

THE
PHYSICAL REVIEW.

THE INFRA-RED ABSORPTION SPECTRA OF ALKALI
HYDROXIDES.

BY G. E. GRANTHAM.

SYNOPSIS.

Infra-red Absorption of Aqueous Solutions of Alkali Hydroxides, 1-3 μ .—The absorption of various concentrations of solutions of *NaOH*, *KOH* and *LiOH* and of one solution each of *NH₄OH* and *CsOH* was determined with reference to that of water, using two like cells with quartz windows, and a suitable spectrometer with thermopile and sensitive galvanometer. All curves show a broad, intense absorption band with a maximum at about 2.29 μ except in the case of the *NH₄OH* solution for which the maximum is at 2.20 μ . This agreement suggests that the band is due to dissociated hydroxide ions; yet in the case of other hydroxide solutions previous observers have not obtained an absorption band at this place. The absorption was found to be proportional to the concentration but not to vary systematically with the atomic weight of the base of the hydroxide. In the case of *KOH* the relative absorption results were checked by actual absorption measurements.

The Coefficient of Absorption of Water, 1.3 to 2.0 μ was measured by comparing the transmissions of cells of different thicknesses. Maximum absorption was observed at 1.48 and 1.98 μ . *The effect of dissolving an alkali hydroxide* is to decrease the absorption of the water in the band at 1.48 μ by an amount proportional to the concentration of the solution and to the atomic weight of the base.

INTRODUCTION.

AN investigation of the ultra-violet and visible absorption spectra of aqueous alkaline solutions of phenoltetrachlorophthalein by Howe and Gibson¹ showed absorption bands at frequency numbers 3590, 2760 and 1740. These bands are approximately harmonic and it seemed desirable to search for the next band of the harmonic series which should have a frequency number of about 900, or a wave-length of approximately 1.1 μ . This search proved fruitless, but in the region 1.7 μ it was found that a given thickness of a ten gram molecule per liter aqueous solution of *NaOH* transmitted less energy than did an equal thickness of phenol-

¹ *PHYS. REV.*, S. II., Vol. X, 1917.

tetrachlorophthalein in a ten gram molecule per liter aqueous solution of NaOH. Further trial showed that NaOH has a strong absorption in this region and that the result just described was due to a di-sodium salt being formed in the cell containing the phenoltetrachlorophthalein, which formation used up n gram molecules per liter of the NaOH, thus, in effect, making this cell contain a less thickness of NaOH. This suggested a study of the absorption spectra of alkaline hydroxides in the region 1.0μ to 3.0μ . The measurements were made by means of a spectrometer in conjunction with a thermocouple and galvanometer.

METHOD.

Owing to the strong absorption of aqueous solutions in this region, a differential method was adopted. The deflection d_1 was taken when the radiation was passing through a given thickness of water, and an instant later the deflection d_2 was taken when the radiation was passing through an equal thickness of the aqueous hydroxide solution. This made it possible to have the two galvanometer deflections of the same order of magnitude, and to work with the galvanometer in a more sensitive condition. The values d_1 and d_2 were taken at least three times for each wave-length, or until consistent results were obtained. Readings were taken at each 0.1μ except in the region of a peak on the transmission curve where they were made more frequently. A sample of the data obtained is shown in Table I. These values were selected at random from a complete set of data for KOH and represent about one third of the values taken for one curve. The per cent. relative transmission was calculated from the equation: $\text{Transmission} = (d_1/d_2) \times 100$.

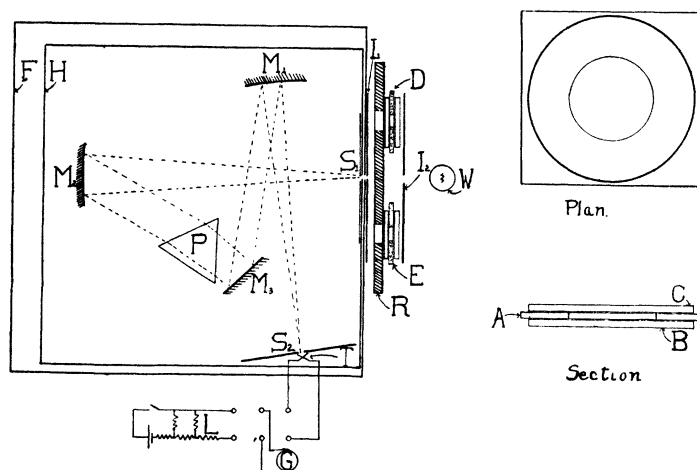


Fig. 1.

APPARATUS.

The apparatus used is shown in Fig. 1. The galvanometer and spectrometer have been quite fully described by the writer in a previous article.¹ The spectrometer was of the Hilger constant deviation type equipped with a rock salt prism *P* and a Coblenz² bismuth-silver thermopile *T*. When adjusted the instrument gave the following values for the three absorption bands of water and the carbon dioxide emission band respectively; 1.48 μ , 1.98 μ , 3.0 μ and 4.36 μ . These points were checked from time to time during this work. The spectrometer was covered by a glass case *H*, which was in turn covered by a sheet iron case *F*. The inside walls of *H* were covered with black cloth to prevent reflection. A 2.5 watt electric lamp was kept burning continuously immediately under the spectrometer to prevent dew formation, and P_2O_5 was used to keep the air surrounding the prism dry. During the experiments the slits *S*₁ and *S*₂ were 0.25 mm. wide.

A Coblenz³ astatic galvanometer *G* was used. The sensibility of the galvanometer was adjusted to approximately 3.3×10^{-11} ampere per mm. at three meters distance. The sensibility was measured by means of the testing box *L*, which was furnished with the galvanometer. No deflection greater than 35 cm. was used.

The source of radiation *W* was a 400-watt nitrogen filled lamp which was supplied with current from a 120-volt storage battery.

The cells which contained the solutions were made as follows: A piece of plane glass was ground until its thickness was uniform and was then cut into two parts, each of which was four centimeters square. Through the center of each of these parts a hole 2 cm. in diameter was ground, making two glass washers. To assemble a cell one of these washers *A* was placed upon a quartz plate *B*, the small volume formed by the hole and the quartz plate filled with the solution, and another quartz plate *C* placed over the glass washer. These three parts were then clamped together and placed upon the slide *R* at *D*. The other cell was made similarly, using the other glass washer filled with water and mounted on the slide at *E*. The four quartz plates used were of equal thickness. Sheet iron screens *I*₁ and *I*₂, with holes 1.5 cm. in diameter, permitted no radiation to enter the slit *S*₁, except that which had come through the water, or solution in a cell. The pairs of washers used for different regions in the spectrum were 3.77 mm., 1.29 mm., 0.84 mm. and 0.15 mm. thick. Unless otherwise stated in this paper the thickness of the cell used was 0.84 mm.

¹ PHYS. REV., S. II., Vol. XVI., 1920.

² Bulletin of the Bureau of Standards, Vol. 9, 1912.

³ Bulletin of the Bureau of Standards, Vol. 4, 1908. Bulletin of the Bureau of Standards, Vol. 9, 1912. Scientific Papers of the Bureau of Standards, No. 282.

TABLE I.
Ten gram molecule per liter aqueous solution of KOH.
Thickness 0.84 cm.

μ	d_1 mm.	d_2 mm.	Transmission, Per Cent.	Average, Per Cent.
1.0	85	85	100	100
	85	85		
1.3	85	85	101	100.3
	199	201		
	195	195		
1.4	202	202	122.3	121.6
	135	165		
	135	163		
1.5	135	164	121.5	135.3
	81	109		
	80	109		
1.7	81	109	135	48.9
	212	103		
	210	103		
2.0	210	103	48.6	49.0
	141	50		
	139	48		
2.1	139	49	35.5	35.1
	137	32		
	132	32		
2.2	131	31	23.3	23.3
	168	25		
	165	26		
2.3	165	26	14.9	15.5
	252	38		
	252	37		
2.5	250	37	15.1	14.9
	59	21		
	59	21		
2.7	59	21	35.6	35.6
	25	18		
	24	17		
2.9	22	16	72	71.7
	24	17		
	18	15		
2.9	18	15	71	72.7
	18	15		
	18	15		
2.9	18	15	71	83.4
	18	15		
	18	15		

RESULTS.

The absorption for different concentrations of NaOH, LiOH and KOH was observed as described above. The absorption for a 0.25 gram molecule per liter aqueous solution of CsOH and for an approximately 15 gram molecule per liter solution of NH_4OH was also observed. The results of these investigations are shown graphically in Figs. 2-7. Figs.

2, 3 and 4 show the absorption curves for different concentrations of the aqueous solutions of the alkali hydroxides. These curves are similar, each showing evidence of strong absorption in the region between 1.5μ and 2.6μ with a maximum of absorption at about 2.29μ . There is

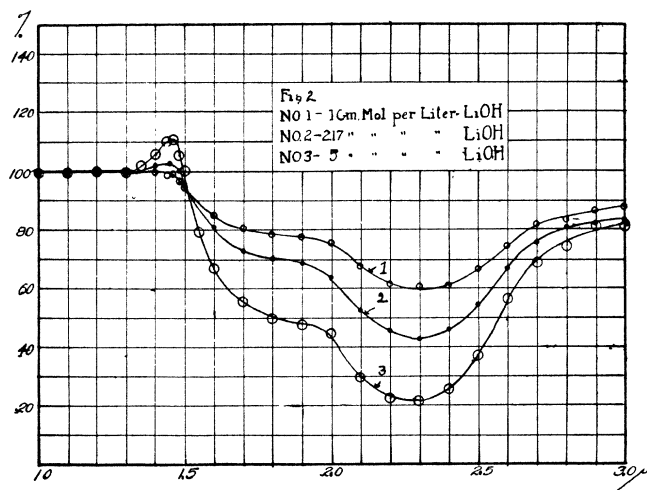


Fig. 2.

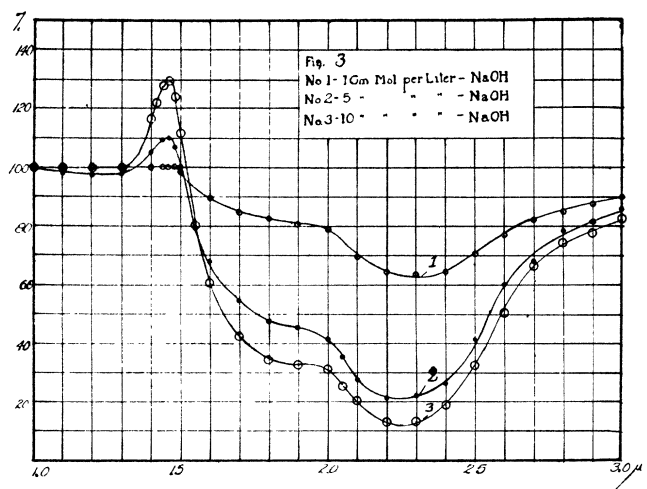


Fig. 3.

practically no difference in the absorption of a given thickness of water such as was used in this investigation, and that of an equal thickness of solution of X-OH in the region from 1.0μ to 1.3μ . From 1.3μ to 1.55μ the absorption of a given thickness of water is much greater than

the absorption of the same thickness of a solution of X-OH. This range (1.3μ to 1.55μ) includes a sharp absorption band due to water at 1.49μ . It also includes a region of weak absorption for X-OH. There is in the X-OH cell a less number of water molecules than in the water cell due to the replacement of water molecules by the X-OH molecules. If the X-OH absorption was weak in this region, a transmission value higher than 100 per cent. would be expected by this method. This explanation, however, does not account for the high values of transmission obtained. The density of a ten gram molecule per liter aqueous solution of KOH was found from chemical tables to be 1.414 grams per c.c. In this

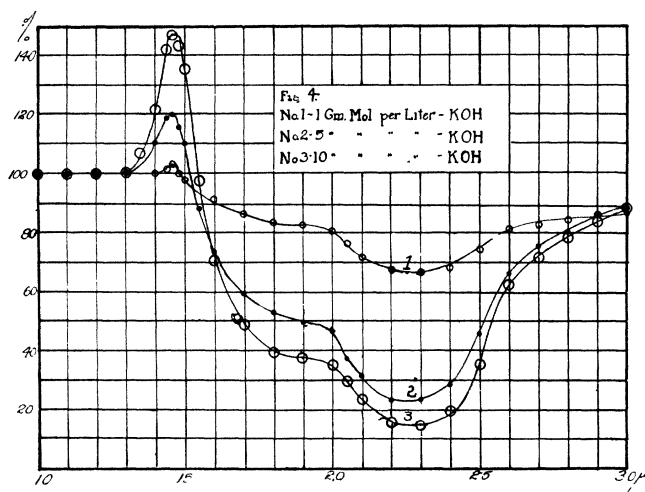


Fig. 4.

solution there were 561.00 grams of KOH per liter. The thickness of the solution used in the cell was 0.84 mm. The actual thickness of the water in this cell was then

$$\frac{1414 - 561}{1000} \times 0.84 = 0.716 \text{ mm.}$$

If the coefficient of absorption of water was known, the per cent. of transmission for equal thicknesses of solution and of water, assuming that the KOH had no effect either as an absorbing agent itself or in modifying that of the water, could be calculated. The coefficient of absorption of water was measured in the following manner: Two cells of different thickness, filled with water, were mounted on the slide and the energy transmitted by each, for wave-lengths in the region 1.3μ to 2.0μ , was measured. The values of the coefficient of absorption were then calculated from the relation:

$$\beta = \frac{I}{c(t_2 - t_1)} \log I_1/I_2$$

where c is the concentration, taken as unity, and I_1 and I_2 the energy transmitted at a given wave-length through cells of thickness t_1 and t_2 respectively. The different values of β were obtained using cells of thickness 0.84 mm. and 1.183 mm. The measurements were then repeated using cells of thickness 0.84 mm. and 1.290 mm. and the mean value for β used. Using these values of β and 0.84 mm. and 0.716 mm. for t_2 and t_1 respectively, the values of I_1/I_2 were calculated for this region of the spectrum. These results are shown graphically in Fig. 5, curve No. 2. Curve No. 1 is the observed per cent. transmission curve for a ten gram molecule per liter aqueous solution of KOH, while No. 2 shows the corresponding values for the same solution calculated in the manner just described. Curve No. 1 shows a maximum ordinate at 1.46μ of

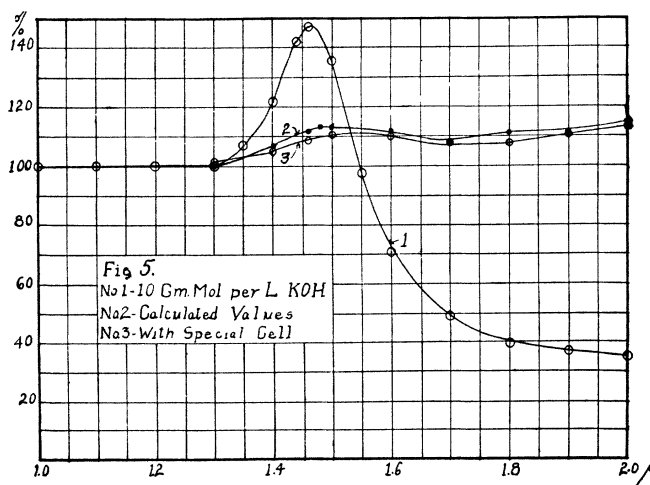


Fig. 5.

value 147 per cent., while, if this increase in transmission was due to the different thickness of water, the maximum value of the ordinate should be 112 per cent. This indicates that the presence of KOH has an effect upon the absorption of water, which effect is to make the transmission greater. A similar calculation with similar results was made for NaOH. The heights of these peaks as seen from Figs. 2, 3 and 4 are roughly proportional to the concentration for a given hydroxide, and to the atomic weight of the base for different hydroxides. The peak of the transmission band is at 1.46μ in each case, while the maximum absorption of water in this region is shown by Fig. 7, curve No. 2 to be at 1.49μ . This apparent shift of 0.03μ toward the shorter wave-lengths is explained by the overlapping of the X-OH absorption band on the transmission band. If it

were not for this overlapping, the maximum of the transmission bands, shown in Figs. 2, 3 and 4 might coincide with the maximum absorption of water.

In order to check the method just described for testing the replacement of water molecules by KOH the following suggestion was acted upon.

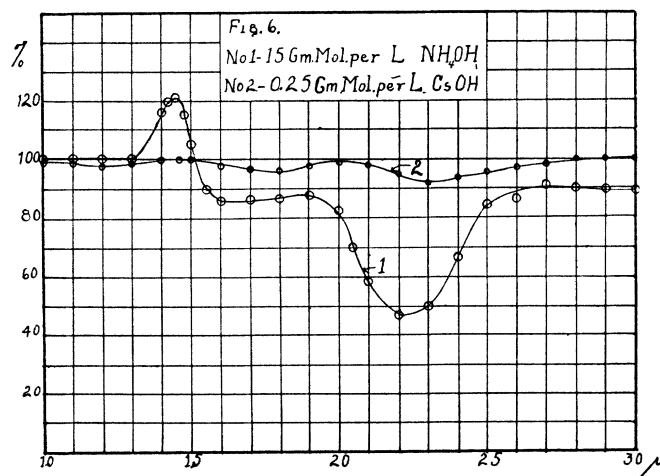


Fig. 6.

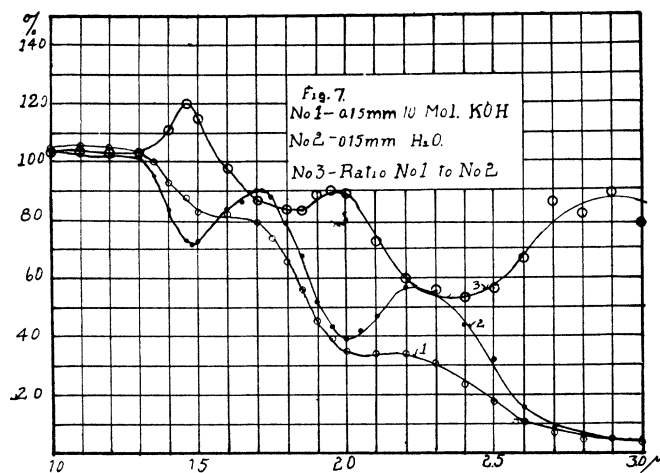


Fig. 7.

By using one cell 0.84 mm. thick and the other of the same thickness as the actual layer of water in a cell 0.84 mm. thick, filled with a ten gram molecule per liter aqueous solution of KOH, namely, 0.716 mm., the per cent. transmission could be obtained directly. In an attempt to

grind a glass washer of this thickness and keep it uniform the grinding was carried too far, and a cell 0.705 mm. thick was obtained. The results of the use of the cells 0.84 mm. and 0.705 mm. thick are shown in Fig. 5, curve No. 3. These results check, as well as could be expected, with those calculated above.

On the transmission curves shown in Figs. 2, 3 and 4 there is a hump at wave-length 2.0μ . This is also the location of a strong absorption band of water, as shown by Fig. 7, curve No. 2. This hump may be due to the same effect as the peak at 1.46μ . It lies, however, in the region of strong absorption of X-OH, and for this reason a similar conclusion cannot be drawn from calculations. Owing to this increase in transmission at 2.0μ the minimum of the transmission curves, which lies at 2.29μ , may be shifted toward the longer wave-lengths, and it is therefore probable that the maximum of absorption of the X-OH solutions is at a slightly shorter wave-length than 2.29μ . Since the absorption curves for the hydroxides of the alkali metals tested are similar, it is evident that the absorption is due to the OH radical. This conclusion is further substantiated by the fact that, at a given wave-length, the magnitude of the absorption for the same strength of different solutions shows no systematic variation with atomic weight of the base. The position of the minimum at 2.29μ does not shift with the change of atomic weight of the base.

Fig. 7, curve No. 1 shows the actual transmission of a 0.15 mm. thickness of a ten gram molecule per liter aqueous solution of KOH, and No. 2 the transmission of the same thickness of water. Curve No. 3 shows the result of plotting the ratio of the ordinates of curves No. 1 and No. 2. This curve is similar to those of Figs. 2, 3 and 4. The relatively strong transmission of the empty cell made it necessary to use the galvanometer at low sensibility, and consequently the accuracy of measurement was not as great for the curves of this figure as for those of Figs. 2, 3 and 4. A study of Fig. 7, curves No. 1 and No. 2 shows the region of the strongest absorption of the KOH to be from 1.8μ to 2.5μ .

Fig. 6, curve No. 1 shows the transmission of an approximately 15 gram molecule per liter solution of NH_4OH . In this curve there is a shift of the minimum to 2.2μ , and the hump in the curve at 2.0μ is much more pronounced than in the case of the hydroxides of the alkali metals. Curve No. 2 shows the transmission of a 0.25 gram molecule per liter aqueous solution of CsOH. The solution was very weak, due to lack of chemicals. No attempt was made to study the absorption of RbOH for the same reason.

Ransohoff¹ has studied the effect of the OH group on absorption using six alcohols. He found bands at 1.71μ and 3.0μ , neither of which falls in the region of the strong absorption found in this investigation. Coblentz² has studied the absorption of $Mg(OH)_2$ and other hydroxides of elements not in the alkali metal group, and his results show no absorption in the region 2.29μ . This would indicate that the band is present only in strongly alkaline hydroxides.

From Fig. 7, curve No. 1 it is seen that the effect of the absorption band of water at 1.49μ is much less marked in the absorption curve of the KOH solution, than the effect of the absorption band of the water at 2.0μ . It is probable that this absorption band of water would disappear, if the concentration of the X-OH were sufficiently high. Coblentz³ has shown that the strong absorption band of solid iodine at 7.3μ disappears when the iodine is placed in solution. This is caused by the action of the solvent upon the absorption of the solute, while the effect here described is the effect of the solute upon the absorption of the solvent.

In papers by Guy, Schaeffer and Jones⁴ and by Schaeffer, Paulus and Jones,⁵ curves appear that show similar effects upon the absorption bands of water at 1.0μ and 1.24μ , when various metallic salts are dissolved in water. The maximum absorption of the solutions does not, in many of the cases shown, occur at the same wave-length as that of the water. The ratio of transmission of solution to the transmission of a layer of water, equal in thickness to that contained in the solution at the positions of maximum absorption for each, is as large as 1.21 for 2.14 normal solution of $MgSO_4$ and 1.16 for 1.02 normal solution of $Al_2(SO_4)_3$.

Livens⁶ in a theoretical paper discusses the effect of solute upon the absorption of a solvent, and points out that a shift in the position of the absorption bands should accompany a change in the intensity of the maximum absorption.

CONCLUSIONS.

The following conclusions may be drawn from these investigations:

1. There is a broad, intense absorption band in the spectra of the alkaline hydroxides in the region 1.5μ to 2.7μ .
2. The absorption is roughly proportional to the concentration of the solution for a given hydroxide.
3. There is no systematic variation of the absorption with the atomic weight of the base.

¹ Berlin Inaugural Dissertation, January, 1896.

² Scientific Papers of the Bureau of Standards, No. 45, 1907.

³ *PHYS. REV.*, XVI., I., 1903.

⁴ *Phys. Zeits.*, Vol. 14, p. 278, 1913; *Amer. Chem. Jour.*, 49, p. 265, 1913.

⁵ *Phys. Zeits.*, Vol. 15, p. 447, 1914; *Chem. News*, 110, p. 223, 1914.

⁶ *Phys. Zeits.*, Vol. 14, p. 660, 1913.

4. The absorption is probably due to the dissociated hydroxide ions, as the absorption is not present in the alcohols, or other compounds which have the OH radical.

5. The presence of an alkaline hydroxide in solution with water decreases the actual absorption of the water present. This effect of the solute upon the absorption of the solvent increases with the concentration. This shows evidence of a change of the physical properties of the water molecule, when it becomes the solvent.

This investigation was carried on in the Physics Laboratory of Cornell University. The writer wishes to thank Professor R. C. Gibbs, under whose direction this work was done, for his interest and advice throughout this investigation and the writing of this report. He wishes also to thank Professor W. R. Orndorff of the Chemistry Department for advice regarding the chemistry involved, Dr. S. D. Jackson and Mr. R. T. K. Cornwell of the Chemistry Department for making up the standard solutions and his wife, Margaret Grantham, for assistance in taking the data and computing the results.

U. S. NAVAL ACADEMY,
ANNAPOLIS, MARYLAND.