THE RELIABILITY OF THE DISSOCIATION CONSTANT AS A MEANS OF DETERMINING THE IDENTITY AND PURITY OF ORGANIC COMPOUNDS

BY HEYWARD SCUDDER

Since the publication of the work of Ostwald¹ on the dissociation constants² of organic acids it has been assumed that this constant furnishes a reliable guide to the identity, strength and purity of organic compounds. Ostwald³ states that the constant gives a satisfactory guide to the purity of analytically pure compounds showing, by a steady diminution of the value found at different dilutions, the presence of isomers or of acids of similar composition which could not be detected by analysis. Nernst⁴ repeats practically the same idea in a note on the experimental work of Wakeman⁵ on isohydric solutions, stating that in the case of a mixture of two acids the variation of the constant at different dilutions gives, as Ostwald had previously pointed out, a criterion of purity. The assumption that it is a suitable means of identification is not explicitly stated in text-books but will become obvious if the articles relating to conductivity measurements are studied.

Unfortunately a study of the literature has shown that the dissociation constant is of no greater reliability than the other physical constants. It is an additional and welcome aid, but can only be used as an aid and not as a crucial test for determining either identity or purity.

¹ *Note*.—Since almost all the references to Ostwald's work are taken from one series of articles, unless otherwise stated they will be found in Vol. 3 of *Zeit. phys. Chem.* and only the page number will be given. *Zeit. phys. Chem.* 3, 173 (1889).

² The dissociation constant is also called the affinity constant.

³ *l. c.* 173.

⁴ *Theoret. Chemie* (3 Aufl.) 473 (1900).

⁵ *Zeit. phys. Chem.* 15, 162 (1894).

The object of this paper is to point out the causes of the errors that may affect the value of the constant, to draw conclusions as to its accuracy as a means of identification and to show that it is not reliable as a guide to purity.

The following symbols for the Ostwald formula will be used;

$$K = 100k = \frac{m^2}{(1-m)v} \cdot m = \frac{\mu_v}{\mu_\infty} \cdot 100m = \text{percent dissociated.}$$

μ = molar conductivity. v = volume in liters.

The temperature at which the measurements quoted were made is 25° unless otherwise stated. The solvent used in all cases was water. For the sake of brevity complete tables will not always be given. The condensed forms will readily be understood. No essential data will be omitted. The expression "limits of K" means the maximum and minimum values found for K at the different dilutions measured. It does not indicate that the variations were regular, giving a steady increase or decrease of K with increasing dilution.

Causes of error

Measurement of conductivity.—Ostwald¹ states that on account of the difficulty of making accurate measurements, and since an error of one percent in the conductivity makes an error of at least two percent in the value of K, there is an allowable error of five percent in the value of K. All subsequent observers have accepted this as the allowable error.

Value of μ_∞ .—Until within a few years the molar conductivities were expressed in terms of the Siemens unit. At the present time they are frequently expressed in reciprocal ohms. It is apparent that this change will not affect the value of K, for m simply expresses the ratio $\frac{\mu_v}{\mu_\infty}$. Since μ_∞ equals the sum of the equivalent conductivities of the anion and kation a change in the equivalent conductivity of the hydrogen or hydroxyl ion will affect the value of K only when the equivalent conductivity of the other ion (kation or anion as the case may

¹ I. c. 173.

be) remains the same. For instance, Ostwald in his measurement of the dissociation constant of acetic acid used different values for H and $C_2H_3O_2$ from those given later by him,¹ but since μ_∞ remains the same the constant is not changed.

H.		$C_2H_3O_2$.	μ_∞	K.
320.5	+	43.5	= 364	0.00180
325	+	38.4	= 363	0.00180

1. c. 172. Lehrb. d. allgemeinen Chemie vol. II [I] 675, 677
2. Aufl.

But if the value for the equivalent conductivity of H is changed while that of $C_2H_3O_2$ remains the same, the difference in K may be considerable.

	H		$C_2H_3O_2$	μ_∞	K
(a)	320.5	+	43.5	= 364	0.00180
(b)	325	+	43.5	= 368	0.00175
(c)	345	+	43.5	= 389	0.00158

The value of H given in (c) is calculated to Siemens units from the value in reciprocal ohms found by Noyes and Sammet.² It will be seen that a variation in the value of H of about one and one-half percent as in (a) and (b) does not change K beyond the limits of allowable error, but that a variation of about six percent as in (b) and (c) changes K about six percent. The equivalent conductivity of H as given at present is,

H	Authority
325	Ostwald l. c. (In Siemens unit.)
345	" Calculated to reciprocal ohms by Noyes and Sammet.
346.4	" Calculated to reciprocal ohms by Muller. ³
346	Bredig. Calculated to reciprocal ohms by Wegscheider. ⁴
365	Noyes and Sammet (In reciprocal ohms).

¹ The change in the values of the equivalent conductivity of the anions was due to a better determination of the equivalent conductivity of the sodium ion.

² Jour. Am. Chem. Soc. 24, 968 (1902).

³ Bull. Soc. chim. Paris, (3) 27, 1012 (1902).

⁴ Monatshefte 23, 613 (1902).

Noyes and Sammet state that their value is 3.8 percent higher than the latest value adopted by Kohlrausch and 5.8 percent higher than the value given by Ostwald. Comparison of this table with the one just given shows that the difference in the value of H calculated to reciprocal ohms by the three different observers would not affect K . But that the difference between Ostwald's value in Siemens unit and in reciprocal ohms or the difference between Ostwald's value in reciprocal ohms and that of Noyes and Sammet would correspond to (b) and (c) and change the value of K considerably.

The same difference may occur in the case of the hydroxyl ion. Bredig¹ in his work on dissociation constants of the bases states that the extrapolated value for OH calculated by Kohlrausch is about 8 percent higher than his own value derived from direct observation, and that if the Kohlrausch value is used the constants of the bases will in general be about 16 percent lower than those given by himself.

Confusion from this source of error is of slight possibility at present, since almost all constants are calculated from the values for different ions given by Ostwald and Bredig.

Temperature. — The difference caused by variation in temperature is so well understood that almost all published results give the temperature at which the measurement was made. The following table is taken from Schaller² omitting measurements between 50° and 90° and at 99°.

<i>o</i> -Toluic acid			K	
ν	25°	40°	50°	90°
128	0.0135	0.0119	0.0107	0.00672
256	0.0134	0.0118	0.0105	0.00660
512	0.0130	0.0115	0.0103	0.00652
1024	0.0130	0.0115	0.0103	0.00652

Guinchard³ gives the following measurements.

¹ Zeit. phys. Chem. **13**, 293 (1894).

² Ibid. **25**, 517 (1898).

³ Ber. chem. Ges. Berlin, **32**, 1728, 1741 (1899).

Levulinic acid		Violuric acid
T	K	K
0°	0.00211	0.00144
25°	0.00228 ¹	0.00273
35.5°	0.00229	0.00333

K = 0.00255 at 25° Ostwald.

He ascribes the considerable change in the value of K in the case of violuric acid to the fact that it is a pseudo acid, since true acids, like levulinic, show no such great differences.

It will be noted that in Schaller's table the change in value of K for a change of ten degrees in temperature is about ten percent, though the values found at different dilutions at each temperature agree well. In the case of other acids the change for ten degrees was in many cases as great as this, in other cases much less.

Decomposition. — Under this head will be described what is commonly known as decomposition, that is, change in molecular composition. Some compounds are decomposed quite rapidly when in solution. The decomposition may be hastened greatly by the influence of the platinized electrodes, though the weight that should be ascribed to this influence is at times a matter of dispute. Bader² states that, partly on account of oxidation the constants of the phenols are in doubt. Hantzsch,³ on the other hand, states that the phenols are not oxidized if pure, and that Bader's trouble was due to the use of impure material. Bader's table for phenol will be given later under the head of Degree of Dissociation. He found that K increased with increasing dilution. Angeli⁴ found that acetonedicarboxylic acid is decomposed by electrolysis, to which fact is due the diminution of the constant with increasing dilution.

Hantzsch and Miolati⁵ in their work on the oximes of ketone-acids found a number of cases of decomposition due to

¹ 0.00239 is the value given on p. 1736.

² Zeit. phys. Chem. 6, 289 (1890).

³ Ber. chem. Ges. Berlin, 32, 3068 (1899).

⁴ Gazz. chim. Ital. 22, II., 31 (1892).

⁵ Zeit. phys. Chem. 10, 19 (1892).

different causes. The next three sets of tables are taken from their work.

ν	K	
21.46	0.0787	K diminishes steadily
171.68	0.0743	
686.72	0.0671	
K = 0.079		

α -Oximino-succinic acid (Syn-)			β -Oximino-succinic acid (Anti-)		
ν	100 <i>m</i>	K	ν	100 <i>m</i>	K
32	—	0.103	32	—	0.3861
64	—	0.113	64	—	0.3874
128	—	0.114	128	49.19	0.3749
256	43.02	0.127	256	59.60	0.3470
512	56.20	0.141	512	71.37	0.3518
1024	69.93	0.159	1024	81.90	0.3860
K = 0.110			K can not be found		

They attribute the increase of K in the case of the α -acid to the effect of the second carboxyl, not to decomposition. The β -acid is rapidly decomposed in water to carbon dioxide, water and cyanacetic acid (K = 0.372 Ostwald). They state that under the conditions of electrolysis the acid is almost instantly decomposed, as shown by the approach of K to the value of K for cyanacetic acid.

They found that the monethyl esters of these acids were decomposed in solution, but in different ways.

Ester of α -acid			Ester of β -acid		
ν	100 <i>m</i>	K	ν	100 <i>m</i>	K
32	—	0.0188	32	—	0.5330
64	—	0.0195	64	—	0.5554
128	—	0.0196	128	54.48	0.5107
256	—	0.0194	256	63.77	0.4391
512	—	0.0193	512	—	0.3427
1024	35.27	0.0188	1024	80.39	0.3220
K = 0.0192			K = 0.533?		

The ester of the α -acid is slowly decomposed by saponification, as shown after standing by the increase of conductivity and by titration.

	Fresh sol.	After 1 hour	After 5 hours
v	μ	μ	u
32	26.59	27.68	33.0

The ester of the β -acid is not changed to the isomer, as was shown by measurements of conductivity and by titration of solutions that had been allowed to stand. It is rapidly saponified to the β -acid, which at once breaks down to cyanacetic acid as just shown.

It will be noted that in most of the illustrations given, except in the case of the phenols where other factors are of influence, K decreases on dilution, because of the effect of the decomposition products in the solution. But there is no regularity in the case of β -oximino-succinic acid.

Change of intramolecular constitution. — This is the change from one isomer to another. It produces in the solution a second compound that may have a value for K and a degree of dissociation quite different from the first, so that a change of K as in the case of impurities might be expected. Optical isomers, however, have the same value for K , so that if a change from one to another occurred, it would not be shown by conductivity measurements.

	K	M. p.	
<i>d</i> -Tartaric acid	0.097	170°	(From Walden) ¹
<i>l</i> -Tartaric acid	0.097	170°	
Racemic acid	0.097	205°	

In the case of all other isomers the change may affect K greatly. The next two tables are taken from Hantzsch and Miolati.²

¹ Zeit. phys. Chem. 8, 465 (1891).

² l. c. 24.

Phenyloximino-propionic acid					
Syn- or stable			Anti- or labile		
ν	100 m	K			
64	—	0.00175	K can not be got. Comparison of μ shows that it is much stronger than the syn-acid.		
128	—	0.00182			
256	—	0.00196			
512	—	0.00224			
1024	14.21	0.00230			
K = 0.0002014			Syn- $\nu = 101.6 \quad \mu = 10.76$ Anti- $\nu = 100.6 \quad \mu = 17.69$		

They state that the change in K on dilution in the case of the syn-acid is due to transformation to the anti-acid.

Phenyloximino-acetic acid					
Syn-			Anti-		
ν	100 m	K	ν	100 m	K
16	—	0.18	16	32.73	1.53
32	—	"	32	50.00	1.56
64	—	"	64	59.58	1.37
128	—	"	128	—	1.15
256	48.65	"	256	—	0.861
—	—	—	512	—	0.638
—	—	—	1024	82.29	0.373
K = 0.18			K = 1.55		

They state that the diminution in K in the case of the anti-acid is due to transformation to the syn-acid and not to impurity.

It will be seen from these examples that the change from one isomer to another may cause K either to increase or to diminish with increasing dilution. If the measurement for α -oximino-succinic acid given under the last head (Decomposition) is examined it will be seen that K increases steadily and shows no sudden great increase after fifty or sixty percent dissociation. This might suggest a change to an isomer.

Great degree of dissociation.—For some reason still in doubt the Ostwald formula is satisfactory only for the so-called half electrolytes, which are but moderately dissociated at ordinary dilutions. This group includes most organic electrolytes. For strongly dissociated compounds the constant varies with varying dilution. Rudolphi and van't Hoff have proposed formulae for such cases, but these have been so little used in measurements of organic compounds that they will not be considered. The constants calculated by their use may vary widely from those obtained by the Ostwald formula.

In the following tables the names of some of the compounds have been slightly altered, so that they correspond to the names given in Beilstein's *Organische Chemie* (3d Aufl.) and *Ergänzungsband*.

Papaveric acid					
Ostwald ¹			Kirpal ²		
v	100 m	K	v	100 m	K
256	77.6	1.05	256	78.0	1.08
512	87.1	1.15	512	87.7	1.20
1024	—	—	—	—	—
K = 0.9 (approx.)			K not given		

4,6-Dibromanilin-2-sulphonic acid			4,5-Dibromanilin-2-sulphonic acid		
v	100 m	K	v	100 m	K
109.8	95.5	18	278	95.8	7.9
439.2	97.5	9	556	97.8	7.8

Both these were measured by Ostwald.³ No constant is given.

¹ l. c. 398.

² Monatshefte, 18, 466 (1897).

³ l. c. 408.

3-Chlor-6-nitro-benzoic acid					
Bethmann ¹			Holleman and de Bruyn ²		
ν	100 <i>m</i>	K	ν	100 <i>m</i>	K
70.4	62.92	1.52	—	—	—
140.8	73.29	1.43	—	—	—
281.6	81.88	1.31	256	81.7	1.44
563.2	89.04	1.29	512	89.3	1.44
1126.4	94.66	—	1024	93.5	1.36
K = 1.52			K = 1.42		

Bethmann ascribes the fall of K to extreme dissociation.

2-Brom-5-nitrobenzoic acid					
			Holleman and de Bruyn ³		
ν	100 <i>m</i>	K			
256	75.4	0.89			
512	85.0	0.93			
1024	91.8	1.01			
K = 0.91					

It will be noted that K falls, rises or remains constant on dilution. Ostwald's constant for papaveric acid is an approximate value obtained by extrapolation. Since the acid is dibasic and is more than seventy percent dissociated at the first dilution measured, this value is of course very doubtful, because the effect of the second carboxyl is unknown. When K has a value much greater than 1.5 it varies greatly. Bethmann does not use an extrapolated value for K or his value would be still higher. Holleman and de Bruyn, measuring the same acid, get constant values. If the acid were as much dissociated as the dibrom-anilin-sulphonic acids such an agreement would be attributed to chance.

Small degree of dissociation.— When a compound is very

¹ Zeit. phys. Chem. 5, 393 (1890).

² Recueil Trav. Pays-Bas, 20, 361 (1901).

³ l. c. 361.

slightly dissociated the constant is so small that its value is affected greatly by small amounts of impurity or by small errors in measurement.

<i>p</i> -Nitro-phenol					
Bader ¹			Hantzsch ²		
ν	μ	K	ν	μ	K
35.6	0.75	0.000012	64	1.28	0.0000098
71.2	1.04	0.000012	128	—	0.0000102
142.4	—	0.000012	512	2.53	0.0000100
284.8	—	0.000013			
569.6	3.01	0.000013			
$\mu_{\infty} = 355$			(K of water used not subtracted)		
K = 0.000012			K = 0.0000096		

Hantzsch had this measurement repeated on other samples of the phenol with the same result. His criticism of Bader's work has already been given under the head of Decomposition.

In the case of compounds that have a smaller constant the difference is still more marked.

Phenol			
Bader ³			Observer
ν	μ	K	K
25	0.14	0.00000056	0.0000005 Hantzsch ⁴ (K of aq. not subtr.)
50	0.23	0.00000077	0.00000042 Van Laar (calculated) ⁵
100	0.41	0.00000012	0.000000013 Walker and Cormack ⁶

$$\mu_{\infty} = 357$$

$$K = ?$$

Walker and Cormack state that values as small as these can be

¹ l. c. 297

² l. c. 3070

³ l. c. 291.

⁴ l. c. 3069.

⁵ Zeit. phys. Chem. 12, 748 (1893).

⁶ Jour. Chem. Soc. 77, 5 (1900).

measured if the conductivity of the water used is not greater than 0.7×10^{-6} . In a revision of this article Walker¹ criticises unfavorably the values given by the other observers which agree in magnitude among themselves but not with the value found by Cormack and himself. He also regards the agreement in magnitude of the value of K for hydrocyanic acid as found by Ostwald, and by Morgan, and calculated by Van Laar as purely accidental.

In this group of cases if K has a value less than 10^{-5} the only possible comparison of values found by different observers is the comparison of the magnitude.

Isohydric solutions. — Wakeman² gives tables of measurements of isohydric mixtures of acids. The following tables are from his paper.

Acetic acid Propionic acid			K = 0.0018 K = 0.00134		
I.			II.		
Acetic acid Propionic acid	50 parts 1 part		Acetic acid Propionic acid	100 parts 1 part	
ν	K	K (calc.)	ν	K	K (calc.)
32.4	0.00184	0.00179	32.72	0.00187	0.00179
64.8	0.00185	"	64.4	0.00188	0.00179
129.6	0.00186	"	128.8	0.00189	0.00179
259.2	0.00187	"	257.6	0.00192	0.00179
518.4	0.00190	"	515.2	0.00195	0.00180
1036.8	0.00194	"	1030.4	0.00198	0.00180

He concludes that in the case of acids as little dissociated as acetic acid and propionic the presence of impurities considerably influences the constant found, and that the presence of a small amount of propionic acid in acetic acid cannot be found by conductivity measurements. He ascribes the rise in value of K to

¹ Zeit. phys. Chem. 32, 137 (1900).

² I. c. 171.

impurities in the water that were not taken into account in calculating K .

Smith¹ measured the so-called meso-camphoric acid which is a mixture of equal amounts of *d*-camphoric acid, $K = 0.00229$, and *l*-iso-camphoric acid, $K = 0.00174$, and found a constant unchanged on dilution though he had expected a change because the solution is not isohydric.

(i) Meso-camphoric acid		
ν	100 <i>m</i>	K
64	—	0.00187
128	—	0.00188
256	—	0.00187
512	—	0.00187
1024	12.82	0.00184
$K = 0.00187$		

He also found that a mixture of equal parts of adipic acid, $K = 0.00376$, and pimelic acid, $K = 0.00323$, gave a constant $K = 0.00345$ (limits of $K = 0.00348$ – 0.00342).

It will be noted in the tables from Wakeman's work that the value of K as calculated and up to $\nu 256$ the value of K as found agrees with K for acetic acid. In Smith's measurement of meso-camphoric acid the value of K is constant within the limits of the error in measurement, so that the small decrease in value could cause suspicion that an impurity was present only because the decrease is fairly regular. There was no regular decrease in the case of the second mixture.

Purity of compound. — It is frequently forgotten that mixtures form which cannot be separated by repeated crystallization from the same solvent or by repeated distillation at the same pressure, but only by crystallization from different solvents or by distillation at different pressures. The instances given under the last head show that widely varying amounts of a second compound may not affect the value of K beyond the allowable

¹ Zeit. phys. Chem. 25, 214 (1898).

error, or in such a way as to cause a suspicion that an impurity is present. The fact that the value of K decreases regularly on dilution might tend to indicate the presence of an impurity, especially if the decrease is great. But if the decrease is within the limits of error of measurement the regularity may be accidental. Smith¹ measured suberic acid and found that K decreased from 0.00307 to 0.00295 in a fairly regular way. He decided that it was impure and recrystallized it. The limits of K then found were 0.00300–0.00294 with no regular decrease. It will be noted that in the first measurement the values of K agree within five percent. If reference is made to Smith's measurements of meso-camphoric acid and of the mixtures of adipic and pimelic acids, it will be seen that in one case there was such a regular decrease, in the other no regularity, though the agreement of the values is good in both. Walden² gives the following data for α -methylglutaric acid: $K = 0.0052$ (limits of K 0.0052–0.0050 at 232–512) m. p. 74°–76°. He ascribes the lack of sharpness in the melting-point to the presence of an impurity.

If the illustrations given under this and the preceding head are grouped, it becomes evident that just as there are "analytically pure" compounds which may contain small amounts of impurity that can not be shown by analysis, so there are "electrolytically pure" compounds containing variable amounts of impurity that can not be shown by conductivity measurements.

Different methods of measurements. — The apparatus used in making conductivity measurements is usually little varied. Schaller³ used a different form, in order to measure at temperatures up to 100°. His constants from measurements at 25° agree well with those of other observers in some cases, but in other cases do not agree, although his own values of K at different dilutions agree closely. This is shown in the case of α -toluic acid, the table for which has been given under the head

¹ l. c. 196.

² Zeit. phys. Chem. 8, 486 (1891).

³ l. c. 517.

of Temperature. He does not give a constant, but from the data a value between 0.0130 and 0.0132 would probably be chosen. Ostwald¹ gives $K = 0.0120$. For *o*-nitro-benzoic acid Ostwald² gives $K = 0.616$, Schaller gives $K = 0.663$ at v_{128} and $K = 0.640$ at v_{1024} ; ³ the fall in value is regular but only about three and one-half percent. This is the strongest of the three isomeric nitro-benzoic acids, so that the presence of an isomer should tend to make the value less than that found by Ostwald.

When the constant is calculated by an entirely different method as by the inversion of sugar, etc., the results are satisfactory only in certain cases. Most of this work has been done with inorganic compounds. With our present limited experimental knowledge, the constants determined for organic compounds only by such means and not by conductivity measurements can not be regarded as more than approximate. Hantzsch and Miolati⁴ calculate the constant for pyroracemic acid as about 0.56 by comparing its effect on the rate of inversion of sugar with that of lactic acid. Ostwald⁵ found a constant of about 0.3 by conductivity measurements. He was unable to get or prepare any acid that did not give a value of K diminishing on dilution (which fact he attributes to the presence of some impurity), but states that by analogy to similar acids a much smaller constant would be expected.

Difficult solubility. — Some compounds are too insoluble to be measured at ordinary dilutions. At great dilutions the influence of impurities in the water and of errors in measurement of v , etc., may be considerable, and since at most only a few dilutions are measured a comparison of the values of K in order to get the best value is impossible. In the following illustration only one dilution was measured.

¹ l. c. 269.

² l. c. 259.

³ NOTE. — Schaller's table for *p*-chlorbenzoic acid, p. 522, from the context and from the value of K is obviously in error from a misprint. It should be for *o*-chlorbenzoic acid, not *p*-chlorbenzoic.

⁴ l. c., p. 7.

⁵ l. c., p. 192.

β -Naphthoic acid			
Bethmann ¹		Bader ²	
ν	K	ν	K
3124	0.00678	3400	0.00523

It has been pointed out in the case of papaveric acid (under the head of Degree of Dissociation) that if a dibasic acid is more than sixty percent dissociated at the first dilution measured there is an error of unknown amount, because the constants for dibasic acids are calculated just as in the case of monobasic acids and the values are rejected which are found after the increase due to the effect of the second carboxyl (this increase is usually marked after an acid is about sixty percent dissociated). But in the case of these difficultly soluble acids of such a degree of dissociation, the values that are usually rejected are the only ones that can be used for getting an approximation of K.

Judgment. — It has been stated previously that the assumption is made that for pure compounds the value of K will remain constant at different dilutions and that in the presence of impurities it will diminish with increasing dilution. But a large number of cases occur in which K changes markedly on dilution, although there is no suspicion of impurity nor is the degree of dissociation such that the formula is unsuitable. In making a choice of the constant that will best represent the compound in these cases it is necessary to consider the cause of the variation. This involves a consideration of the structure of the compound, of the possibility of associated molecules, complex ions, impurity, isomers, etc. It therefore furnishes a fruitful field for extremely ingenious speculations, some of which are of value.

Since judgment is always necessary in selecting the proper value for K from the measurements made, an attempted classifi-

¹ l. c., p. 399.

² l. c., p. 311.

cation of the cases specially calling for the use of judgment is open to adverse criticism, for at best it can be but rough, and many of the examples already given could properly be put under this head. But it aids an analysis of the subject under consideration by allowing emphasis of certain conditions that often affect the choice of a constant.

(a) *Value of K increases with increasing dilution.*—This occurs in quite a large number of cases, e. g., phenols, amino-acids, etc. Ostwald¹ gives the following measurements:

Amino-benzoic acids				
ortho-		meta-	para-	
<i>v</i>	K	K	K	
64	0.00066	0.00650	0.00072	Benzoic acid K = 0.00600
1024	0.00096	0.00806	0.00105	

The value of K increases steadily. He gives no constant. The increase of K is ascribed to the fact that the acids are at the same time both weak acids and bases and probably form intermolecular salts which dissociate on dilution. To the same cause he ascribes the strength of the meta-acid which is stronger than benzoic acid, contrary to the ordinary chemical experience that the introduction of an amino group into an acid weakens it. Berthelot² two years later measured these acids and found that the meta-acid is weaker than benzoic acid.

ortho-		meta-	para-	
<i>v</i>	K	K	K	T = 17°
100	0.00065	0.00084	0.00068	K of water not subtracted
1000	0.00099	0.00099	0.00118	

The meta-acid was measured by Bersch for Ostwald,³ who states

¹ l. c., p. 261.

² Ann. Chim. Phys. (6) 23, 95 (1891). Berthelot in this paper uses the value $K = 10^8 k$ instead of $10^2 k$, as used ordinarily. In the table in the text K has been changed to $10^2 K$ to correspond to the other tables.

³ Zeit. phys. Chem. 8, 428 (1891).

that some error had been made in the earlier measurement and that Bersch had found $K = 0.0012$, bringing the meta-acid into the same relation to the ortho- and para-acids and to benzoic acid as found by Berthelot. No extended table is published, but the value of K probably is an extrapolated value or else the value of K at v 1024.

In a case of this sort there is no definite guide. It would not be expected that the introduction of an amino group would strengthen an acid nor would the analogy to the isomeric acids support such a supposition. But on the other hand it must be remembered that the influence of the substituting group varies greatly both with its position and with its nature. If Ostwald's constants of the nitro- and oxy-benzoic acids are considered,

Nitrobenzoic acids	Oxy-benzoic acids
o -K = 0.616	o -K = 0.102
m -K = 0.0345	m -K = 0.00867
p -K = 0.0396	p -K = 0.00286

it will be seen that the order of strength of the different isomers varies in the two groups and that the constant of o -oxy-benzoic acid is about twelve times as great as that of the next strongest isomer, while in Ostwald's measurements of the amino-benzoic acids the constant of the meta-acid is about nine times as great as that of the next strongest isomer. The introduction of the amino group caused an increase of K on dilution contrary to the usual rule for pure compounds, so that it might actually cause an increase in the strength of benzoic acid because of some unsuspected influence of space relations.

Walden¹ measured asparagic acid (amino-succinic acid).

v	100 m	K	
32	—	0.0067	Succinic acid $K = 0.00665$ (Ostwald)
1024	31.05	0.0137	
	$K = ?$		

¹ l. c., p. 481.

The minimum value of K (which increased steadily) is slightly greater than that of succinic acid. Walden gives a clever theoretical explanation based on a structural formula for the acid different from that usually given. I have found no repetition of the measurement of this acid (Walker's work¹ is in a different direction), so that it is not possible to say whether this case will have the history of *m*-amino-benzoic acid or whether Walden's explanation is correct. [See foot-note.]

Ostwald² measured protocatechuic acid:

v	100 m	K	
32	—	0.00290	(K increases five units for each succeeding dilution except the last, for which the increase is six units)
1024	16.68	0.00326	
$K = 0.0033$			

This value (which is extrapolated) he considers as correct because confirmed by its agreement with the value calculated from the constants found for the oxy-benzoic acids.

(b) *Value of K decreases with increasing dilution.*—This is characteristic of certain groups, such as the alkyl succinic acids. It also occurs in isolated cases. No definite explanation has been given. The following table is taken from Walden.³

NOTE.—I overlooked Berthelot's measurements which confirm those of Walden. $K = 10^2 k$ instead of $10^3 k$ as given by Berthelot.

Succinic acid		Asparagic acid	
v	K	v	K
100	0.00635	100	0.00813
500	0.00634	500	0.0114

$T = 17^{\circ}$

$T = 15.4^{\circ}$

Conductivity of water not subtracted

Ann. Chim. Phys. (6) 23, 54, 99 (1891).

¹ Zeit. phys. Chem. 4, 332 (1889).

² l. c., p. 250.

³ l. c., p. 462.

s-Diethylsuccinic acids				
Anti- M. p. 128°			Para- M. p. 192°	
ν	100 <i>m</i>	K	100 <i>m</i>	K
32	—	0.0343	—	0.0245
64	—	0.0342	—	0.0245
128	—	0.0338	—	0.0249
256	—	0.0330	—	0.0241
512	—	0.0320	—	0.0235
1024	33.1	0.0291	37.9	0.0225
K = 0.0343			K = 0.0245	

The highest value of K was taken in these cases.

3,5-Diamino-benzoic acid		
ν	K	Bethmann ¹
36	0.00108	(The first two dilutions are omitted here as being unessential. At $\nu = 9$ K = 0.00316.)
72	0.00069	
144	0.00051	
288	0.00045	
576	0.00049	
K = 0.00048		

Bethmann repeated this measurement with a sample that had been recrystallized, to make sure that there was no impurity. The second measurement gave the same values with the minimum at ν 248. The only explanation that he offers is that it may be due to the fact that this acid is also a base, although it is sufficiently strong to be titred.

It will be recalled that the basic nature of the amino-benzoic acids was used in explaining the increase of K on dilution in their case.

(c) *Place in a series.* — If homologous compounds are arranged in order, the difference in value of their constants is sometimes so regular that it affords a guide to the probable value

¹ l. c., p. 388.

of constants that are in doubt. The following table of constants of monobasic fatty acids is taken from values found by Ostwald¹ and by Franke². The boiling-points are from Beilstein's *Organische Chemie*.

Acid	Ostwald	Franke	Boiling-point
Formic	0.0214	—	100.8°
Acetic	0.00180	—	118.1° (corr.)
Propionic	0.00134	—	140.9°
<i>n</i> -Butyric	0.00149	0.00152	162.3°
<i>iso</i> Butyric	0.00144	0.00143	154°-155°
<i>n</i> -Valeric	(0.00161)	0.00150	186°-186.4° (corr.)
<i>iso</i> -Valeric	—	0.00167	173.7°
Caproic	0.00145	0.00138	205°
<i>iso</i> -Butylacetic	—	0.00145	200°-201° (207° corr.)
Diethylacetic	—	0.00189	190° (I. v.)
Heptoic	—	0.00131	223°-223.5°
Caprylic	—	(0.00144)	236°-237° (I. v.)
Pelargonic	—	(0.00112)	253°-254° (I. v.)
—	—	—	I. v = thermometer im-
—	—	—	mersed in the vapor.

Constants enclosed by brackets are regarded as doubtful, Ostwald's because the measurement was made before the importance of having pure water was understood and the water used contained some ammonia, Franke's for reasons which will be given. Both observers state that there is no regular difference between the constants of the acids in this series. Franke, however, doubts his value for caprylic acid, because it is stronger than heptoic acid. His measurements are

Caprylic acid. B. p. 237.5° (corr.)

<i>v</i>	K	
259	0.00144	(No other dilutions were measured) K = (0.00144)
512	0.00143	
1024	0.00144	

in which the values of K agree admirably.

¹ l. c., p. 174 et seq.

² Zeit. phys. Chem. 16, 486 (1895).

It is not obvious why caprylic acid should not be stronger than the acid which immediately precedes it, since propionic and the butyric acids offer a striking illustration of the same sort and it is admitted that there is no regular difference in the constants for the acids in this series. The question of regularity in such a series is often a matter of arrangement. If, omitting formic acid, acetic acid is taken as the starting point and the acids are arranged in two series, placing on one side the normal acids considered as monalkyl derivatives, methylacetic acid, etc., and on the other side the acids that do not have a straight chain considered as dialkyl derivatives, dimethylacetic acid, etc., it will be seen that the difference becomes much more regular and that caprylic acid might be considered to be in its proper place when stronger than heptoic.

Franke regards Ostwald's caproic acid as iso-butyl acetic. The constants of the two acids differ slightly less than five percent, and the boiling-points are so close together that it would be difficult to tell whether the acid measured was one or the other. It will be noted that, excluding formic and pelargonic acids, the constants of these acids differ only forty-four percent between the extremes, and that the difference between any two acids is often less than ten percent. The table of dibasic acids that will be given later under Identification offers another illustration of how the place in a series influences the judgment of what the proper constant for a compound ought to be.

(d) *Analogy*. — It is found that substituting groups affect the value of K in a fairly regular way under limited conditions. Thus Ostwald found the following constants :

Benzoic acid	$K = 0.00600$
<i>m</i> -Oxy-benzoic acid	$K = 0.00867$
<i>p</i> -Oxy-benzoic acid	$K = 0.00286$

If the ratio of the constants of the substituted acids to the constant of benzoic acid is considered to be a factor representing the influence of meta- or para-hydroxyl, the value of K for a *m*-, *p*-dioxy benzoic acid could be calculated by multiplying the

constant for either of the oxy-acids by the factor for the other hydroxyl,

$$\begin{array}{l} 0.00867 \times 0.48 = 0.0038 \\ 0.00286 \times 1.4 = 0.0040 \end{array}$$

$$K \text{ found} = 0.0033$$

This acid is protocatechuic acid which has been given under (a) of this head. It will be noted that the calculated values only offer a suggestion of the real value. Wegscheider¹ in his work on the influence of constitution on the dissociation constant, in which he gives tables of factors for the different substituting groups, states that constants calculated by the help of factors do not as a rule agree very exactly with those found by direct measurement and sometimes do not agree at all.

But since these factors give approximations in closely allied cases, there is a temptation to apply the knowledge of the effect of a certain group, gained by experimental work on a small number of compounds, to all apparently similar compounds. Hantzsch and Miolati² finding in their work on ketone acids that the substitution of the oxime group for oxygen weakens the acid, conclude that the work of Bader³ on the oxime of papaveric acid needs revision because the oxime could not be so strong. For papaveric acid $K = 0.9$ (Approximated. The measurement has been given under the head Degree of Dissociation.) Bader found the oxime stronger than oxalic acid ($K =$ about 10. Ostwald). But since they measured no acids of the same type containing both a benzene and pyridine ring, their judgment must be accepted with caution, for in all cases space relations may cause an unsuspected difference. In their own work they found that in the case of the α - and β -oximino-acids, there is such a difference in apparently analogous acids which they ascribe to a difference in the space relation of the oxime group to carboxyl. Engler and Hantzsch⁴ give the following constants for the diazophenols:

¹ Monatshefte, 23, 300 (1902).

² l. c., p. 13.

³ l. c., p. 418.

⁴ Ber. chem. Ges. Berlin, 33, 2148 (1900).

$C_6H_5NNOHK = 0.123$.

$CH_3OC_6H_4NNOH$ Nearly as strong as KOH, etc., therefore K can not be found.

They found that *p*-anisidine hydrochloride is more dissociated than aniline hydrochloride, but give no measurements by which the effect of methoxyl in the two cases can be compared.

We are in the habit of thinking loosely that the same group always has the same effect when it is substituted, the aliphyl groups, CH_3 , etc., for instance, weakening acids, while the aryl groups, such as phenyl, strengthen.¹ There are so many exceptions to such a principle that it can hardly be called general. The halogens and the nitro and sulphonic groups show a fairly fixed character when substituted. In the following tables, taken from Ostwald, Bethmann, and Walden, the effect is reversed.

Glutaric acid	$K = 0.00475$
α -Methylglutaric acid	$K = 0.0054$
β -Methylglutaric acid	$K = 0.0059$
Acrylic acid	$K = 0.0056$
Phenyl-acrylic acid (Cinnamic acid)	$K = 0.00355$
Succinic acid	$K = 0.00665$
anti-Dimethylsuccinic acid	$K = 0.0123$
para-Dimethylsuccinic acid (Cf. Judgment <i>b</i>)	$K = 0.0191$
Benzoic acid	$K = 0.00600$
<i>o</i> -Methylbenzoic acid (<i>o</i> -Toluic acid)	$K = 0.0120$

Such effects are ascribed to space relations. It is evident that here as elsewhere the argument from analogy is often weak because the analogy is only apparent and not real. It is also evident that the attempt to argue from a particular case or group of cases to all similar organic compounds will fail.

¹ Cf. Nernst. Theoret. Chemie, p. 469 (3 Aufl.).

Frequency of errors

The error in measurement at present always may cause an unavoidable error of five percent in the value of K .

The errors from using different values of μ_∞ , different temperatures of measurement, different methods of measurement and different formulae for calculating K , will not often be met with. They may cause considerable variation, so that the possibility of their occurrence must be borne in mind.

This leaves, as affecting most cases, the errors due to decomposition, change of constitution, isohydric solutions, impurity of the compound, difficult solubility, degree of dissociation, and errors of judgment in selecting a proper value for K . Inspection will show the possibility of error due to degree of dissociation. Values of K outside the limits 1.5 — 0.00001 are of doubtful accuracy.

Causes affecting the value of K in one set of measurements at different dilutions

In the following classification no unusual cause such as variation of temperature is considered.

On dilution	Cause
K remains constant	Purity of compound Impurity of compound Isohydric solution Difficult solubility Inaccuracy of formula
K increases	Dissociation of associated molecules Change of intramolecular constitution Impurity of compound Inaccuracy of formula (Compound may be pure)
K decreases	Impurity of compound Decomposition Change of intramolecular constitution Isohydric solution Inaccuracy of formula Unknown reasons (Compound may be pure)

This classification is made from the examples previously given. The distinction between isohydric solution and impurity is of course artificial, since the presence in a solution of any other compound beside the one that is being measured is strictly the presence of an impurity.

Identification

If it is assumed that the value of K can be found with an accuracy of five percent and that the purity of the compound is shown by the agreement of the values of the constant found at different dilutions, yet for the same compound two observers find values of K differing by ten percent or more, although each one gets an excellent agreement for his own value of K at all dilutions measured, the question arises whether the compound actually is the same. If the difference is ten percent or less, the true value might lie between the reported values, in which case each would agree with the true value. But if the difference is greater than ten percent the conclusion is evident, either that one of the reported values is in error or that two different compounds were measured. Of course it is easy to assume that the compounds were isomers and that the difference is due to space regulations, for even such a simple acid as propionic acid gives at least three possible isomers from different space relations of the methyl and carboxyl groups. But unless the existence of such an isomer is shown directly or is shown to be probable, the *onus probandi* lies on the man making such an assumption. This leaves the other alternative, that one of the values is in error. From the illustrations already given it is evident that the agreement in the values of K at different dilutions does not exclude the possibility of impurity, so that an error is quite probable. It has also been shown that on account of a number of reasons the value of K as found by two observers may differ more than five percent. These facts make the primary assumptions invalid.

In the following table of some of the lower dibasic fatty acids, the observers are arranged in chronological order. Since each one found concordant values of K in his own measurements,

extended tables will not be given. Oxalic and malonic acids are the only acids more than twenty-five percent dissociated at v 1024. The melting-points are taken from Beilstein's Org. Chemie. If the values given differ by more than one degree the extremes are taken, as in the case of pimelic acid.

	Ostwald ¹	Bethmann ²	Brown & Walker ³	Smith ⁴	Melting-point
Oxalic	(10).	—	—	—	98°; 189.5° ^{aq. free}
Malonic	0.158	0.171	—	—	130°; 132°
Succinic	0.00665	—	0.0068	—	185° (corr.)
Glutaric	0.00475	—	—	0.00473	97.5°
Adipic	0.00371	—	0.00365	0.00376	149°; 153° (corr.)
Pimelic	0.00357	—	—	0.00323	114°; 118°
Suberic	0.00258	0.00311	0.00296	0.00299	140°
Azelaic	—	0.00296	—	0.00253	106°
Sebacic	0.00234	—	0.00276	0.00238	133°-133.5°

Walden⁵ found for malonic acid $K = 0.163$. This, if correct, brings the values of Ostwald and Bethmann, which differ by about eight percent, into agreement with a mean value.

Ostwald could get no constant for oxalic acid because it is too strongly dissociated. He regards the value for pimelic acid as doubtful because it does not come in its proper place in the series which has a value of K steadily diminishing with increased molecular weight and separation of the two carboxyl groups. The poor value he attributes to the presence of impurity (although K did not diminish on dilution) which could not be removed on account of the small amount of material available.

Bethmann found that his new values for malonic and suberic acids improved the series and gave a regular difference. If a table of differences is made it will be seen that the

¹ l. c., p. 284.

² l. c., p. 401.

³ Liebig's Ann. **261**, 116 (1891).

⁴ l. c., p. 198.

⁵ l. c., p. 448.

magnitude of the difference varies with alternate acids, not with succeeding acids as in Ostwald's table.

The work of Brown and Walker is of special interest, because they made by electrolysis the four acids given in the table and tried to identify them by the constant. The constants of succinic and adipic acids agreed well with Ostwald's, but of the other two did not agree within ten percent, and the constant of suberic acid differs a little more than five percent from Bethmann's. They measured samples of the last two acids prepared in the usual way and found for suberic acid $K = 0.00293$, for sebacic acid $K = 0.00271$, values which agreed well with their own for the synthetic acids. Ostwald¹ accepts all their constants as better than his own.

Smith found that his new values for pimelic, suberic and azelaic acids make a much better series than that of Bethmann, giving a regular decrease in K (as found by Ostwald) except in the case of suberic and azelaic acids where the difference is too great, showing a possible error. Both Bethmann and himself found that in the case of azelaic acid the value of K increases on dilution. He regards his own value as better than Bethmann's because it makes the difference between azelaic and sebacic acids more regular, and finds confirmation of the probable accuracy of this value in the fact that his constant for suberic acid agrees well with that found by Brown and Walker. In the case of sebacic acid his value fits in well in his series and agrees with that of Ostwald.

It will be noted in this series that the values regarded as most accurate are those that give desired differences between the constants of two adjacent acids, except in the work of Brown and Walker, who simply made and measured four acids without reference to any such considerations. Ostwald regards his constant for pimelic acid with doubt on this account. Smith's value would fit much better in Ostwald's series. Bethmann introduces into the series a new acid and finds a new value for suberic acid which gives a better series. Smith regards his

¹ Zeit. phys. Chem. 7, 235 (Review).

value for suberic acid as better than Bethmann's because it makes a better series and is confirmed by its agreement with the value found by Brown and Walker. This agreement in the case of suberic acid he also regards as showing that his value for azelaic acid is better than Bethmann's. But he rejects Brown and Walker's value for sebacic acid (which Ostwald had accepted) because his own makes a better series and agrees with that of Ostwald. The difference in the value of the constant for the last three acids is so great that identification would be impossible. If the proper value for each acid from glutaric acid on is chosen, two series can be made, one corresponding to Bethmann's in which the regularity is between alternate acids, the other corresponding to Ostwald's in which the regularity is between adjacent acids. Neither series is perfect. But there is no way of deciding which series is the better one to take as a guide in selecting the most probable value of the constants. The same difficulty occurred in the series of monobasic fatty acids. It is due to imperfect knowledge.

Itaconic acid. — Ostwald¹ found $K = 0.0120$. Smith² measured preparations from different makers and found for one, $K = 0.0149$; for the other, $K = 0.0151$. This agreement makes him suppose that Ostwald may by mistake have measured the wrong acid. The difference, however, is little greater than that found in many other cases.

Oxaluric acid. — Ostwald found the acid too much dissociated to get a constant, except by approximation.

	Ostwald ³	Trüsbach ⁴
v	μ	μ
64	284	98.8
128	311	108.8
$K = 4.5$ (approx.)		

¹ l. c., p. 383.

² l. c., p. 211.

³ l. c., p. 287.

⁴ Zeit. phys. Chem. 16, 713 (1895).

Trübsbach found that this acid decomposes in solution, finally breaking down to oxalic acid. This decomposition is the probable explanation of the great difference between the two measurements which would seem to be of different compounds. The illustration shows the danger of depending on agreement of the molar conductivities at the same dilution as a means of identification in all cases.

The only other point that is of interest in identification is the agreement in value between the constants of compounds of closely related composition. The tables of constants of the monobasic and dibasic fatty acids give several instances of this sort in which the difference is less than five percent. The following table is from Walden :¹

	K	M. p.	
Methylsuccinic acid	0.0086	111°	(Note that these acids are stronger than succinic acid. K = 0.00665)
Ethylsuccinic acid	0.0085	98°	
Propylsuccinic acid	0.00886	91°	

The agreement is of course accidental. It is of theoretical interest because of the slight difference caused by different substituting groups.

In conclusion it seems advisable to make a brief statement about certain points that have been brought up by inference. In the choice of illustrations care has been taken to give no isolated or unusual cases, but to select only those that can be duplicated by a number of similar cases which have been published. This has restricted the illustrations chiefly to acids, since the constants of most organic bases can not satisfactorily be found by conductivity measurements. Many of these acids are dibasic, so the question naturally arises whether some of the differences may be due to the fact that the influence of the second carboxyl varies in different cases. This hardly seems possible because the agreement found is so often good.

It will be noted that few cases have been given in which

¹ l. c., p. 460.

different observers found values for K that agreed well, though many such cases are reported. This is because the reliability of a constant is shown by the relative number of cases in which it is found wanting. If the relative number of such cases tends to increase with increased knowledge, the reliability decreases accordingly.

The availability of conductivity measurements is greatly limited by the fact that the compound must be in solution when measured, and that the use of organic solvents gives results that are of doubtful value in our present state of knowledge.

Unless extended tables of measurements are given it is impossible to compare justly two different values for the constant of any compound, since there is no guide to the circumstances that affected the choice of each value. For instance, if one is an extrapolated value and the other is the value found at the first dilution measured, the agreement may be better or may be worse than it would be if both values were chosen in the same way.

In all cases where the value of K steadily decreases or increases with increasing dilution it is possible that the cause may be a change from one isomer to another.

Conclusions

The dissociation constant is a moderately reliable aid to identification. Its use is limited.

If, for any compound, the constants found by different observers agree within ten percent, the agreement is satisfactory.

The agreement between the values of the constants at different dilutions does not give a satisfactory guide to the purity of the compound that is being measured. This fact lessens the reliability of the constant as a means of identification.

*Massachusetts Institute of Technology,
February, 1903.*