

more than 25% transformed before the color change corresponding to the hydrogen-ion concentration at the correct end-point for a morphine titration is reached. According to Noyes,³ the best transformation value for an indicator lies between 5 and 25%.

The conflicting values for the dissociation constants of alkaloids, given in the literature, preclude anything more than an approximate comparison of the optimum value for the indicator function obtained by calculation, and that determined empirically, for any particular titration.

Summary

1. The Sørensen values of various alkaloidal salts in aqueous solution have been determined by the potentiometer method. From these values the indicator giving the most accurate results in titrations of the corresponding alkaloid has been selected and experimental results are given to justify the selection.

2. The greater accuracy of some of the sulfonphthalein indicators in alkaloidal titrations has been pointed out.

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THE DIFFUSION OF HYDROGEN AND HELIUM THROUGH SILICA GLASS AND OTHER GLASSES¹

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Introduction

Villard,² in 1900, noted that gas leaked into an evacuated silica glass vessel when the latter was heated over a Bunsen flame to 1000° and because he found that this gas would diffuse readily through platinum, he concluded that it was hydrogen. His work was followed by that of other investigators; Jaquerot and Perrot,³ Berthelot,⁴ Richardson and Richardson,⁵ Bodenstein and Kranendieck,⁶ Mayer⁷ and Wüstner.⁸

The probable permeability of our modern water-clear silica glass can hardly be predicted from these results. Several reasons may be assigned for this, such as the qualitative nature of most of the work; the discrepancies between the observations of the various workers and the fact that

¹ Presented in part at the Rochester meeting of the American Chemical Society, April, 1921.

² Villard, *Compt. rend.*, **130**, 1752 (1900).

³ Jaquerot and Perrot, *Arch. sci. phys. nat. Geneve*, [4] **20**, 128 (1905).

⁴ Berthelot, *Compt. rend.*, **140**, 821 (1905).

⁵ Richardson and Richardson, *Phil. Mag.*, **22**, 704 (1911).

⁶ Bodenstein and Kranendieck, *Nernst-Festschrift*, **1912**, 100.

⁷ Mayer, *Phys. Rev.*, **6**, 283 (1915).

⁸ Wüstner, *Ann. Physik*, **46**, 1095 (1915).

the latter, with the exception of Wüstner, do not indicate to what extent their glasses had devitrified.⁹ We have, therefore, carried out experiments with silica glass, Pyrex glass and Jena combustion glass, using air, hydrogen and helium.

Experimental Apparatus and Procedure

Inasmuch as we were primarily interested in the permeability of silica glass to hydrogen, we thought it best to determine the amount of the gas that would leak into an evacuated vessel rather than the amount that would leak out of a vessel initially filled with the gas. Especially did this appear desirable since the results of both Bodenstein and Kranendieck, and Wüstner were obtained by the latter method.

The Gage System.—This was made up of a McLeod gage, a phosphorus pentoxide drier, the tube under test and the connecting tubes and glass bulbs. The volume of the system which ranged from 183 cc. to 1490 cc. during different experiments, was varied by sealing in or cutting off of glass bulbs of known capacity. The gage could be easily read to 0.001 mm. The silica tubes were cemented to the rest of the system by means of De Khotinski cement. The test-tubes were approximately 20 cm. long with walls from 1 mm. to 2 mm. thick. The silica tubes¹⁰ were water-clear and almost free from bubbles. For the quantitative work, they were sealed to suitable capillary tubes and the latter only were in the region of non-uniform temperature in the furnace.

The Casing.—For experiments at temperatures¹¹ above 632°, the test-tubes were inserted into the gas-filled furnace. At and below this temperature a Pyrex glass casing was used to hold the gas. It was connected to the gas supply, to a manometer and to a vacuum pump and enabled much smaller quantities of gas to be used as well as gave more ready control of the gas pressure.

Heating Element.—An electrically-heated tube furnace was used for this. It was constructed by winding a large silica glass tube with Nichrome wire and insulating with magnesia-asbestos pipe covering. The furnace had a region at the center, approximately 20 cm. in length, in which the temperature was uniform within 5°.

Pump.—A mercury diffusion pump with a fore-pump was used for the evacuations.

⁹ When silica glass devitrifies, cristobalite usually forms and this undergoes a volume change in passing from the high temperature modification to that of the low temperature. Tubes that had become well crystallized might, therefore, be expected to be porous. See C. N. Fenner, *Am. J. Sci.*, **36**, 360 (1913); Endell and Rieke, *Z. anorg. allgem. Chem.*, **79**, 239 (1912); *C. A.*, **7**, 4052 (1913).

¹⁰ We are indebted to the Thermal Syndicate Company of New York for 6 especially fine tubes.

¹¹ We found that Pyrex glass would not keep its shape when subjected to a pressure difference of 1 atmosphere at temperatures much in excess of 630°.

Temperature Measurements.—The temperatures were measured by means of a Chromel-alumel thermocouple, placed just outside the casing, in conjunction with a portable potentiometer.¹² The element was compared with a carefully standardized platinum-platinrhodium element before and after use.

The hydrogen was a commercial electrolytic product containing 0.5% of air, and was dried over sulfuric acid. The helium¹³ contained initially between 10 and 15% of methane and was purified by passing through charcoal cooled in liquid air.

In the earlier experiments the gage system was all of glass and was without stopcocks. In the later work an excellent stopcock was inserted between the pumping system and the gage system.

A typical experiment is as follows.

The casing and the gage system were tested in the cold for several hours for air-tightness. They were then placed in the furnace, the latter brought up to temperature, and were again tested for air-tightness. Hydrogen was then admitted to the casing, the air having previously either been replaced by nitrogen or pumped out. The gage system was then finally evacuated and sealed off. Manometer, temperature and gage readings were taken from time to time. The pressure of the gas in the casing was kept constant during a run. After the rate of change of the gage reading had remained constant for several hours the hydrogen was replaced either by nitrogen or air. The gage readings were continued for some time and a final reading was usually taken the next morning.

Sometimes the tests for air-tightness were made at the beginning and at the end of a series of experiments.

Discussion of Results¹⁴

With gas pressures up to 1 atmosphere and temperatures up to 881°, we have never observed any leakage of air or nitrogen gas through a sound silica glass tube. The data from a typical experiment follow.

Temperature, 750°; pressure, 1 atm. of air. The pressure in the gage system rose from 0.018 mm. to 0.020 mm. of mercury in 66.4 hours while the tube was in air. Upon displacing the air with hydrogen the pressure rose to 0.173 mm. in the next 5 hours.

Such experiments as this, together with those of Wüstner who obtained only dubious evidence that silica glass absorbs nitrogen at temperatures and pressures up to, respectively, 1000° and 900 atmospheres, lead us to believe that silica glass is practically impervious to these gases. Mayer's conclusions are at variance with this.

Neither Pyrex glass nor Jena combustion glass¹⁵ was found to be permeable to hydrogen gas at 1 atm. pressure and 640°, but the Pyrex glass slowly

¹² Made by the Leeds and Northrup Co.

¹³ We are indebted to Professor J. C. McLennan of our Department of Physics for the supply of helium and the method of purification.

¹⁴ We wish to thank Dr. J. B. Johnson for certain qualitative results which he kindly placed at our disposal.

¹⁵ Mayer also concluded that Jena combustion glass was impermeable to hydrogen.

blackens. This blackening becomes appreciable at temperatures above 500° and is not a surface effect for the color appears to extend into the glass as though the hydrogen had diffused into the glass and reacted with it.

Within the limits of the experimental errors, identical pressure changes were noted with pure hydrogen and with a gas containing small amounts of moisture, air, nitrogen or carbon dioxide when silica glass tubes were used. Similarly a slight surface devitrification of the silica glass was without noticeable effect. Below 630° these tubes did not devitrify. The tendency to devitrify was more pronounced in an atmosphere of hydrogen than we had ever observed to be the case in air with similar tubes.

Using a fresh tube of silica glass, a constant rate of pressure increase was obtained within 10 minutes at 880° , within 30 minutes at 750° , and in slightly over an hour at 440° . When a tube was first used with helium and then hydrogen, the hydrogen rate was at first high, decreasing to a constant value slowly with time, due no doubt to the slow evolution of helium.

For purposes of comparison, the permeabilities are taken as the rates in cubic centimeters per hour at 0° and 760 mm. at which the gas would diffuse through a glass wall 1 mm. thick and 1 sq. cm. in area into a vacuum. The calculations were made either by averaging the inner and outer areas of the tubes and assuming the rate inversely proportional to the thickness, or by the use of a shape factor.¹⁶

The relation of pressure to the permeability of silica glass, to hydrogen gas and helium gas is shown in Fig. 1.

Bodenstein and Kranendieck made use of the formula $dx/dt = k(a - x)$ and calculated k from their results. They obtained constant values for k over a considerable range of pressures. Wüstner carried out two experiments at 600° , one at 400 atmospheres and one at 1000 atmospheres. He noted that the changes in gas volume in the two cases were approximately identical (a difference of 15%) and concluded that the absorption of the gas by the silica glass was proportional to the gas pressure. Our results would indicate a similar relation between permeability and pressure to that just given. Such a relation for helium renders improbable the conclusion of Richardson and Richardson that helium leaked into an evacuated silica glass tube from the air when the tube was heated in air. One would rather believe that the helium came from the glass itself.

In Fig. 2 the logarithms to the base 10 of the permeabilities are plotted against the temperatures and the permeabilities appear to be exponential functions of the temperatures. Wüstner's results are thus confirmed.

The permeability of rubber to hydrogen, helium and carbon dioxide

¹⁶ Langmuir, Adams and Meikle, *Trans. Am. Electrochem. Soc.*, **24**, 53 (1913).

was found by Edwards and Pickering¹⁷ to bear a like relation to the temperature.

When Bodenstein and Kranendieck calculated the permeability of

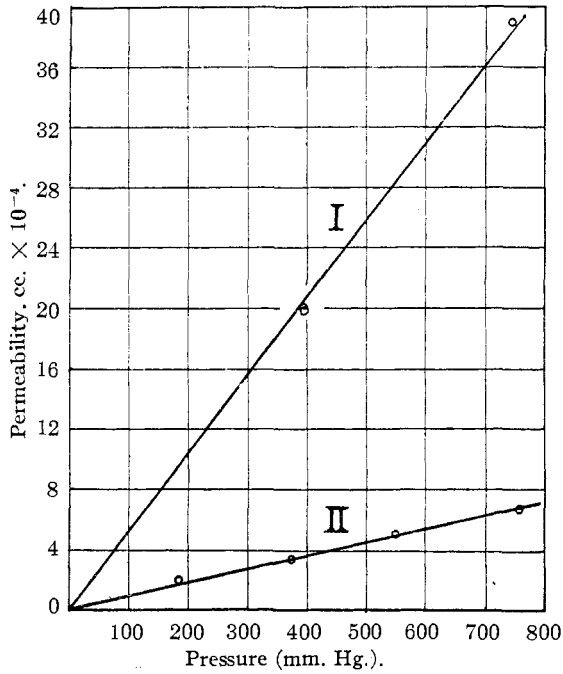


Fig. 1.—The relation of permeability to pressure.
Curve I, helium at 441°; Curve II, hydrogen at 625°.

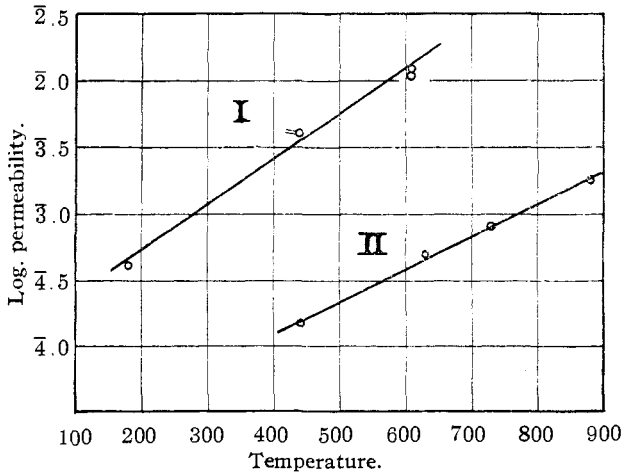


Fig. 2.—The relation of permeability to temperature.
Curve I, helium (760 mm.); Curve II, hydrogen (760 mm.).

¹⁷ Edwards and Pickering, *Bur. Standards Sci. Paper*, 387 (1920).

silica glass to hydrogen at 880°, they neglected to take account of the volume of their system although they had determined it. If we correct their value for this oversight, we obtain 21.6×10^{-4} cc. instead of 8.65×10^{-6} cc.¹⁸ The correct calculation for 732° gives a value of 11.0×10^{-4} cc., a result in accord with ours.

Jaquerot and Perrot do not give enough data for a calculation of the permeability. If we assume that their vessel had a minimum wall thickness of 1 mm., and this seems a fair assumption, then their results lead to values considerably higher than those of Bodenstein and Kranendieck. This fact led us to view their hydrogen results with suspicion at first and indirectly their helium results also. The relative permeabilities for hydrogen and helium may be calculated from their work. At 500° for helium it is 27 times the value for hydrogen. Our curves indicate a similar ratio of 22 for this temperature.

In Table I are collected the values obtained with several tubes. The underlined values were picked from curves since, unfortunately, the experiments were not carried out at quite the desired temperatures. Tubes 1, 2, 4 had a wall thickness of 1 mm., Tube 9 of 1.2 mm. and Tube 10 of 2 mm.

TABLE I
THE PERMEABILITIES OF DIFFERENT SILICA GLASS TUBES TO HYDROGEN

Temperature ° C.	Tube 1	2	4	9	10	Remarks
440	1.61	1.5	..	1.6	<u>1.7</u>	
440	1.9	
610	5.15	<u>4.6</u>	..	<u>7.1</u> (high)	<u>6.2</u>	The high value is due to the experiment having followed one with helium. The rate had not quite become constant.
727	<u>9.5</u>	8.0	7.7	...	<u>12.0</u>	
881	..	17.7	15.0	

Wüstner's experiments were carried out at pressures between 800 and 900 atmospheres in most cases, and at temperatures up to 1100°. He determined the amount of gas that disappeared in 5 minutes from a gas-filled silica glass vessel; the walls of the vessel were about 0.2 mm. thick. By combining these results with his results upon the absorption of hydrogen by the glass at these temperatures, he calculated the diffusion constants for the different temperatures. He assumed the absorption to be proportional to the pressure and that the concentration of gas at one surface was zero and at the other corresponded to a state of saturation. For the purpose of comparison we have calculated the diffusion constants for hydrogen from the results plotted in Fig. 2 and the absorption coefficients

¹⁸ Kurt Arndt has unfortunately quoted the incorrect value for 880°, "Handbuch der physikalisch-chemischen Technik," Enke, Stuttgart, 1915, p. 28.

given by Wüstner. Together with the values obtained by Wüstner in his first series of experiments, these constants are given in Table II.

TABLE II
THE CALCULATED DIFFUSION CONSTANTS

Temperature °C.	Wüstner Cm. ² sec. $\times 10^{-8}$	Williams and Ferguson Cm. ² sec. $\times 10^{-8}$
400	1.1	0.5
600	1.7	1.5
700	1.8	2.0
800	3.2	3.0

All values in Wüstner's second series are somewhat higher. This might be easily explained if he used a different sample of silica glass.

The agreement between the results of Bodenstein and Kranendieck, Wüstner and ourselves (results obtained under a variety of conditions) is such as to inspire confidence in their correctness. The effect of slight impurities in the silica glass, as evidenced by the different results obtained with different samples of glass, is such that if an exact value of the permeability were required for a new sample, a determination would be necessary.

The permeability of Pyrex glass at 610° to helium at one atmosphere pressure was found to be 5.2×10^{-4} cc. The tube used was impervious to hydrogen after this experiment.

The surprising thing about our results with silica glass is the great rapidity with which helium will pass through it as compared to hydrogen. Were it a case of effusion the ratio would be less than unity, whereas at 500° we found a ratio of 22. Jaquerot and Perrot obtained a ratio with porcelain which is in substantial agreement with the value calculated for a case of effusion. Similarly the ratios obtained for rubbered balloon fabrics¹⁹ and for thin soap bubbles²⁰ also agree with this assumption. On the other hand Sir James Dewar²¹ offers no general theory for the rates at which various gases pass through pure rubber. We likewise have not sufficient information on which to base a theory to explain our results.

The suggestion that the slow rate for hydrogen might be due to chemical action seems unreasonable since a discoloration of the tubes was never noted.

We hope to be able to continue our work and shed some light on this phase of the subject.

Summary

1. Silica glass is permeable to hydrogen at high temperatures. The permeability is proportional to the gas pressure and is an exponential function of the temperature. Above 300° it becomes appreciable.

¹⁹ R. T. Elworthy and V. F. Murray, *Trans. Roy. Soc. Canada*, **13**, Sec. III, 37 (1919).
J. D. Edwards and S. F. Pickering, *Bur. Standards Sci. Paper*, **387** (1920).

²⁰ J. C. McLennan and W. W. Shaver, *Phil. Mag.*, **40**, 272 (1920).

²¹ Sir James Dewar, *Proc. Roy. Inst. Gt. Britain*, **23**, 813 (1918); *J. Chem. Soc. (London)*, **114**, 2, 186 (1918).

2. Silica glass is similarly permeable to helium. This may be easily measured at 180°. At 500° this permeability is about 22 times that of hydrogen.

3. Neither Pyrex glass nor Jena combustion glass was found to be permeable to hydrogen, but the gas apparently reacts with the Pyrex, causing it to blacken. The latter is also permeable to helium.

4. The permeabilities of a number of samples of glass were determined and the results correlated with the work of previous experimenters.

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THE DETERMINATION OF LEAD IN LEAD AMALGAM

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The determination of lead in lead amalgam, or of both the lead and the mercury, has been accomplished by several methods. A brief account of the types of these methods which have been so employed was presented in a preliminary paper.¹ At this time it seems sufficient to mention merely the principles involved in the various procedures.

Two electrolytic methods have been proposed. For amalgams prepared electrolytically Lindeck² and Stähler and Alders³ claim success in the calculation of the concentration of the lead from the weights of mercury used as cathode and of the resulting amalgam. Vortmann⁴ reported difficulty from oxidation of the amalgam while drying, and the author has had the same experience. Smith⁵ reported the simultaneous electrodeposition of small amounts of lead and mercury from a solution in nitric acid.

The gravimetric procedures involve a solution of the amalgam in nitric acid and a subsequent separation of the two elements by precipitation. The lead may be precipitated by means of sulfuric acid and the mercury taken by difference, or determined as the sulfide.⁶ Humphreys volatilized a considerable portion of the mercury before dissolving the amalgam. Treadwell,⁷ and also Scott,⁸ recommend precipitating the two elements together as the sulfides and then effecting a later separation.

¹ Mellon and Reinhard, *Proc. Ind. Acad. Sci.*, 1921, p. 189.

² Lindeck, *Wied. Ann.*, 35, 311 (1888).

³ Stähler and Alders, *Ber.*, 42, 2685 (1909).

⁴ Vortmann, *ibid.*, 22, 2756 (1891).

⁵ Smith and Moyer, *J. Anal. Chem.*, 7, 252 (1893). Smith and Heidenreich, *Ber.*, 29, 1585 (1896). Jordan, *J. prakt. Chem.*, 10, 439 (1837).

⁶ Horsford, *Am. J. Sci.*, [2] 13, 305 (1852). Bauer, *Ber.*, 4, 449 (1871). Guthrie, *Phil. Mag.*, [5] 16, 321 (1883). Crookes, "Select Methods in Analytical Chemistry," 1894, p. 324. Humphreys, *J. Chem. Soc.*, 69, 243 (1896).

⁷ Treadwell-Hall, "Analytical Chemistry," John Wiley & Sons, 1919, II, p. 194.

⁸ Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand, 1917, p. 271.