1. With five mono-azo dyes the effect of the methyl *iso*propyl substitution was that of a deepening of color corresponding to a displacement of the absorption band in the direction of longer wave length amounting to approximately 10 $\mu\mu$.

2. With Victoria green the effect of the *iso*propyl substitution in the non-aminated nucleus in a *para* position to the methane linking was that of a displacement of the two absorption bands in the visible spectrum in opposite directions, the spectral interval between their maxima being decreased.

3. The absorption of a homolog of phenolsulfonephthalein, derived from *p*-cymene, in which the substitution occurred in the sulfonated residue, was practically identical with that of phenolsulfonephthalein. With the *p*-cymene derivative the transition to the alkaline form occurred at somewhat higher points in the Sörensen scale than with phenolsulfonephthalein.

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THE SOLUBILITY OF HELIUM AND HYDROGEN IN HEATED SILICA GLASS AND THE RELATION OF THIS TO THE PERMEABILITY[1]

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According to the law of Graham and Bunsen, the rates of effusion of helium and hydrogen should be inversely proportional to the square root of their densities; that is, the helium rate should be 0.7 times the rate for hydrogen. In the cases of rubber,[2] rubbered balloon fabrics[3] and soap bubbles[4] the permeabilities observed are in approximate agreement with this law but in the case of silica glass this is not true. For example, at 500° the helium rate is approximately 22 times the hydrogen rate, the ratio increasing slightly at higher and diminishing slightly at lower temperatures. Such a wide discrepancy between theory and experiment seems to indicate that the phenomenon cannot be one of simple effusion.[5] On the other hand, to call it a case of true solution and diffusion at once raises the question of the relative solubilities of these gases in this medium.

Wüstner[6] has determined the solubility of hydrogen but no one appears to have made solubility measurements with helium gas. Measurements

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[1] Experimental work by G. A. Williams.

[2] Elworthy and Murray, *Trans. Roy. Soc. Canada,* [III] **13,** 37 (1919).

[3] Edwards and Pickering, *Bur. Standards Sci. Paper,* **387** (1920).

[4] McLennan and Shaver, *Phil. Mag.,* **40,** 272 (1920).

[5] Williams and Ferguson, THIS JOURNAL, **44,** 2160 (1922).

[6] Wüstner, *Ann. Physik,* **46,** 1095 (1915).

were carried out by us with both gases, using as nearly as possible the same method and apparatus in the hope that the results would be strictly comparable.

Apparatus and Experimental Method.—Small fragments of silica glass were broken from a tube of clear glass of 0.2cm. thickness of wall. They were sealed in a Jena combustion glass container.[7] The container was placed in an electric furnace and the capillary tube was connected externally to a glass apparatus by means of a joint of DeKhotinsky cement. The glass apparatus consisted of several parts: the gasometers and pressure gages for the saturating gases, the vacuum pumps, and a McLeod gage with phosphorus pentoxide drier. The volume of the gage system during measurements was 1000 cc. The temperatures were determined by means of a calibrated thermel and a potentiometer.

The silica glass was exposed for a given time at a determined temperature to the saturating gases at a known pressure. The furnace was then removed from the container and the latter allowed to cool to room temperature. When cold, the excess gas was removed by pumping. Once evacuated, the container was connected to the already evacuated gage system and then reheated in the furnace to a temperature 100° in excess of the temperature of saturation. The increase of pressure in the gage system was taken as a measure of the gas dissolved. The final pressures were always less than 0.1 mm. of mercury and this pressure was low enough to ensure the practically complete evolution of the gas. Care was taken that the gage system and the sample were not exposed to the air of the room so that errors from possible air leakage from the walls of the system were avoided. The part of the apparatus containing the gasometers was cut off from the gage system by means of a mercury seal.

Experimental Results.—Careful blank determinations were carried out. The helium blanks on two containers were found to be proportional to their respective areas. In a case in which the same container was used for both helium and hydrogen, the helium blank was 0.023 mm. while the hydrogen blank was 0.012 mm.

The times allowed for saturation of the sample were for helium and hydrogen 2.5 and 3.25 hours, respectively. Experiments showed that these times were sufficient.

A possible source of error would be in the evolution of gas from the cold sample during the evacuation of the container tube after the saturation and cooling of the sample. In the case of hydrogen, some slight evidence of such an evolution was obtained but in the case of helium the evidence

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[7] This material was more impervious to helium or hydrogen than Pyrex or silica glass and was not noticeably attacked by the latter gas. The container was usually 12 cm. long, of 2 cm. bore and was sealed to a capillary tube 40 cm. long and of 0.3cm. bore.

was fairly conclusive. In both cases the evolution was much too slow to affect our results. Another source of error might arise from readjustments during the cooling of the samples. To obviate this, special precautions were taken to cool the samples as rapidly as the glass container would allow. In view of the known rates of diffusion, there seems little doubt that the adjustments were inappreciable in the case of hydrogen. With helium the adjustments were undoubtedly larger. These would tend to make the solubilities correspond to lower temperatures than those indicated, but would not mask any large temperature coefficient. Since the results obtained do not indicate any appreciable temperature coefficient the errors from this source are probably slight.

Our solubility determinations are given in Table I, α is the number of cubic centimeters (under standard conditions) of gas dissolved in 1 cc. of glass[8] when the saturating pressure is one atmosphere. The values of α are calculated on the apparently justifiable assumption that the solubility is proportional to the saturating pressure.

TABLE I

THE SOLUBILITIES OF HYDROGEN AND HELIUM

Series A	Saturating pressure Mm.	α	Series D	Saturating pressure Mm.	α
Hydrogen-silica glass	763	0.0092	Helium-silica glass	747	0.0103
Sample 16.12 g.	750	.0091	Sample 16.12 g.	575	.0103
Temperature 515°	474	.0098	Temperature 515°	357	.0097
	376	.0088			
				Av.	.0101
	Av.	$.0092_1$			
Series B			Series E		
Hydrogen-silica glass	757	.0099	Helium-silica glass		
Sample 14.71 g.	755	.0095	Sample 16.12 g.	750	.0103
Temperature 515°	754	.0097	Temperature 445°		
	Av.	.0097			
Series C			Series F		
Hydrogen-silica glass	800	.0100	Helium-pyrex glass	755	.0082
Sample 14.71 g.	767	.0099	Sample 17.57 g.	752	.0085
Temperature 445°	755	.0098	Temperature 515°		
	460	.0099			
				Av.	$.0083_5$
	Av.	$.0098_9$			

Discussion of Results.—The hydrogen results may be compared with those of Wüstner. The latter worked at saturating pressures of 900 atmospheres. His values of α varied from 0.0088 to 0.01195 for temperatures running from 700° to 1000° but the variations are not simply related to the temperatures. For 600°, 400° and 300°, the values were, respectively,

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[8] The density of silica glass was taken as 2.22 and that of Pyrex as 2.25.

0.00819, 0.005669 and 0.005483. As previously stated, the permeability of silica glass to helium is many times the permeability to hydrogen, although according to the simple theory, they should be as 7 to 10. This would seem to indicate that the controlling factors or factor must differ in kind or degree in these cases. The solubility is one factor which might be expected to differ sufficiently in degree to account for the permeabilities but our results do not bear this out. In this connection the work done on other systems is of interest. In the case of hydrogen through nickel,[9] or of hydrogen through platinum,[10] the rates are proportional to the square roots of the pressures and in the latter case this has been explained upon the assumption that the hydrogen dissociates in the metal and that the monatomic hydrogen plays practically the whole role in the diffusion. In the case of silica glass the rates are proportional to the pressure and this might be taken as indicating that in this instance diatomic hydrogen diffuses. The helium molecule is considered to be smaller than the hydrogen molecule and one might try to connect this with the rates of diffusion. However, in the case of rubber the rates are also proportional to the pressures of the diffusing gases so that the hydrogen would seem to be in the same state as in the case of silica, but with rubber the rates for helium and hydrogen agree fairly well with the theory and these facts prevent one developing a theory based upon the size of the molecules. Nevertheless, it would be of much interest if the rates for helium and hydrogen were determined in some case in which the hydrogen acts in the monatomic state.

The great dependence of permeability upon the temperature has been noted by most investigators in this field but to date no one has advanced a generalization that covers the facts. In our previous paper, we showed that there was a linear relation between the temperature and the logarithm of the permeability for both helium and hydrogen and silica glass. More recently Lombard has indicated that the same kind of relation holds in the case of hydrogen and nickel. Re-plotting the results of other investigators shows that a similar relation holds in the case of hydrogen and rubber, of helium and rubber (Edwards and Pickering), of hydrogen and nickel, and of hydrogen and copper (Deming and Hendricks).[11] The rule is probably not an exact one. Some slight deviations occur and these might almost be ascribed to experimental error, were it not for the fact that similar but much larger deviations occur in the cases of carbon dioxide and rubber (Edwards and Pickering) and of hydrogen and platinum (Richardson). The fact that such a relation holds at all for the diverse cases cited above indicates that in these cases the controlling factors are

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[9] Lombard, *Compt. rend.*, **177**, 116 (1923).

[10] Richardson, *Phil. Mag.*, [6] **8**, 1 (1904).

[11] Deming and Hendricks, THIS JOURNAL, **45**, 2857 (1923).

probably similar. This assumption rules out the tentative suggestion of Venable and Fuwa[12] regarding the relation between viscosity and permeability since this suggestion could hardly be applied to silica glass.

The electrolytic conductance of typical solid salts is usually an exponential function of the temperature[13] and one may question if the resistance offered the migrating ions by the solids in these cases is not somewhat akin to the resistance offered to the diffusing gases in the cases cited by us.

The actual solubilities are of some interest to the geochemist. Clarke cites several cases[14] in which the gases given off by heated rocks and minerals can hardly be due to chemical reactions brought about by the heat treatments, that is, cases which are exceptions to the generally accepted rule. Since hydrogen dissolves in silica glass and also apparently in Jena glass (see blanks), and since also the solubility is proportional to the pressure, one might reasonably expect that in certain cases some of this gas might be held in true solution.

Summary

The solubilities of helium and hydrogen gases in silica glass have been determined at two temperatures. The solubility of helium in Pyrex glass was also obtained for one temperature.

The solubilities of helium and hydrogen differ but little and hence do not explain the marked differences in the rates at which these gases diffuse through silica glass.

The relation between temperature and permeability is shown to be similar for many of the cases which have been investigated.

The phenomenon in general is discussed.

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[12] Venable and Fuwa, *J. Ind. Eng. Chem.*, **14**, 139 (1922).

[13] Kraus, *Am. Chem. Soc. Monograph*, "The Properties of Electrically Conducting Systems," Chemical Catalog Co., **1922**, p. 360.

[14] Clarke, *Bull. U. S. Geol. Survey*, **695**, 270 (1920).