, and also from the facts that  $D/\sqrt[3]{m}$  for the same temperature interval is not strictly constant, and further that it varies rapidly with the temperature, and at different rates for different gases, Winkler's suggestion that  $K$  in (1) is the cube root of the molecular weight of liquid water—which between  $0^\circ$  and  $20^\circ$  he takes to be  $3 \times 18$ —is hardly justified.

What appears to be the quantity which is independent of the temperature and which might therefore be expected to be related to the chemical nature of the gas, is the factor  $N^1$ ; although  $N^1$  diminishes with diminution in molecular weight, there does not appear to be a simple relation between them.

The conclusions which seem warranted by the foregoing discussion are therefore:—

(1.) For the same gas, the diminution in the absorption coefficient, for any temperature interval, is approximately proportional to the corresponding diminution in the viscosity coefficient of the solvent.

(2.) For any gas, the factor of proportionality is greater the greater its molecular weight.

The entire question is one of considerable interest, and, as Winkler suggests, would best be attacked by obtaining absorption coefficients for solvents other than water, where they are larger and can be more accurately determined. Measurements of the viscosity coefficients of a large number of organic liquids at different temperatures have now been carried out, and lack of observations on solubility alone delays the investigation of this question. This note may possibly be of service in calling the attention of chemists to the necessity for such determinations.