

maintaining, and dried as above, in an atmosphere of known moisture content. The platinum dish and salt were placed in a desiccator which contained sulfuric acid so diluted as to give to the air above it a humidity of 70%, which is not likely to be exceeded in the air of a laboratory. From time to time during 47 days the dish and contents were weighed. The gain or loss as compared with the previous weight never exceeded 0.002 g. and at the end of the period, summing up the gains and losses, there was found a loss of 0.0001 g.

These 2 sets of experiments seem to show that the hygroscopicity of potassium hydrogen phthalate is practically nothing, and in using it and weighing it attention need be directed only to the containing vessel. By use of an open platinum crucible in weighing it, it is believed that this source of error has been almost completely avoided.

In the preparation of potassium hydrogen phthalate it is desirable to know its solubility in hot and cold water, and this was determined at 25 and 35 degrees and at the boiling point of its saturated solution. At the lower temperatures the method used was one devised by the writer.¹ For the solubility at the boiling point the method of Pawlewski² was used.

Solubility of Potassium Hydrogen Phthalate in Water.

Temp.	Wt. solution.	Wt. acid phthalate.	% in sol.
At 25 degrees.....	21.025	2.1531	10.23
	21.028	2.1553	10.25
At 35 degrees.....	21.198	2.6859	12.67
At boiling point.....	9.18	3.3158	36.12

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

THE EFFECT OF SOLVENT ON THE ULTRA VIOLET ABSORPTION SPECTRUM OF A PURE SUBSTANCE.

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In a previous paper³ some quantitative measurements were described showing the absorption of acetone and its homologues in the pure liquid condition. A large quartz spectograph fitted with a spectrophotometric arrangement was used and by this means the extinction coefficient, ϵ , is given by $\epsilon = 1/d (\log I_0/I)$, where I_0 is the intensity of the incident light, I the intensity of the emergent light, and d the thickness of the absorbing layer. ϵ may, therefore, be defined as the reciprocal of that thickness of medium which reduces the intensity of the light to $1/10$ of its original value. If c be the normality of the ketone (sp. gr. \times (1000/mol. wt.)) the molecular extinction is given by $M = \epsilon/c$.

¹ *Proc. Iowa Acad. Sci.*, **23**, 31 (1916).

² *Ber.*, **32**, 1040 (1899).

³ *Proc. Roy. Soc. (London)*, **91A**, 76 (1914).

The molecular extinction curves are obtained by plotting the values of M on the ordinate against the corresponding wave lengths on the abscissa. Known thicknesses of the various ketones were obtained by making up a number of cells consisting of 2 plain parallel quartz plates cemented together with a wire ring of known diameter. The error in measuring the center of the absorption band was in most cases about 3 Ångström units, but in certain cases in the present investigation where the solvent had comparatively high absorptive power the error may be as great as 6 units. The error in the value of the molecular extinction is in general about 6%.

The ketones as ordinarily purchased contain small quantities of unsaturated substances which cannot be entirely removed by fractional distillation. This can be shown by treating a few drops of a carefully distilled ketone with dil. aqueous potassium permanganate, when immediate oxidation takes place. These impurities must be removed because their absorptive power may be up to 500 times that of the ketone, and the presence of only $\frac{1}{2}\%$ may completely mask the absorption of the ketone itself. This fact was not realized in previous investigations, and most of the published work is quite valueless, due to the use of impure specimens of ketones. Throughout the present work the greatest care was taken to ensure the purity of the ketones, and the methods used have been described in previous papers by the author.

When the pure liquid ketones were examined certain striking regularities were observed in their absorptive action towards light. It can be stated that all saturated aliphatic ketones are practically diactinic between 7,000 A. U. and 3,200 A. U. Between 3,200 A. U. and 2,300 A. U. there is an absorption band and from 2,300 to 2,100 A. U. all of the ketones again become diactinic. There are no exceptions to the rule, such ketones as hexamethyl acetone and methylonyl ketone behaving precisely like acetone in this respect. The wave length between 3,200 and 2,300 A. U. at which maximum absorption occurs varies with the ketone and depends on the number of hydrogen atoms in the α or β position which are substituted by alkyl radicals. Substitution of other hydrogens has no effect on the absorption so that all ketones of the general formula $\text{CH}_3\text{COCH}_2\text{-CH}_2\text{R}$ have maximum absorption at 2,790 A. U.

This effect of substituting α or β hydrogens is in general to move the absorption maximum towards the red end of the spectrum; thus the absorption maxima for acetone, pinacolone, $(\text{CH}_3)_3\text{CCOCH}_3$, hexamethyl acetone, $(\text{CH}_3)_3\text{CCOC}(\text{CH}_3)_3$ are, respectively, 2747, 2850, 2950 A. U., intermediate effects being obtained with other ketones.

With regard to the value of M , the molecular extinction at the point of maximum absorption, all of the ketones with the exception of acetone and methylethyl ketone have the same value, namely 21.2. The values for these 2 ketones are 17.1 and 19.4, respectively, and this deviation is

probably due to association. Assuming that the absorption power of the associated molecules is inversely proportional to the number of simple molecules in the complex, the association factor of these 2 ketones can be calculated.

The foregoing is a brief summary of the author's work on the absorptive power of the pure liquid ketones. In the present paper the effect of dissolving the ketones in various solvents is examined.

The first question which came up was whether or not it was necessary to submit the solvent used to the same rigorous purification as was necessary with the pure ketones. In the spectrophotometer the actual mechanical absorption of the solvent was corrected for by placing in the lower beam of light the amount of solvent used, the solution being in the path of the upper beam. There remains, however, the possibility of some further effect between the dissolved ketone and the impurities, as for example, in cases of catalysis where an impurity may have an effect out of all proportion to its concentration. To test this point some acetone was freshly prepared from the bisulfite compound, dried with the greatest care, and placed in a specially dried cell and its absorption at once measured.

Acetone, which had been exposed to air and a specimen to which 1% of water had been added, were also examined, but in all 3 cases the center of the absorption band was at $\lambda = 2747$. That the presence of small quantities of water has a negligible effect is also shown by experiments with acetone dissolved in various solvents. An 0.8 molar solution in ordinary absolute alcohol (99.6%) showed the center of absorption at $\lambda = 2725$. Absolutely dry alcohol was prepared by the method of Young and Fortey,¹ and the center of the band when acetone was dissolved in this solvent was also at $\lambda = 2725$, so that the small quantity of water present in ordinary absolute alcohol makes no difference.

Experiments with dry chloroform and chloroform saturated with water (about 0.3%) gave the same result as did chloroform containing a small quantity of piperidine. Generally it may be stated that in no case did a small quantity of a second solvent (up to 1 or 2%) cause any appreciable movement of the centre of the absorption band with acetone or any of the aliphatic ketones. This result is important because it shows that there is no need to purify a solvent rigorously, small traces of impurities having no appreciable effect on the absorption band. It must be noted, however, that this holds good only when the absorption of the impurity is corrected for by placing an equivalent quantity of the solvent in the path of the lower beam of light. The ketone studied must also be optically pure, for if it contains any impurity, the absorption of the latter would be superimposed on that of the ketone itself and would thus lead to error.

¹ *J. Chem. Soc.*, 81, 717 (1902).

It was soon found that any effect produced in the absorptive power of acetone by a solvent was produced also on any of the higher ketones, but in a less degree. (See Table I.) It will be noticed that hexamethyl acetone gives no movement of the absorption band when dissolved in alcohol, nor does it give any movement when dissolved in water-alcohol mixtures. This accords well with the fact that this ketone does not form an oxime, hydrazone or semicarbazone, due probably to the steric effect of the adjacent methyl groups which also apparently prevent any hydrating of the carbonyl group by the solvent. In the case of solvents, such as hexane and carbon tetrachloride, where there is a movement of the band towards the red, hexamethyl acetone behaves normally.

TABLE I.—EFFECT OF SOLVENT ON ABSORPTIVE POWER OF KETONES.

Ketone.	Pure liquid. λ.	Aqueous.			Ethyl alcohol.			Heptane.			Chloroform.		
		M.	λ.	Shift.	M.	λ.	Shift.	M.	λ.	Shift.	M.	λ.	Shift.
Acetone	2747	18.8	2645	—102	18.6	2725	—22	17.1	2785	+38	17.1	2745	0
Methylethyl	2770	20.9	2665	—95	19.8	2750	—20	19.4	2799	+29	19.4	2770	0
Methyl-													
propyl	2790	21.2	2695	—95	21.2	2770	—20	21.2
Methylbutyl	2790	21.2	2700	—90	21.2	2770	—20
Methyl													
isopropyl	2820	21.2	2735	—85	21.2	2800	—20	21.2	2845	+25
Methyl													
isobutyl	2810	21.2	2725	—85
Methyl													
tert. butyl	2850	21.2	2760	—90	21.2	2870	+20	21.2	2850	0
Diethyl	2780	21.2	2690	—85
Ethylpropyl	2800	21.2	2720	—80	21.2	2790	—20	21.2	2815	+15	21.2	2800	0
Hexamethyl	2950	21.2	2950	0	21.2	2968	+18	21.2	2950	0

M = molecular extinction of the ketone at the wave length of maximum absorption λ . The concentration of the ketones was about 0.1 molar.

The extinction coefficient ϵ of a ketone dissolved in a solvent will vary with the concentration of the solution, but if the molecular extinction is calculated by dividing ϵ by the concentration of the ketone in gram moles per liter, then according to Beer's law¹ the value of the molecular extinction will not be affected by solvents or dilution. There has been much controversy regarding the reasons why some substances do not obey this law, which, of course, presupposes that the molecules of the ketones are not affected by the solvents.

In this investigation it was found that deviations from Beer's law occurred only with acetone and methylethyl ketone, and the molecular extinctions of all other ketones are constant (21.2) whether the ketone is in the pure state or in solution.

The value of M for pure liquid acetone is 17.1, and this value is not changed by solution in hexane, chloroform, or other non-dissociating sol-

¹ *Pogg. Ann.*, 86, 78 (1852).

vents. Solutions of acetone of about 0.1 molar concentration in ethyl alcohol and water give values of M equal to 18.6 and 18.8, respectively.

TABLE II.—CHANGE IN THE POSITION OF THE ABSORPTION MAXIMUM WITH GRADUAL ADDITION OF WATER.

Normality.	L .	λ .	$\lambda_1 - \lambda$.
13.8	0.07	2747	0
10.9	0.09	2716	31
8.4	0.12	2687	70
5.7	0.17	2662	85
2.4	0.42	2659	88
1.0	1.0	2657	90
0.24	4.2	2651	96
0.12	8.3	2645	102
0.04	25.0	2640	107
0	...	2637	110

L = liters of solution containing one g. mol. of acetone.

λ = wave length of maximum absorption.

λ_1 = wave length of maximum absorption for pure acetone.

It seems very probable, therefore, that the deviation of acetone and methylethyl ketone is due to part association of the molecules and partial breaking down of this association by an ionizing solvent such as water. The value of the molecular extinction for aqueous acetone is nearer to the normal value 21.2. In the case of the aliphatic ketones there is no deviation from Beer's law in passing from the pure state to solution in many different solvents except in the cases of acetone and methylethyl

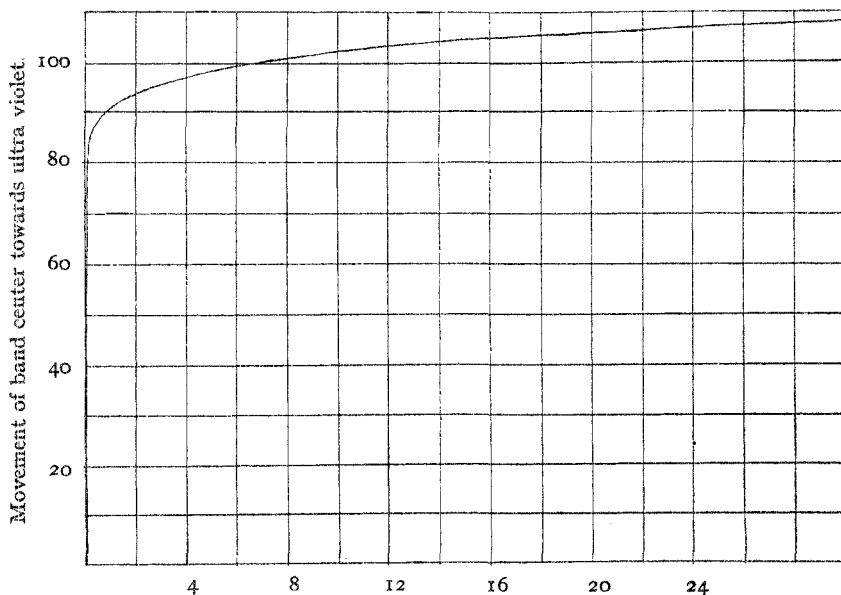


Fig. 1.—Liters of aqueous solution containing 1 g. mol. of acetone.

ketone, when deviations are to be ascribed to disruption of associated molecules by an ionizing solvent. Table II shows the change in the position of the absorption maximum with gradual addition of a solvent (water) to pure acetone, the last line of the table being obtained by extrapolation. The water causes the center of the absorption band to move towards the ultra violet, the movement increasing with dilution up to wave length 2637, at which point (see Curve I) it becomes asymptotic.

Exactly analogous effects were observed when other solvents were gradually added to acetone, but owing to the much smaller shifts of the

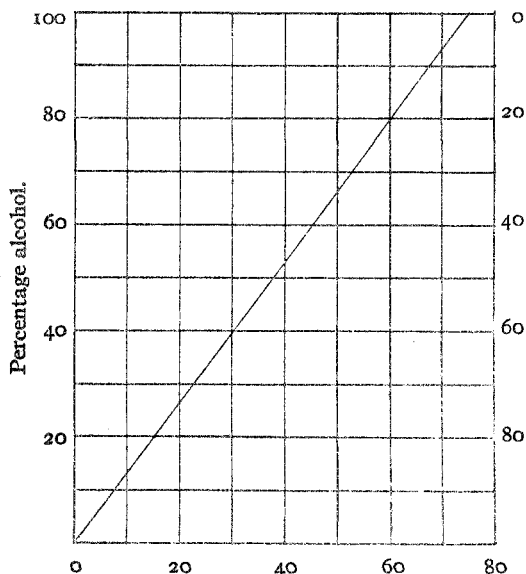


Fig. 2.

band center the experimental error was too great to allow accurate curves to be drawn.

Fig. 2 was obtained by starting with an 0.8 *M* solution of acetone in water and gradually displacing the water by alcohol, the strength of acetone being kept constant. In this case the effect is directly proportional to the quantity of alcohol added. This was found to hold generally for mixtures of 2 solvents, and enables us to state the general rule that if an absorbing substance is dis-

solved in one solvent and if this solvent is gradually displaced by another solvent (the strength of the solute being kept constant) the movement of the absorption band is directly proportional to the percentage of the second solvent present.

Let A and B be the two solvents; and let λ_A = the point of maximum absorption in A; and λ_B = the point of maximum absorption in B; and let $x\%$ of B be present in the mixed solvent; then the maximum absorption in the mixed solution will be given by

$$\lambda_1 = \lambda_A + x/100 (\lambda_A - \lambda_B).$$

It will be seen that a small quantity of impurity (where $x = 1$ or 2%) in a solvent will have a negligible effect, providing its mechanical absorption is corrected for in the usual way.

The variation in the position of the absorption maximum with the

nature of solvent, was first studied by Kundt,¹ who stated that with increasing refractivity of solvent the absorption band moved nearer the red. As a rough generalization (see Table III) Kundt's rule undoubtedly appears to hold good for in the case of these solvents with higher refractivity the band is generally nearer the red end of the spectrum. There are, however, several indications that it is not a hard and fast rule as, for example, in Table III, methyl acetate, which should give a shift similar to hexane, does not affect the position of the band.

TABLE III.—KUNDT'S RULE.

Solvent.	Mol. refractivity.	Shift.
Hexane.....	29.7	38
Carbon tetrachloride.....	26.4	43
Methyl acetate.....	29.36	0
Ether.....	22.31	27
Chloroform.....	21.31	0
Propyl alcohol.....	17.4	-11
Acetic acid.....	12.9	-47
Formamide.....	8.5	-42
Methyl alcohol.....	8.13	-44

In the column headed "shift" is given the difference between the centre of the absorption band of pure acetone and of acetone dissolved in the various solvents.

With regard to the dielectric constants a similar effect may be observed, for in the cases of those solvents with low values of the dielectric constant the centre of the band is nearer the red end of the spectrum. But as before, this is only a rough generalization.

An interesting study was made of the effect of using an homologous series of compounds as solvents, the case of the aliphatic alcohols being shown in Table IV, acetone of about 0.08 *M* being used as solute.

TABLE IV.—EFFECT OF HOMOLOGOUS SERIES, WITH ACETONE AS SOLVENT.

Solvent.	Center of band.	Shift.
Methyl alcohol.....	2720	-27
Ethyl.....	2730	-17
Propyl.....	2737	-10
Isopropyl.....	2737	-10
Butyl.....	2736	-11
Isobutyl.....	2734	-13
Tert. butyl.....	2735	-12
Iso amyl.....	2736	-11
Sec. amyl.....	2740	-7
Octyl.....	2738	-9

It will be seen that with the exception of methyl and ethyl alcohols which are abnormal the alcohols give a constant shift of 11 units. This shift is similar to the series constant in other physical measurements, such as refractivity and magnetic rotation. The saturated hydrocarbons also show a series constant, those examined being pentane, hexane, heptane,

¹ *Ann. Phys.*, 4, 34 (1878).

octane, decane, and cyclohexane, and giving a constant shift of 38 units towards the red. The chlorine derivatives of the paraffins examined were chloroform, dichloro-ethane, trichloro-ethane and chloropropane, all of which gave no movement of the band center. The series of fatty esters also gave no shift. The ether series (only one member examined) gave a shift of +27 units.

These results are tabulated in Table V, acetone again being used as solvent.

TABLE V.—COMPARISON OF SERIES OF HOMOLOGUES, USING ACETONE AS SOLVENT.

Solvent.	Number examined.	Average center.	Series constant.
Hydrocarbons.....	6	2785	38
Chlorohydrocarbons.....	4	2747	0
Alcohols.....	10	2736	—11
Acids.....	2	2724	—23
Esters.....	3	2747	0
Ethers.....	1	2774	27

A summary of the effect of solvents, on the absorption by acetone, is given in Table VI and it will be seen that solvents fall into 2 main classes, namely those which move the band center toward the ultra violet and those which do not affect it or which move it towards the red.

TABLE VI.—EFFECT OF SOLVENTS ON THE ABSORPTION BY ACETONE.

Solvent.	Normality.	Mol. extinction.	Center.	Shift.
Water.....	0.1	18.8	2745	—102
Methyl alcohol.....	0.1	18.2	2703	—44
Ethyl alcohol.....	0.1	18.6	2720	—27
Higher alcohols.....	4.0	17.1	2736	—11
Acetic acid.....	4.0	17.8	2700	—47
Propionic acid.....	4.0	17.1	2724	—23
Phosphorus oxychloride.....	4.0	...	2718	—29
Formamide.....	4.0	18.8	2755	—45
Hydrocarbons (6).....	4.0	17.1	2785	+38
Chlorocarbons (4).....	4.0	17.1	2747	0
Chlorocarbons.....	0.1	11.1	2745	0
Carbon tetrachloride.....	4.0	17.1	2789	+42
Ethyl ether.....	4.0	17.1	2774	+27
Methyl acetate.....	0.1	17.1	2747	0
Ethyl acetate.....	0.1	17.1	2747	0
Ethyl propionate.....	0.1	17.1	2747	0
Propyl acetate.....	0.1	17.1	2747	0

The difference between the two sets of solvents seems to be connected with their physico-chemical properties, especially their ionizing powers. The replacement of hydrogen atoms which either ionize themselves or confer ionizing properties on the solvent, causes the band of acetone to be displaced towards the red end of the spectrum.

This may be illustrated by the 3 compounds, water, ethyl alcohol, and ether. The very highly ionizing compound water, the slightly ionizing

compound ethyl alcohol, and the non-ionizing compound ethyl ether, shift the band of acetone by -102 , -22 and $+27$ units, respectively. Another example of this is given by the ionizing compound acetic acid, which displaces the acetone band 47 units towards the ultra violet, whereas the replacement of the hydrogen atom to give ethyl acetate entirely neutralized this effect, no shift being observed when acetone is dissolved in the ester.

Summary.

1. All of the aliphatic ketones except acetone and methylethyl ketone follow Beer's law, *i. e.*, the molecular extinction is independent of the concentration, and solvent.

With acetone and methylethyl ketone there are deviations when ionizing solvents are used, due to partial disruption of the associated molecules.

2. Kundt's Rule, which states that with increasing refractivity of solvent the band moves towards the red, holds good if regarded as a rough generalization.

3. When a pure substance is dissolved in an ionizing type of solvent the absorption center moves toward the ultra violet; if a pure substance is dissolved in a neutral non-ionizing type of solvent the absorption center is unaffected or moves towards the red end of the spectrum. It is probable that this is a general rule which holds good for all classes of absorbing substances.

The whole of the experimental part of this work was carried out in the Spectroscopic Department of Liverpool University, England. The author desires to express his sincere thanks to Prof. E. C. C. Baly for permitting him to make such full use of the facilities available there for this work.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE DETERMINATION OF POTASSIUM AS PERCHLORATE. II.

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Not long ago¹ we reported the results of experiments upon the quantitative handling of potassium perchlorate with special reference to its solubility in various washing media. After presenting additional evidence of the fact, already known, that the salt is soluble to a marked degree in even very concentrated alcohol containing perchloric acid, we supported the proposal of Davis² of using as a washing liquid alcohol containing

¹ THIS JOURNAL, 39, 249 (1917).

² *J. Agr. Sci.*, 5, 52 (1912).