

7. The change in salt effects for a P_H range from 3.97 to 12.55 was determined. Specific salt effects over the secondary hydrogen ion change only become important in the extreme range of P_H values.

WASHINGTON, D. C.

NOTES

The Atomic Weight of Chlorine. The Solubility of Silver Chloride.—

I am grateful to Messrs. Scott and Johnson¹ for calling my attention to an erroneous statement in the paper by Hönigschmid and Chan² on the atomic weight of chlorine.

Our reason for deciding that it was unnecessary to apply a correction for the silver chloride removed in making the nephelometric tests, when the precipitate was subsequently to be weighed, was that we had assumed its solubility under the conditions of the analysis at 0° to be 0.05 mg. per liter. At that time we had not determined this value ourselves but, through an error in reading, had taken from the paper by Richards and Willard³ this value instead of the true one, 0.5 mg. per liter. After reading the communication of Scott and Johnson, we determined this solubility in analyses both of sodium and potassium chlorides at the equivalence point, after the usual shaking and cooling in ice for several days. Portions of the perfectly clear solution were pipetted into nephelometer tubes and, after addition of silver and chloride ion, respectively, showed the same opalescence as a standard containing 0.53 mg. of silver chloride per liter, thus completely confirming the work of Richards and Willard. When an excess of 0.3 mg. of silver was added, the solubility was 0.42 mg. or only 80% as much. This common ion effect makes the correction uncertain.

The nature of the precipitate obtained by us was probably different from that obtained by Scott and Johnson, and this doubtless accounts for the lower solubility found by us. In making the correction we prefer to use our own value because we consider it more applicable.

A calculation of the correction to be applied was easily made by referring to the laboratory notebook which contained all the data. Usually only two or three tests were necessary, because the proper amount of silver was carefully weighed to within 0.1 or 0.2 mg. It was assumed that 100 cc. of the solution contained 0.05 mg. of silver chloride, as already determined, because although it may have been less in the first test, when an excess of one ion was present, this value is certainly a maximum. Each nephelometer tube contained 22 cc. The corrections are shown in Table I.

¹ Scott and Johnson, *THIS JOURNAL*, **52**, 3586 (1930).

² Hönigschmid and Chan, *Z. anorg. allgem. Chem.*, **163**, 315 (1927).

³ Richards and Willard, *THIS JOURNAL*, **32**, 4 (1910).

TABLE I
 CORRECTION VALUES

No.	No. of nephelometric tests	Vol. of soln. removed, cc.	AgCl in soln., mg.	Corr. wt. AgCl in vac., g.
1	2	88	0.044	11.54010
2	2	88	.044	9.11889
4	3	132	.066	9.94704
5	4	176	.088	13.58106
6	4	176	.088	11.96637
7	3	132	.066	8.94863
8	3	132	.066	12.30290
9	3	132	.066	8.80133

In Table II are shown the corrected gravimetric values for the atomic weight of chlorine, together with the weights of silver plus chlorine taken and found.

 TABLE II
 THE ATOMIC WEIGHT OF CHLORINE

No.	Wt. of Cl in vac., g.	Wt. Ag in vac., g.	Wt. AgCl in vac., g.	Diff., mg.	Cl:AgCl	At. wt., Cl
1	2.85458	9.68543	11.54010	-0.09	0.2473618	35.4558
2	2.25569	6.86312	9.11889	-0.08	.2473645	35.4563
4	2.46049	7.48635	9.94704	-0.20	.2473590	35.4553
5	3.35955	10.22139	13.58106	-0.12	.2473702	35.4574
6	2.96007	9.00620	11.96637	-0.10	.2473657	35.4565
7	2.21357	6.73502	8.94863	-0.04	.2473641	35.4562
8	3.04333	9.25949	12.30290	-0.08	.2473669	35.4568
9	2.17711	6.62409	8.80133	-0.13	.2473615	35.4558
	21.32439	64.88109	86.20632	-0.84	.2473646	35.4563

The average value for the atomic weight of chlorine is 35.4563, and that obtained nephelometrically is 35.4567. The average deviation between the weight of silver chloride found and calculated is 0.10 mg. and the total for eight gravimetric determinations is 0.84 mg.

Because silver chloride retains traces of other salts, it is probable that the weight obtained in the gravimetric process tends to be too great and that an exact agreement between the gravimetric and volumetric methods, if it occurs, is due to a chance compensation of errors in both directions.

In most of our atomic weight determinations the error due to uncertainty in the amount of silver chloride removed for nephelometric tests is, as shown above, very small, because the solution is almost always so near the equivalence point that very few tests are necessary.

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Note on the Third Law Calculation of the Entropy and Free Energy of Ammonia.—A calculation of the molecular entropy and free energy of formation of ammonia has been made by means of the third law of thermodynamics using the low temperature heat capacity data of this compound. The calculated molecular entropy and free energy of formation are, respectively, 46.7 entropy units, and -4150 calories at 298.1°K .

There has been considerable uncertainty regarding the proper value of the entropy of hydrogen to be used in thermodynamic calculations in combination with other molecular entropies obtained by means of the third law. For this purpose, Giauque¹ has recommended a value derived from the absolute entropy of ordinary hydrogen obtained from spectral data, modified by the principle of nuclear spin cancellation.² This value has been found satisfactory for systems of monatomic and diatomic substances, but has not been conclusively tested for larger molecules. Since the thermal data and equilibrium in the ammonia synthesis, $\frac{1}{2}\text{N}_2(\text{g}) + 1\frac{1}{2}\text{H}_2(\text{g}) = \text{NH}_3(\text{g})$, are known with a high order of precision,³ and since there are now sufficient measurements upon ammonia at low temperatures to permit a calculation of the molecular entropy, this substance serves as a test of the applicability of the third law, and more particularly of Giauque's value for the entropy of hydrogen.

The low temperature heat capacity measurements used in the present calculation are those of Clusius, Hiller and Vaughen,⁴ also Eucken and Karwat.⁵ Heats of vaporization and fusion were taken from the work of Eucken and Donath.⁶ Extrapolation to 0°K . was carried out by the Debye function with $\theta = 215$. For the heat capacity of the gas, the values of Osborne⁷ and associates were used. The molecular entropy thus obtained is 46.7 entropy units at 298.1°K .

Assuming Giauque's value of 31.23 for the entropy of hydrogen, and 45.6 for that of nitrogen,⁸ the entropy change accompanying the formation of ammonia is -22.9 E. U. The heat of formation, $\Delta H_{298.1}$, which is equal to $-10,985$ calories, is obtained from Lewis and Randall's equation⁸

$$\Delta H = -9500 - 4.96T - 0.000575T^2 + 0.0000017T^3$$

The free energy of the ammonia synthesis can be derived from the above results by means of the second law, and is found to be: $\Delta F_{298.1}^\circ = -4150$,

¹ Giauque, *THIS JOURNAL*, **52**, 4816 (1930).

² Gibson and Heitler, *Z. Physik*, **49**, 465 (1928).

³ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 556-557.

⁴ Clusius, Hiller and Vaughen, *Z. physik. Chem.*, **8B**, 427 (1930).

⁵ Eucken and Karwat, *ibid.*, **112**, 467 (1924).

⁶ Eucken and Donath, *ibid.*, **124**, 181 (1926).

⁷ Osborne, Stimson, Sligh and Cragoe, Bur. Standards Sci. Paper No. 501, Washington, D. C., 1925.

⁸ Lewis and Randall, Ref. 3, p. 464.

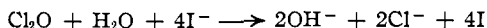
which may be compared with the experimental $\Delta F_{298.1}^{\circ} = -3910$ given by Lewis and Randall.⁸ If the previously accepted value⁹ of 29.6 for the entropy of hydrogen be used instead of that later recommended by Giauque,¹ $\Delta F_{298.1}^{\circ} = -4900$ is obtained. It is obvious that Giauque's value gives the better agreement with experiment.

Villars¹⁰ has calculated the molecular entropy of ammonia from spectroscopic data. His figure, 44.0 E. U., is not given on the same basis as the above value. When Villars' result is made comparable with the entropy of hydrogen used here (31.23), his value becomes 46.5, in close agreement with the 46.7 given above.

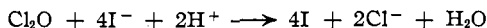
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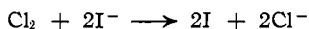
The Analysis of Chlorine Monoxide-Chlorine Mixtures.—Chlorine monoxide may be determined by absorption in potassium iodide solution and titration of the iodine liberated.



It is necessary to acidify the solution before titrating with thiosulfate.¹



The liberation of OH^- provides a further means for the determination of chlorine monoxide and indicates a method for the analysis of chlorine monoxide-chlorine mixtures.



Excess of standard sulfuric acid is added and after titration of the total iodine with thiosulfate the excess acid is found by back titration with standard alkali. Bowen² used methyl orange as indicator, while Hinshelwood³ used *N*/10 baryta and phenolphthalein. If x cc. of thiosulfate is used and then y cc. of sulfuric acid is required to neutralize the OH^- ; $\text{Cl}_2\text{O} \propto y$ and $\text{Cl}_2 \propto x - 2y$. Acid, base and thiosulfate must all be of the same normality or correcting factors are necessary.

The analysis can be simplified by an adaptation of the method used by Bodenstein⁴ for the analysis of chlorine-ozone mixtures.

As before, the gases are absorbed in potassium iodide solution and excess standard *N*/10 sulfuric acid added and the total iodine found.

⁹ Giauque and Wiebe, *THIS JOURNAL*, **50**, 121 (1928).

¹⁰ Villars, *ibid.*, **53**, 2006 (1931).

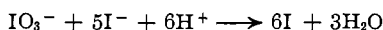
¹ Kistiakowsky, *Z. physik. Chem.*, **116**, 371 (1925).

² Bowen, *J. Chem. Soc.*, **123**, 1203 (1923).

³ Hinshelwood, *Proc. Roy. Soc. (London)*, **A131**, 177 (1931).

⁴ Bodenstein, Schumacher and Padelt, *Z. physik. Chem.*, **5B**, 209 (1929).

The excess sulfuric acid is estimated by addition of a slight excess of $N/10$ potassium iodate solution and titration of the iodine liberated.



The acid may be standardized by addition of potassium iodide and a slight excess of $N/10$ potassium iodate solution, the results agreeing very well with those by other methods.

The agreement between this method and that used by Hinshelwood³ may be seen by comparing the amounts of standard $N/10$ sulfuric acid used to neutralize the OH^- liberated by the chlorine monoxide contained in 5 cc. of a solution of chlorine monoxide-chlorine in carbon tetrachloride.

	Solution A	Solution B	Solution C
H_2SO_4 estimated by KIO_3 method, cc.	7.40	5.67	7.88
H_2SO_4 estimated by baryta method, cc.	7.42	5.74	7.89

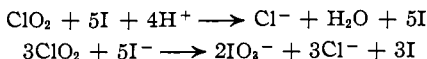
Doing duplicate experiments showed an agreement to about one-half of one per cent. but the method could be brought up to the usual accuracy of iodine titrations using calibrated apparatus and greater care than in these preliminary experiments. The concentrations of chlorine monoxide and chlorine were between 0.05 and 0.30 g. moles per liter in these experiments.

This method would appear to have the advantage of speed, simplicity and a convenient end-point. Since the acid can be standardized in terms of the thiosulfate, only the latter need be determined absolutely and, furthermore, the ratio of chlorine to chlorine monoxide can be found without a knowledge of the actual normality of the thiosulfate.

The method could also be used for the analysis of chlorine dioxide-chlorine mixtures, the excess acid being determined as above by addition of potassium iodate solution.



Bowen² analyzed chlorine dioxide-chlorine mixtures by absorption in potassium iodate solution, followed by thiosulfate titration in acid and in neutral solution according to Bray's⁵ method.



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⁵ Bray, *Z. physik. Chem.*, **54**, 731 (1906).

The Ultraviolet Light Absorption of Ethyl Alcohol Purified by Different Methods.—According to Bielecki and Henri¹ the first ultraviolet absorption band of pure ethyl alcohol begins at about $\lambda 2500 \text{ \AA.}$, and extends, with increasing strength, down at least to 2100 \AA. On the other hand, many of the impurities ordinarily found in ethyl alcohol (*e. g.*, aldehydes, resins, etc.), shows strong absorption bands at longer wave lengths. It follows that measurements of the absorption coefficients of ethyl alcohol in the threshold region, $\lambda 2500\text{--}3000 \text{ \AA.}$, should provide a very delicate method for the detection of impurities of this type.

We have observed a considerable variation in the absorption spectra in the threshold region of samples of ethyl alcohol purified by different methods, and believe that absorption measurements can be used to determine to some extent the efficiency of different methods of purification.

In Table I, and on Fig. 1, are compared the absorption coefficients of samples of ethyl alcohol which have been subjected to the following treatments. All distillations were made through a fractionating column, only the center portion of the distillate being collected in each case.

A. Stock 95% ethyl alcohol, without purification.

B. Alcohol "A" was dried over calcium oxide, then 1 g. of iodine added per liter of alcohol. The solution was allowed to stand for several days and then distilled. To this was added 1 g. per liter of pure powdered zinc, the mixture being refluxed for several hours and again distilled.²

C. To alcohol "A" was added, per liter, 25 cc. of 12 *N* sulfuric acid. The mixture was refluxed for several hours and distilled.

D. The product from "C" was treated with 20 g. of potassium hydroxide and 10 g. of silver nitrate per liter, the mixture being refluxed and distilled.

E. Alcohol "D" was allowed to stand for one week over specially prepared pure calcium oxide, then distilled slowly on a water-bath.

F. Treatment same as in "E" except that the solid matter (calcium oxide and hydroxide) was filtered off before distillation.

G. Same as "E" except that the whole process, from first addition of calcium oxide, was carried out in an atmosphere of pure nitrogen.

H. Alcohol "D" was allowed to stand for one week over active aluminum amalgam, filtered and distilled.

The absorption measurements show clearly that the treatment of stock alcohol with dilute sulfuric acid, followed by distillation, produces a tremendous improvement in purity (curve C). Another marked improvement is produced by the treatment with alkaline silver oxide (curve D). This is no doubt due principally to the removal of aldehydes.

If the next step be distillation in air from calcium oxide, after standing, in the usual manner, a very pronounced increase in absorption is observed (curve E), indicating the formation of some absorbing impurity. Upon filtering off the calcium oxide before distillation, a less marked

¹ Bielecki and Henri, *Ber.*, **45**, 2819 (1912); *Compt. rend.*, **155**, 456 (1912).

² Castille and Henri, *Bull. soc. chim. biol.*, **6**, 299 (1924).

TABLE I
ABSORPTION COEFFICIENTS

λ	$K \times 10^3$								
	A Stock 95%	B I ₂ + Zn method	C H ₂ SO ₄ + H ₂ O distillation	D "C" + Ag ₂ O	E "D" + CaO distillation	F "D" + CaO filtered	G "D" + CaO in N ₂	H "D" + Al amal.	I Henri values
3710	2.8					
3500	8.2					
3320	13.0		1.1		2.9				
3160	18.1		1.9		3.1				
3020	25.1		2.9	...	9.7		..		
2890	34.8	0.5	3.1	0.02	10.2	...	0.15	..	
2780	50.4	2.0	5.1	.4	13.7	1.7	.43	0.30	..
2675	77.5	3.8	5.5	.5	15.1	3.1	.65	.45	..
2585	..	6.0	6.7	.9	17.6	4.5	1.2	.58	4.0
2500		8.8	9.6	2.0	20.3	6.4	2.2	1.33	6.2
2430		12.4	14.5	3.3	24.8	9.7	3.5	2.85	10.0

increase in absorption is obtained (curve F), and upon keeping the alcohol in an atmosphere of nitrogen during the entire treatment and distillation, no change in absorption is observed (curve G).

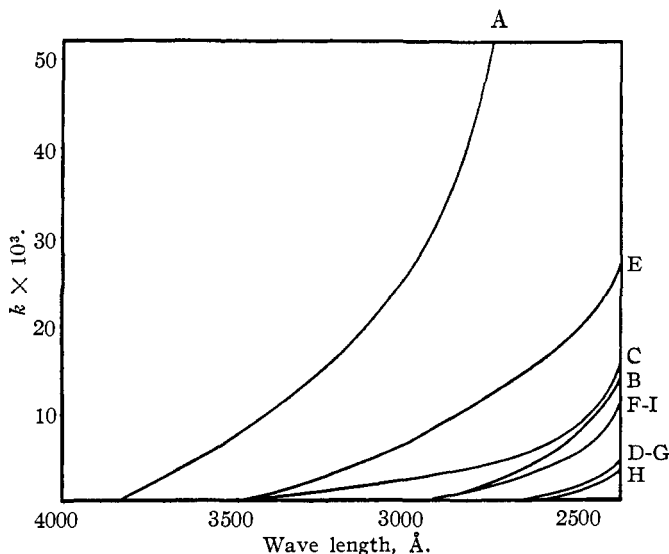


Fig. 1.—Absorption coefficients for various alcohol samples.

This suggests that the alcohol is oxidized by calcium oxide in the presence of air, the reaction proceeding very slowly at room temperature, and much more rapidly during distillation. The oxidation does not occur in the absence of oxygen, and hence the drying of ethyl alcohol over calcium oxide should be carried out in nitrogen.

Drying over aluminum amalgam gives the lowest absorbing, and hence

the purest alcohol of any of the methods used here. It should be pointed out, however, that non-absorbing impurities, such as water, are not detected by absorption measurements. The electrical conductivity may be used to detect the presence of small amounts of water, and a comparison of the conductivities of the different samples indicated that aluminum amalgam is fully as efficient a drying agent as calcium oxide. Metallic calcium, used as a drying agent, failed to give any better results than calcium oxide, either for light absorption or conductivity.

The iodine-zinc method of purification (curve B) does not give quite as good results as the other methods.

It is of interest that the absorption measurements of Bielecki and Henri (column I) which are the lowest hitherto reported, agree almost exactly with our alcohol F, while our samples D, G and H show a lower absorption in this threshold region.

In short wave lengths, however, where alcohol itself absorbs strongly, one would expect the difference between the various samples to be slight.

Summarizing, light absorption measurements indicate that the standard practice of drying ethyl alcohol over calcium oxide should be carried out in an oxygen-free atmosphere. The highest degree of purity, as measured by the absorption spectrum, is obtained by the use of aluminum amalgam for drying.

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SOME FACTORS AFFECTING THE CATALYTIC ACTIVITY OF COBALT OLEATE IN THE AUTOXIDATION OF PENTENE-2¹

By JULIUS HYMAN AND C. R. WAGNER

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(A) Introduction

In a paper published some months ago,² the authors noted the catalytic activity of certain substances on the autoxidation of cracked gasolines. It was ascertained at that time that hydrogen chloride, for example, was a strong autoxidizing catalyst, whereas acetic acid was almost without effect. These reactions, as well as numerous other indications, prompted the authors^{2,3} to propose a new theory of autoxidation based on the acidic

¹ Presented before the Petroleum Division of the American Chemical Society at Cincinnati, Ohio, September 9-13, 1930.

² Wagner and Hyman, 10th Annual Meeting, A. P. I. Report, 3rd section, pages 118-123.

³ Hyman and Wagner, *J. Inst. Pet. Tech.*, 15, 645 (1929).