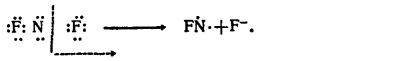
The NF_2^- ion is a species limitingly saturated with electrons, which should stimulate its tendency to stabilisation, leading to a decrease in this saturation, by the elimination of a fluoride anion:



Depending upon the conditions (the presence or absence of solvents and catalysts) the temperature, the difluoramine concentration, pH of the medium or basicity of the reagent, etc.) the process can proceed either quietly (for example, in aqueous alkaline solutions or under the action of potassium and rubidium fluorides) or explosively (for example, in pure difluoramine or upon reaction with caesium fluoride).

It cannot be excluded that the existence of the difluoramide anion for a sufficiently prolonged period outside the molecule of difluoramine, adducts, transition states, etc. (that is, not in a bound state) is impossible in general.

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ACIDITY FUNCTIONS OF AQUEOUS SOLUTIONS OF STRONG ACIDS

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CONTENTS

1. Acidity scale for aqueous solutions of strong acids 803
2. Indicators for measuring acidity functions 805
3. Values of H_0 for aqueous solutions of strong acids and oleum 807
4. Accuracy of measurements of H_0 812
5. Physical significance of the concept of "acidity of the medium" 813
6. Relation between the acidity of the medium and the thermodynamic activity of water 814

1. ACIDITY SCALE FOR AQUEOUS SOLUTIONS OF STRONG ACIDS

In investigating the kinetics of chemical processes in a homogeneous solution it is necessary to take into account the influence of the solvent on the thermodynamic properties of the reactants. The properties of the medium are of particular importance in chemical reactions taking place in aqueous solutions of strong acids and bases. The great tendency to form hydrogen bonds and the higher concentration of ions in such solutions promotes the formation of various complexes and ions with participation of the reagents.

In kinetic equations for liquid-phase processes allowance is made for the effect of the medium on the thermodynamic properties of the reagents, intermediates, and activated complex by the use of activity coefficients. In solutions of acids and bases, the reagents are usually ionised. In most instances the ionised form exhibits a greater reactivity than the un-ionised form. The catalytic action of an acid or base in such instances consists in the conversion of the reagent into an ionised form. The possibility of the chemical process occurring at the moment of collision of the reagent with a proton, hydroxide ion, or molecules of undissociated acids and bases is also not ruled out. The kinetic equation for a chemical reaction will be the same for processes in which the species capable of reaction are ions formed in the interaction of the reagent with an acid or base (if the relative concentration of the ions is small) and for processes in which the rate-limiting state occurs during the collisions of the reagent molecules with protons or hydroxide ions.

We will consider the chemical reaction for the conversion of substance M into Q taking place in an acid medium. The process is first order with respect to M. It is assumed that the ionised form MH^+ is reactive. The MH^+ concentration is low in comparison with that of M. The rate of reaction W is expressed by Eqn. (1):

$$W = \frac{dC_Q}{dt} = k\frac{a^*}{f^*} = k'\frac{a_M a_{H^+}}{f^*} = k'\frac{C_M a_{H^+} f_M}{f^*}. \qquad (1)$$

$$\frac{W}{C_M} = k_{eff} = k' a_{H^+}\frac{f_M}{f^*},$$

where a^*, a_M, and a_{H^+} are the activities of the activated complex, the reacting substance M, and the proton respectively; C_M is the concentration of M; f^* and f_M are the activity coefficients of the activated complex and substance M.

According to Eqn. (1) the change in k_{eff} is connected with change in the quantity $a_{H^+}(f_M/f_{MH^+})$. In aqueous solutions of strong acids the protons are present as hydroxonium ions; therefore the activity of protons a_{H^+} must be expressed in terms of the concentration of hydroxonium ions $C_{H_3O^+}$ and the activity coefficient of the protons f_{H^+}:

$$a_{H^+}\frac{f_M}{f^*} = C_{H_3O^+} f_M \frac{f_{H^+}}{f^*}.$$

The experimentally observed proportionality between k_{eff} and the concentration of hydroxonium ions $C_{H_3O^+}$ in extremely dilute solutions of acids is connected with the constancy of the ratio $f_M f_{H^+}/f^*$.

In concentrated aqueous solutions of strong acids k_{eff} rises more sharply than the hydroxonium ion concentration; this is connected with an increase in the ratio $f_M f_{H^+}/f^*$. Consequently, to predict how the catalytic activity of an acid medium varies with change in the acid concentration it is necessary to know how the quantity $a_{H^+}(f_M/f^*)$ varies. The activity coefficient of the un-ionised form f_M can be measured. The activity coefficients f_{H^+} and f^* cannot be measured experimentally in isolation. Here assumptions must be made which allow measurable quantities to be introduced into the kinetic equation. When an activated complex is formed from a molecule of the reagent and a proton, then in composition and charge it corresponds to the ionised form of the reagent. Therefore it can be taken that as the composition of the medium is varied the activity coefficients of the activated species f^* and of the protonised form f_{MH^+} will change similarly. On making this assumption, f^* in Eqn. (1) can be replaced by f_{MH^+}.

$$k_{eff} = k' a_{H^+}\frac{f_M}{f_{MH^+}}.$$

The change in the catalytic activity of the acid medium is determined by the activity of the protons a_{H^+} and by the ratio of the activity coefficients of the un-ionised and ionised forms of the reagent. The proton activity a_{H^+} is determined by the properties of the medium. The activity coefficients f_M and f_{MH^+} reflect the properties of the reagent M dissolved in the acid. The quantity $a_{H^+}(f_M/f_{MH^+})$ also characterises the ratio of the concentrations of the protonated and unprotonated forms of the substance dissolved in the acid.

We will use k_{BH^+} to denote the equilibrium constant for the ionisation of substance B, expressed in terms of activity:

$$B + H^+ \rightleftharpoons BH^+,$$

$$k_{BH^+} = \frac{a_B a_{H^+}}{a_{BH^+}} = \frac{C_B a_{H^+} f_B}{C_{BH^+} f_{BH^+}}.$$

Hammett has proposed[1] that in concentrated aqueous solutions of strong acids the change in the ratio f_B/f_{BH^+} is determined by the properties of the acid medium and is independent of the chemical nature of the substance. Hence according to Hammett the following equality holds for solutions of substances (for example, M, B, C, and D):

$$\frac{f_M}{f_{MH^+}} = \frac{f_B}{f_{BH^+}} = \frac{f_C}{f_{CH^+}} = \frac{f_D}{f_{DH^+}}.$$

If Hammett's hypothesis is correct, then it becomes possible to find a quantitative characteristic for the ionising ability of acid media. Kinetic and indicator methods can be used for this purpose.

To obtain a quantitative measure of the catalytic activity of the acid medium by the kinetic method it is necessary to study the kinetics of some process over the required concentration range of the solution of the acid. A simple unimolecular chemical reaction for which the ionisation mechanism and rate-determining steps have been established in detail should be chosen for this purpose. It is desirable that the degree of ionisation of the reagent should be negligible over the whole concentration range of the acid, that is, the reagent should be almost wholly in its un-ionised form. When on going from dilute to concentrated solutions of a strong acid the mechanism of the process and also the activation energy and preexponential factor of the rate-determining step remain unchanged, the rate constant of such a process could serve as a quantitative measure of the catalytic activity of the acid media. The problem is to select a chemical process for which the rate constant at constant temperature would change by 12–14 orders of magnitude on changing the acid concentration.

Modern techniques of kinetic investigation allow processes to be studied where the rate constant varies only by 4–5 orders of magnitude at constant temperature. It is therefore necessary to choose several reagents with different reactivities. However, there is then no certainty that the reagents chosen as the models ionise by the same mechanism and that in all instances the mechanism of the rate-limiting step is the same.

A quantitative measure of the ionising ability of aqueous solutions of strong acids over a wide range of concentrations can be obtained using the indicator method proposed by Hantzsch[2] and worked out in detail by Hammett. By indicator is meant a chemical substance which is ionised in solutions of acids and bases, the un-ionised and ionised forms of which have different absorption spectra. An indicator should be chemically stable in the medium being investigated.

The concentrations of the ionised and un-ionised forms of the indicators are determined spectrometrically.

The simplest type of ionisation is protonation. This is an acid–base process, as a result of which base B is converted into acid BH^+, Eqn. (2). With a rather large number of substances ionisation finishes at the protonation stage.

In the ionisation of alcohols and organic acids, the ionised form can be dehydrated:

$$\left.\begin{aligned} &BOH + HA \rightleftharpoons BOH_2^+ + A^- \\ &BOH_2^+ \rightleftharpoons B^+ + H_2O \end{aligned}\right\} \qquad (3)$$

The protonated form BH^+ and also the cations B^+ which are formed in the dehydration of the ions BOH_2^+ can form ion pairs:

$$\left.\begin{aligned} &BH^+ + A^- \rightleftharpoons BH^+.A^- \\ &B^+ + A^- \rightleftharpoons B^+A^- \end{aligned}\right\} \qquad (4)$$

The possibility of the reagent forming a specific complex with some acid or with the solvent cannot be excluded. The ionisation mechanism is determined by the chemical structure of the reagent and by the properties of the medium.

Naturally, in studying the ionising ability of a medium by some mechanism indicators must be chosen which ionise by the same mechanism. To establish an acidity scale, Hammett selected a series of indicators which are mainly derivatives of the nitroanilines. The ionisation of these indicators proceeds by Eqn. (2). Such indicators are termed simple. Hammett took the equilibrium constant of process (2), K_{BH^+} as a measure of the strength of the base. The negative logarithm of the quantity K_{BH^+} is denoted by pK_{BH^+}:

$$pK_{BH^+} = -\log K_{BH^+}.$$

K_{BH^+} for strong bases is small and pK_{BH^+} is positive. The weaker are the basic properties of the substance, the greater the value of K_{BH^+} and the more negative the value of pK_{BH^+}.

Hammett proposed that the quantity $a_{H^+}(f_B/f_{BH^+})$ be termed the acidity of the medium. This is denoted by the symbol h_0 and its negative logarithm is termed the acidity function and given the symbol H_0:

$$h_0 = a_{H^+}\frac{f_B}{f_{BH^+}}; \qquad H_0 = -\log h_0.$$

On taking logarithms of Eqn. (2) for the constant K_{BH^+} and replacing $-\log K_{BH^+}$ by pK_{BH^+} and $-\log a_{H^+}(f_B/f_{BH^+})$ by H_0, we obtain an equation which relates the acidity function of the medium to the ratio of the concentrations of the ionised and un-ionised forms of the indicators:

$$H_0 = pK_{BH^+} + \log\frac{C_B}{C_{BH^+}}. \qquad (5)$$

If the acidity of the medium is known it is possible to calculate the basicity constant and the ratio of the concentrations of the base and the conjugate acid form of the substance. Hence to measure the acidity function of the medium by the use of some indicator it is necessary to know its basicity constant (K_{BH^+}) and the ratio of the concentrations of the un-ionised and ionised forms (C_B/C_{BH^+}) in the given medium. The concentrations C_B and C_{BH^+} are usually measured spectrophotometrically or colorimetrically. A single indicator can be used to investigate a medium whose acidity function changes within the limits of 2–3 units, which corresponds to a change in the C_B/C_{BH^+} ratio from 30–10 to 0.1–0.03. To investigate a medium with a wider range of acidities, several indicators must be used.

Infinite dilution of an aqueous solution of a strong acid is selected as the standard state for the scale. In an infinitely dilute aqueous solution the activity coefficients f_B and f_{BH^+} are taken to be unity and the thermodynamic activity of the protons is taken as numerically equal to the hydroxonium ion concentration. In such solutions the acidity of the medium equals the hydrogen ion concentration, and H_0 equals the pH.

The essence of the indicator method of measuring H_0 consists in determining pK_{BH^+} and the values of C_B/C_{BH^+} of the indicators in the medium of unknown acidity. At first it is necessary to find the values of pK_{BH^+} for the indicators, which are strong bases, for which the quantity C_B/C_{BH^+} can be determined in extremely dilute solutions of acids, where $h_0 = C_{H_3O^+}$. For example, aminoazobenzene (which we will denote by the symbol B) is already appreciably ionised in 10^{-4} m HCl† and almost completely so in 0.024 m HCl. From the dependence of $\log(C_B/C_{BH^+})$ for aminoazobenzene on the concentration of the acid in the range of C_{HCl}, its pK_{BH^+} is calculated by Eqn. (5). Another indicator is chosen for the determination of the acidity of more concentrated solutions of hydrochloric acid, for example, benzeneazodiphenylamine, which is a weaker base than aminoazobenzene. This indicator (which we will denote by the symbol C) is only partly ionised in 1×10^{-4}–2×10^{-2} m HCl and is completely ionised in more concentrated solutions, where $-\log C_{H_3O^+}$ is no longer equal to the pH.

We will compare the logarithms of the ratios of the concentrations of the un-ionised and ionised forms for the two indicators mentioned above (for example, B and C) in the same solution of acid:

$$-\log a_{H^+} = pK_{BH^+} + \log\frac{C_B}{C_{BH^+}} + \log\frac{f_B}{f_{BH^+}} = pK_{CH^+} + \log\frac{C_C}{C_{CH^+}} + \log\frac{f_C}{f_{CH^+}},$$

or

$$pK_{BH^+} - pK_{CH^+} = \log\frac{C_C}{C_{CH^+}} - \log\frac{C_B}{C_{CH^+}} + \log\frac{f_C f_{BH^+}}{f_{CH^+} f_B}.$$

† Here and subsequently the symbol m denotes the molality of the solution [in the translation, *m* is employed as the symbol for the molality and m as the abbreviation for the unit of molality, as usual (Ed. of Translation)].

When

$$\frac{f_C f_{BH^+}}{f_{CH^+} f_B} = 0,$$

it becomes possible to determine pK_{CH^+} of the indicator C, provided pK_{BH^+} of another indicator B and the quantities C_B/C_{BH^+} and C_C/C_{CH^+} in the same medium are known.

$$pK_{BH^+} - pK_{CH^+} = \log \frac{C_C}{C_{CH^+}} - \log \frac{C_B}{C_{BH^+}}. \quad (6)$$

Since pK_{BH^+} of aminoazobenzene is determined in extremely dilute solutions‡, where $H_0 = pH = -\log m_{H_3O}$, then Eqn. (6) can be used to calculate pK_{CH^+} of the less basic indicator, for example, benzeneazodiphenylamine. By determining pK_{CH^+} by Eqn. (5), the acidity of solutions of stronger acids can be calculated where the ratio of the concentrations of the un-ionised and ionised forms of benzeneazodiphenylamine can be measured with good accuracy. To measure H_0 of more concentrated solutions, an indicator D is chosen which exhibits an even lower basicity but partly overlaps the region of acid concentrations where the indicator C is still incompletely ionised. pK_{DH^+} of the indicator and H_0 for the acid solutions are calculated as described above.

Hence by means of several indicators the acidity function is measured over a wide range of concentrations of aqueous solutions of strong acids. For example, to measure the acidity function of the $HCl-H_2O$ system from dilute solutions to 16 M HCl, it is necessary to use seven or eight indicators, and to measure H_0 of the $H_2SO_4-H_2O$ system from dilute solutions to 100% H_2SO_4 10–12 indicators are required.

2. INDICATORS FOR MEASURING ACIDITY FUNCTIONS

Table 1 gives the indicators used for measuring acidity functions and the values of their pK_{BH^+}. The ionisation of such indicators involves the addition of a proton. In acid media the indicator is present in two equilibrium forms: un-ionised and ionised.

Cryoscopic and electrical conductivity results are usually used to establish the ionisation mechanism. 100% sulphuric acid acts as an ionising solvent. The indicators chosen by Hammett for measuring H_0 were investigated cryoscopically by Hammett and coworkers [6] and also by other authors [7]; the latter [7] also investigated the electrical conductivity of the solutions. The value of the van't Hoff i factor for simple indicators is near or equal to 2. On this basis it is concluded that when these substances ionise two species are formed:

$$B + H_2SO_4 \rightleftharpoons BH^+ + HSO_4^-. \quad (7)$$

This conclusion does not seem unambigous. The i factor being 2 only signifies that in 100% sulphuric acid and in H_2SO_4 solutions with low water and sulphur trioxide concentrations (sulphuric acid only slightly diluted with water and with a low oleum concentration) the substance ionises according to Eqn. (7). On the basis of this fact it is impossible to maintain that the indicator is present solely as an ionised and an un-ionised form also in more dilute aqueous solutions of sulphuric acid, when the concentration of HSO_4^- anions is high. In 100% sulphuric acid§ the HSO_4^- ions are formed as a result of autoprotolysis:

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-,$$

and their concentration is not high. For example, at 25° the concentration of HSO_4^- anions in 100% H_2SO_4 is $\sim 3 \times \times 10^{-2}$ M. [8,9] In 78–80% H_2SO_4 the concentration of HSO_4^- anions is 10.6 M at 25°. [10,11]

The possibility of the ion pairs $BH^+.HSO_4^-$ being formed in solutions of acids where there is a high concentration of anions is not ruled out:

$$BH^+ + HSO_4^- \rightleftharpoons BH^+.HSO_4^-.$$

In this instance the dissolved indicator or reagent will now be present in the acid solution as the equilibrium forms: un-ionised form, protonised form, and ion pair. When the indicators form ion pairs over some range of acid concentrations then they can be used for measurements of H_0 only if it is possible to determine the concentrations of all

TABLE 1*.

Values of pK_{BH^+} of acid indicators (at 22–26°)

Indicator	pK_{BH^+} in $HCl-H_2O$	K_{BH^+} in $HBr-H_2O$	pK_{BH^+} in $HClO_4-H_2O$	pK_{BH^+} in $H_2SO_4-H_2O$	pK_{BH^+} in HNO_3-H_2O	pK_{BH^+} in $P_2O_5-H_2O$
p-Aminoazobenzene	+2.82	—	+2.82	—	—	—
m-Nitroaniline	+2.50	—	+2.50	—	—	—
2,4-Dichloroaniline	+2.0	—	—	—	—	—
Benzeneazodiphenylamine	+1.42	—	—	—	—	—
p-Nitroaniline	+1.0	+0.9	—	+1.0	+1.03	+1.0
Diphenylamine	+0.78	—	-	+0.77	—	—
o-Nitroaniline	−0.29	−0.23	−0.29	−0.33	−0.28	−0.2
Pyrocatecholsulphonic acid	−0.08	—	—	—	—	—
NN-Dimethyl-2,4-dinitroaniline	—	—	—	−1.0	—	—
4-Chloro-2-nitroaniline	−0.99	—	−1.07	−1.02	−1.11	−0.98
5-Chloro-2-nitroaniline	−1.44	−1.45	—	−1.55	—	−1.6
2,5-Dichloro-4-nitroaniline	—	—	−1.79	−1.90	—	—
2-Chloro-6-nitroaniline	—	—	−2.41	−2.43	—	—
4-Nitrodiphenylamine	−2.37	—	—	−2.50	—	−2.28
2,6-Dichloro-4-nitroaniline	—	—	−3.2	—	−2.55	—
2,4-Dichloro-6-nitroaniline	−3.33	−3.24	—	−3.28	−3.3	−3.02
2,4-Dinitroaniline	−4.58	−4.39	−4.26	−4.45	—	−4.96
2,6-Dinitroaniline	—	—	−5.25	−5.64	—	—
4-Chloro-2,6-dinitroaniline	—	—	−6.12	−6.25	—	—
2,4-Dinitro-1-naphthylamine	—	—	−6.5	—	—	—
6-Bromo-2,4-dinitroaniline	—	—	−6.69	−7.09	—	—
3-Methyl-2,4,6-trinitroaniline	—	—	−8.56	−8.34	—	—
3-Bromo-2,4,6-trinitroaniline	—	—	−9.77	—	—	—
2,4,6-Trinitroaniline	—	—	—	−9.98	—	—
p-Nitrotoluene	—	—	—	−11.27	—	—
p-Chloronitrobenzene	—	—	—	−12.63	—	—
Nitrobenzene	—	—	—	−12.19	—	—
2,4-Dinitrotoluene	—	—	—	−13.53	—	—
m-Nitroanilinium cation (second protonisation of *m*-nitroaniline)	—	—	—	−14.14	—	—

pK_{BH^+} at other temperatures

Indicator	Temperature, °C		
	40	60	80
p-Nitroaniline	+0.81	+0.60	+0.43
o-Nitroaniline	−0.41	−0.55	−0.70
4-Chloro-2-aniline	−1.17	−1.28	−1.41
2,4-Dichloro-6-nitroaniline	−3.07	−3.14	

* The errors in the determination of the pK_{BH^+} of the indicators are not given in Table 1, as this problem receives detailed discussion in Section 4. Pyrocatecholsulphonic acid is used as an indicator for determining the acidity of aqueous solutions of hydrochloric acid in the presence of ions of copper(I) chloride [4] at 20–80°. New information has been published recently [5] on the values of pK_{BH^+} for *p*-nitroaniline at elevated temperatures: at 30°, 40°, 50°, and 60°, it is 0.96, 0.9, 0.83, and 0.77 respectively.

‡ Before Paul's work [3], pK_{BH^+} for strong bases were determined by comparison of $\log (C_B/C_{BH^+})$ with the logarithm of the mean ionic activity $a_\pm$. When f_B is constant in very dilute solutions of acids the activity coefficient of the ionised form f_{BH^+} changes according to the Debye–Hückel law. Therefore it is correct to compare $\log (C_B/C_{BH^+})$ with the H_3O^+ ion concentration. Then the electrostatic contributions to f_{H^+} and f_{BH^+} are reduced.

§ Here and subsequently weight percentages of acids are given.

three forms separately. However, this is a rather difficult task. The spectrophotometric method in such instances is inapplicable since the free ions and ion pairs have similar absorption spectra.

It can be reliably stated that during the ionisation of indicators chosen for the measurement of acidity function free ions are formed in dilute solutions of strong acids and close to 100% H_2SO_4, where the concentration of anions is low. As for the region of moderate acid concentrations, where the anion concentration is high, there is still no direct proof of the absence of the ion pairs $BH^+.HSO_4^-$ from such solutions, but there are certain facts which can serve as indirect evidence that the measurable ratio C_B/C_{BH^+} for the indicators characterises the acidity of the medium h_0. The unimolecular reaction selected must be one which can be investigated in both concentrated and dilute solutions of the acid, for example, sulphuric acid, which encompass 7–8 units of the H_0 scale (from +1 to -7 units). The degree of the ionisation of the reagent should be negligible ($C_{BH^+} \ll C_B$) over the whole H_0 range being investigated. When k_{eff}/h_0 = const for all the solutions, this will be proof that in both concentrated and dilute solutions of the acid the mechanism of ionisation is the same.

As already mentioned, it is difficult to select a unimolecular chemical reaction for which the dependence of k_{eff} on H_0 can be studied over such a wide H_0 range under the condition $C_{BH^+} \ll C_B$. Nevertheless a single example can be given: the hydrolysis of β-propiolactone in sulphuric acid. This hydrolysis¶ has been studied in aqueous solutions of sulphuric acid from dilute solutions to 65% H_2SO_4. At 25°, k_{eff} increases in proportion to the acidity of the medium [13]. It is interesting to investigate a similar reaction over a wider range of acid concentrations. For this purpose it would be possible to select the exchange of hydrogen for deuterium and the subjects of the investigation could be the very indicators which are used to measure H_0. There are also considerations based on the method of measurement of the quantity C_B/C_{BH^+}. The un-ionised forms of nitroaniline indicators absorb, and the ionised forms do not absorb, in the visible region of the spectrum. The concentration of the un-ionised form C_B is determined from the intensity of the colour of the indicator solution in the visible region of the spectrum. The concentration of the ionised form C_{BH^+} is determined as the difference between the total concentration of the indicator and C_B.

The formation of ion pairs cannot be deduced from the measurements of the C_B/C_{BH^+} ratio when salt formation starts under conditions where the indicator is present almost entirely as the ionised form. When the salt-formation constant is such that ion pairs are formed in solutions with a low degree of protonation, it is impossible to determine C_B/C_{BH^+} from the change in the colour of the solution.

The problem of possible ion pair formation in the ionisation of acid–base indicators in concentrated acids requires detailed investigation. It is especially important to show the possibility of ion-pair formation in sulphuric acid solutions containing from 65 to 90% H_2SO_4 and in aqueous solutions of nitric acid with >60% HNO_3. Not all the substances which are used to measure H_0 satisfy the requirements applicable to indicators.

In concentrated solutions of sulphuric acid benzalacetophenone is unstable and undergoes isomerisation [14]. It is also unstable in polyphosphoric acid solutions [15]. Anthraquinone has several absorption bands in the visible and ultraviolet regions of the spectrum. On changing the acid concentration, in addition to the change in its degree of ionisation there is a displacement of the absorption maximum. Owing to the shift in the absorption maxima of *p*-nitrodiphenylamine and anthraquinone it is impossible to determine their degree of ionisation accurately.

Benzalacetophenone, anthraquinone, and *p*-nitrodiphenylamine are unsuitable for measuring the acidity of the medium. With *N*-substituted nitroanilines the concentration of the un-ionised form in aqueous solutions of sulphuric [16] and nitric [17] acids — and also in solutions of sulphuric acid in acetic acid [18] — falls anomalously. It can be assumed that in these materials ion pairs are formed during ionisation as well as the protonated species†.

As already mentioned above, a spectrophotometric method is now used for determining the concentrations of the ionised and un-ionised forms of indicators. The degree of ionisation of the indicator is most frequently determined by measuring the absorption coefficient at a single wavelength which is convenient for measurements. With the indicators of the nitroaniline series the absorption intensity is measured at some wavelength in the visible region of the spectrum. When the change in the spectrum of an indicator on raising the acid concentration is due not just to the appearance of an ionised form but also to a change in the optical properties of the medium, then it is difficult to judge the degree of ionisation of the indicator from the optical density of the solution. Usually in measurements of H_0 of acids the applicability of Beer's law is verified for particular wavelengths and during this the indicator concentration is varied over wide limits in solutions with the same acid concentration. The absorption coefficient for some form (ionised or un-ionised) is determined in solutions of acid with such an acidity that one of the forms is almost absent. In calculating C_B and C_{BH^+} it is assumed that the absorption coefficient of the forms B and BH^+ does does not depend on the composition of the medium in the range of acid concentrations at which the measurements are made. To avoid any possible effect when the medium is changed, the absorption coefficient of the un-ionised form is determined in acid solutions in which the ratio $C_B/C_{BH^+} \simeq 100$, and the absorption coefficient of the ionised form in solutions with $C_B/C_{BH^+} \simeq 0.01$. There are occasions when the change in the degree of ionisation of the indicator is not the only reason for a change in the spectrum. An example of this is the spectrum of 6-bromo-2,4-nitroaniline in sulphuric acid solutions [19]. This indicator has maximum absorption at 360 nm, due to the un-ionised form. In solutions of sulphuric acid with <67% H_2SO_4, the indicator is almost completely in the un-ionised form. In more concentrated solutions of the acid the intensity of the absorption maximum decreases (Fig. 1). The absorption coefficient also decreases at longer wavelengths. The position of the absorption maximum is almost unchanged in the interval 59–98% H_2SO_4, where ionisation of this substance takes place. When the absorption coefficients of the ionised and

¶ The hydrolysis of β-propiolactone has a complex mechanism. As Long and coworkers have shown [12], the experimentally observable rate constant is the sum of the rate constants of a non-catalytic and a catalytic process. Here we are considering the dependence of the rate constant of the catalytic process of hydrolysis on the acidity of the medium. This process is unimolecular.

† Possibly, in the ionisation of *N*-substituted nitroanilines, Hammett's hypothesis of the equality of the ratios of the activity coefficients of the un-ionised and ionised forms is not satisfied.

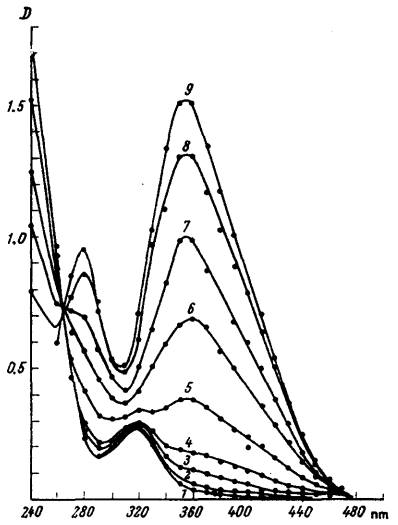


Fig. 1. Absorption spectra of 6-bromo-2,4-dinitroaniline in aqueous solutions of sulphuric acid with concentrations from 58.86 to 98.21%, from Vinnik and coworkers[19]. The optical densities D were obtained for the same indicator concentration. H_2SO_4 concentrations, %: 1) 98.21; 2) 88.07; 3) 85.24; 4) 82.72; 5) 79.93; 6) 77.5; 7) 75.36; 8) 72.18; 9) 58.96.

TABLE 2. Values of $\log(C_B/C_{BH^+})$ for 6-bromo-2,4-dinitroaniline, calculated from intensities at different wavelengths and from the area of the absorption contour from λ_{max} to the side of greater wavelengths.

H_2SO_4, %	Wavelength, nm	$\log\frac{C_B}{C_{BH^+}}$	H_2SO_4, %	Wavelength, nm	$\log\frac{C_B}{C_{BH^+}}$	H_2SO_4, %	Wavelength, nm	$\log\frac{C_B}{C_{BH^+}}$
85.24	280	−1.32	79.93	280	−0.46	75.36	280	+0.26
	360	−1.19		360	−0.50		360	+0.24
	370	—		370	−0.49		370	+0.24
	380	−1.15		380	−0.49		380	—
	390	−1.13		390	−0.44		390	+0.29
	400	−1.11		400	−0.41		400	+0.37
	410	—		410	−0.40		410	+0.38
	420	−1.18		420	−0.36		420	+0.41
	430	−1.02		430	−0.31		430	+0.54
	440	—		440	−0.27		440	+0.55
	450	—		450	−0.16		450	+0.53
	from area	−1.21		from area	−0.52		from area	+0.30
82.72	280	−1.03	77.51	280	−0.06			
	360	−0.96		360	−0.1			
	370	−0.90		370	−0.05			
	380	−0.90		380	−0.04			
	390	−0.87		390	−0.02			
	400	−0.83		400	−0.01			
	410	−0.82		410	+0.01			
	420	−0.80		420	−0.08			
	430	−0.70		430	+0.14			
	440	−0.66		440	+0.19			
	450	−0.64		450	+0.29			
	from area	−0.95		from area	−0.08			

un-ionised forms for different wavelengths do not depend on the concentration of the acid, then the change in the observed absorption coefficients should be due only to the change in the degree of ionisation of the indicator. In this instance the same values of C_B/C_{BH^+} should be obtained for all wavelengths. As the data of Table 2 show, the values of C_B/C_{BH^+} for 6-bromo-2,4-dinitroaniline in a particular medium depend on the wavelength chosen for the measurements. The explanation is that a change in the observed absorption coefficients for different wavelengths is due not only to the change in the C_B/C_{BH^+} ratio but also to the change in the absorption coefficients of the individual dual forms of the indicator. Such an effect is also observed for 2,4-dichloro-6-nitroaniline, and it is even more prominent with p-nitrodiphenylamine[20]. With o-nitroaniline, 2,4-dinitroaniline, 2,4,6-trinitroaniline, and p-nitroaniline at 25° the ratio C_B/C_{BH^+} is almost independent of the wavelength at $\lambda > \lambda_{max}$.[19]

In solutions of 2,4-dinitroaniline in concentrated phosphoric and polyphosphoric acids[15], there is a slight displacement of the absorption maximum and the absorptivity of this indicator varies under conditions where there is still no appreciable ionisation.

The concentration of a substance is characterised by the area under the curve plotted as absorption intensity against frequency. Therefore in measuring the acidity of a medium by the indicator method, even in instances where the absorption maximum of the indicator is not displaced by changing the acid concentration, integral intensities should be used. The measurement of integral intensities is rather laborious and is not always feasible. When there is the above-mentioned complication, the values of $\log(C_B/C_{BH^+})$ obtained from the intensity for maximum absorption agree with the values obtained from the area under the curve from the absorption maximum towards longer wavelengths. This is shown by the example of 6-bromo-2,4-dinitroaniline and 5-chloro-2-nitroaniline[19], where there is hardly any displacement of the absorption maximum. Table 2 gives the values of C_B/C_{BH^+} for 6-bromo-2,4-dinitroaniline calculated for different wavelengths and from the area under the absorption curve, taken from Vinnik and coworkers[19].

When it is impossible to use integral intensities in determining the indicator ratio C_B/C_{BH^+} then it is desirable to measure the intensity at the absorption maximum.

3. VALUES OF H_0 FOR AQUEOUS SOLUTIONS OF STRONG ACIDS AND OLEUM

The problems which related to the quantitative characteristic of acid media were discussed in detail in Shatenshtein's monograph[2]. Paul and Long[21] published a thorough review of work on the acidity of aqueous and non-aqueous solutions of acids in 1957, and subsequently papers appeared in which the values of H_0 were refined and the acidities of new solutions were measured. The present review only gives values of the acidity function for aqueous solutions of strong acids and oleum.

a. Sulphuric Acid

The acidity function of sulphuric acid was first measured in work by Hammett and Deyrup[1] published in 1932. The results of these authors for the region from dilute solutions up to 68% H_2SO_4 were repeatedly confirmed in later investigations[20,22,23], but the acidity function for more concentrated solutions was determined[1] with greater error, as the indicators used were benzalacetophenone and anthraquinone, which do not satisfy the requirements applicable for indicators. The indicators used by Jorgenson and Hartter[24] to measure the acidity function of sulphuric acid solutions

from 65 to 90% H_2SO_4 were: 2,6-dinitroaniline, 4-chloro--2,6-dinitroaniline, 2-bromo-4,6-dinitroaniline, 3-methyl--2,4,6-trinitroaniline, 3-chloro-2,4,6-trinitroaniline, and 3-bromo-2,4,6-trinitroaniline. For the same acid concentration range the observed difference in $\log(C_B/C_{BH^+})$ was satisfactorily constant between 2,4-dinitroaniline and 2,6-dinitroaniline, and also between 2,6-dinitroaniline and 4-chloro-2,6-dinitroaniline.

The data on the ionisation of 6-bromo-2,4-dinitroaniline obtained by Vinnik and coworkers [19] differ somewhat from those of Jorgenson and Hartter [24]. As we determined [19] the value of C_B/C_{BH^+} from the area under the absorption curve, these results are naturally more accurate. The acidity of acid solutions with $>90\%$ H_2SO_4 can be measured by using 3-methyl-2,4,6-trinitroaniline, 2,4,6-trinitroaniline, and *p*-nitrotoluene [25]. Jorgenson and Hartter [24] also propose 3-bromo-2,4,6-trinitroaniline and 3-chloro-2,4,6-trinitroaniline for this purpose. As the acid concentration is raised, the C_B/C_{BH^+} ratio for 3-bromo-2,4,6-trinitroaniline and 3-chloro-2,4,6-trinitroaniline falls more sharply than would be expected by the acidity of the medium measured by 3-methyl-2,4,6-trinitroaniline (from Jorgenson and Hartter's results [24]) and 2,4,6-trinitroaniline‡ (Vinnik and Ryabov [9]); the reason for this is still not clear. Possibly it is connected with errors in the measurements, or with the quantity $f_B f_{CH^+}/f_{BH^+} f_C$ not being constant for these substances.

Table 3 gives published [19] values of H_0 at 25° for aqueous solutions of sulphuric acid. The acidity function for sulphuric acid at elevated temperatures was measured by Gel'bshtein and coworkers [22] by a photometric method. Table 4 gives their results for the interval from 4% H_2SO_4 to 54% H_2SO_4 (the measurements were made with *p*-nitroaniline, *o*-nitroaniline, 4-chloro-2-nitroaniline, and 2,4-dichloro-6-nitroaniline). The H_0 for more concentrated solutions of sulphuric acids are not given here for the following reasons. In addition to the indicators mentioned, 2,4-dinitroaniline (from 60.2 to 73.4% H_2SO_4), 6-bromo-2,4-dinitroaniline (from 78.0 to 89.5% H_2SO_4), and 2,4,6-trinitroaniline (from 97.1 to 99.6% H_2SO_4) were used [22]. pK_{BH^+} for the last two indicators cannot be determined by comparing $\log(C_B/C_{BH^+})$ since the acidity has not been measured by another indicator in the chosen ranges of H_2SO_4 concentrations. The ionisation regions of 2,4-dichloro-6-nitroaniline and 2,4-dinitroaniline overlap in the range 60.2–64% H_2SO_4. However, it is impossible to determine pK_{BH^+} for the latter indicator since the difference in $\log(C_B/C_{BH^+})$ for these substances depends significantly on the acid concentration.

TABLE 3. Acidity function of sulphuric acid at 25°.

H_2SO_4, %	H_0	H_2SO_4, %	H_0	H_2SO_4, %	H_0
1	+0.84	45	−2.95	92	− 9,33
3	+0.31	47	−3.13	94	− 9.59
5	−0,02	50	−3.41	96	− 9.88
8	−0.28	52	−3.60	98	−10,27
10	−0.43	55	−3.91	99	−10.57
12	−0.58	57	−4.15	99.1	−10.62
14	−0.73	60	−4.51	99.2	−10.66
16	−0.85	62	−4.82	99.3	−10.72
18	−0.97	65	−5.18	99.4	−10.77
20	−1.10	67	−5.48	99.5	−10.84
22	−1.25	70	−5.92	99.6	−10,92
25	−1.47	72	−6.23	99.7	−11,01
27	−1.61	75	−6.72	99.8	−11.18
30	−1.82	77	−7.05	99.85	−11.28
32	−1.96	80	−7,52	99.90	−11.43
35	−2.19	82	−7.84	99.95	−11.64
37	−2.34	85	−8.29	100	−11.94
40	−2.54	87	−8.60		
42	−2.69	90	−9.03		

TABLE 4. Acidity function of sulphuric acid at elevated temperatures*.

H_2SO_4, %	H_0			H_2SO_4, %	H_0		
	40°	60°	80°		40°	60°	80°
4	+0.19	+0.17	+0.15	28	−1.61	−1.63	−1,64
6	−0.11	−0.14	−0.13	30	−1.74	−1.76	−1.77
8	−0.29	−0.34	−0.35	32	−1.87	−1.89	−1.90
10	−0.44	−0.50	−0.52	34	−2.01	−2.03	−2.03
12	−0.58	−0.63	−0.66	36	−2.16	−2.15	−2.15
14	−0.69	−0.75	−0.79	38	−2.31	−2.31	−2.31
16	−0.82	−0.85	−0.89	40	−2.46	−2.47	−2.47
18	−0.95	−0.98	−1.01	44	−2.76	−2.78	−2.78
20	−1.07	−1.11	−1.14	48	−3.08	−3.09	−3.09
22	−1.21	−1.24	−1.26	50	−3.23	−3.24	−3.25
24	−1.34	−1.37	−1.39	54	−3.61	−3.59	−3.58
26	−1.47	−1.49	−1.51				

* In calculating H_0 for 40°, 60°, and 80° it was assumed that the quantity pK_{BH^+} for *p*-nitroaniline in sulphuric acid is the same as that in hydrochloric acid. The pK_{BH^+} for the other indicators were determined as usual. The values of pK_{BH^+} are given in Table 1.

b. Solutions of SO_3 in Sulphuric Acid

The acidity function of oleum has been measured by Brand and coworkers [25,26] and by Vinnik and coworkers [9]. In solutions with up to 36% SO_3 the following can serve as indicators: *p*-nitrotoluene, *p*-chloronitrobenzene, *p*-fluoronitrobenzene, *p*-bromonitrobenzene, *p*-butylnitrobenzene, *m*-nitrotoluene, and nitrobenzene. 2,4-Dinitrotoluene and the *m*-nitroanilinium ion [26] (addition of a second proton to *m*-nitroaniline) ionise in more concentrated solutions. Trinitrobenzene and 2,4,6-trinitrotoluene ionise only 20–30% in 65% oleum [26]. Table 5 gives values of H_0 for oleum solutions at 25°. There is no doubt that in dilute oleum the ionisation of the aforementioned indicators consists in the addition of a proton. In concentrated oleum the activity of sulphur trioxide rises sharply and the latter can be attached to the indicator as an aprotic acid. The indicator method for measuring acidity does not distinguish between protonation and ionisation by addition of an aprotic acid.

TABLE 5. Acidity function of oleum at 25°.

SO_3, %	$-H_0$	SO_3, %	$-H_0$	SO_3, %	$-H_0$
0.15	12.1	3.0	12.74	14	13.39
0.2	12.13	3.5	12.78	16	13.47
0.4	12.26	4.0	12.83	18	13.55
0.5	12.30	5.0	12.90	20	13.62
0.6	12.33	6.0	12.98	22	13.68
0.8	12.38	7.0	13.04	25	13.76
1.0	12.43	8.0	13.1	27	13.81
1.5	12.54	9.0	13.15	30	13.91
2.0	12.62	10.0	13.21	32	13.98
2.5	12.68	12.0	13.31	36	14.13

‡ The data on the ionisation of 2,4,6-trinitroaniline obtained by Jorgenson and Hartter [24] differ considerably from those of Vinnik and Ryabova [9].

More precise information about the ionisation mechanism of indicators in concentrated oleum could be obtained by studying the dependence of the rate of deuterium exchange with the hydrogen of the aromatic ring for the indicator (type RNO_2). It should be noted that in dilute oleum there is a marked rise in acidity with increase in SO_3 concentration. In more concentrated solutions the acidity of the medium increases in proportion to the activity of the sulphur trioxide.

c. Hydrochloric and Hydrobromic Acids

Hammett and Paul[27] measured the acidity function of aqueous solutions of hydrogen chloride from dilute solutions to 20% HCl, and their results were confirmed in later investigations[3,28]. The acidity function of more concentrated solutions has been measured[29,30]. The following indicators were used: aminoazobenzene; benzeneazodiphenylamine, *p*-nitroaniline, *o*-nitroaniline, 4-chloro-2--nitroaniline, 5-chloro-2-nitroaniline, *p*-nitrodiphenylamine, 2,4-dichloro-6-nitroaniline, and 2,4-dinitroaniline. In solutions of acid where indicators with similar values of pK_{BH^+} overlap, a constant difference in $\log(C_B/C_{BH^+})$ for these indicators is observed satisfactorily.

Table 6 shows values of H_0 for aqueous solutions of HCl at 22–26°. Table 7 gives values of the acidity function for hydrochloric acid at 40°, 60°, and 80°, from Gel'bshtein and coworkers[28].

The acidity function of solutions of hydrobromic acid[30] at 25° was measured with the indicators: *p*-nitroaniline, *o*-nitroaniline, 5-chloro-2-nitroaniline, 2,4-dichloro-6--nitroaniline, and 2,4-dinitroaniline (Table 8).

d. Perchloric Acid

The acidity function of aqueous solutions of perchloric acid from 6% $HClO_4$ to 63.9% $HClO_4$ was measured by Hammett and Deyrup[1], using *p*-nitroaniline, *o*-nitroaniline, 4-chloro-2-nitroaniline, 2,4-dichloro-6-nitroaniline, 2,4-dinitroaniline, and *p*-nitroazobenzene. The last indicator overlaps with 4-chloro-2-nitroaniline and 2,4-dichloro-6-nitroaniline. However, it is impossible to calculate its pK_{BH^+} since the difference in $\log(C_B/C_{BH^+})$ for *p*-nitroazobenzene and other indicators changes with the concentration of the acid. Bonner and Lockhart[31] measured the acidity function of concentrated solutions (from 49.6 to 71.3% $HClO_4$) with 2,4-dinitroaniline and 2,4-dinitro-1-naphthylamine. For the same solutions of the acid the values of $\log(C_B/C_{BH^+})$ in these works differ by 0.25–0.28 units. The reason for this difference is still difficult to explain. In recent work by Yates and Wai[32] the acidity of aqueous solutions of perchloric acid at 25° was measured again over the range 4.9 to 78.6% $HClO_4$ using the indicators: *o*-nitroaniline, 4-chloro-2-nitroaniline, 2,5-dichloro-4-nitroaniline, 2-chloro-6-nitroaniline, 2,6-dichloro-4-nitroaniline, 2,4-dinitroaniline, 2,6-dinitroaniline, 4-chloro-2,6-dinitroaniline, 2-bromo-4,6-dinitroaniline, 3-methyl-2,4,6-trinitroaniline, and 3-bromo-2,4,6-trinitroaniline. The Hammett relation is observed by all the indicators mentioned. The results[32] for dilute solutions differ from the earlier data[1]. For example, the values of $\log(C_B/C_{BH^+})$

TABLE 6. Acidity function of aqueous solutions of HCl at 22–26°.

HCl, %	H_0	HCl, %	H_0
0.1	+1.56	16	−1.68
0.2	+1.36	18	−1.93
0.5	+0.81	20	−2.17
0.7	+0.62	22	−2.43
1.0	+0.4	24	−2.72
2.0	+0.17	26	−3.0
3.0	+0.03	28	−3.28
4.0	−0.17	30	−3.52
5.0	−0.33	32	−3.78
7.0	−0.61	34	−4.05
10	−0.95	36	−4.35
12	−1.17	38	−4.6
14	−1.40	−4,6	−4.99

TABLE 7. Acidity function of aqueous solutions of HCl at 40°, 60°, and 80°*.

HCl, wt. %	H_0		
	40°	60°	80°
0.5	+0.79	+0.80	—
1.0	+0.43	+0.38	—
1.5	+0.23	+0.18	—
2.0	+0.08	+0.02	—
3.0	−0.13	−0.21	−0.28
4.0	−0.3	−0.38	−0.34
5.0	−0.46	−0.54	−0.59
6.0	−0.62	−0.68	−0.73
8.0	−0.92	−0.89	−0.96
10	−1.05	−1.10	−1.16
12	−1.27	−1.33	−1.39
14	−1.50	−1.55	−1.61
16	−1.73	−1.77	−1.84
18	−1.95	−2.01	−2.05
19	−2.06	−2.12	−2.16

* Gel'bshtein and coworkers[28] determined the pK_{BH^+} of *p*-nitroaniline by a comparison of $\log(C_B/C_{BH^+})$ with the logarithm of the mean ionic activity $\log a_\pm$. In compiling this table, pK_{BH^+} for *p*-nitroaniline was calculated by comparison of $\log(C_B/C_{BH^+})$ with C_{HCl} in the interval 0.04–0.099 m. The pK_{BH^+} of *o*-nitroaniline and of 4-chloro-2-nitroaniline were determined in the usual way.

TABLE 8. Acidity function of aqueous solutions* of HBr at 22–26°.

HBr, %	H_0	HBr, %	H_0	HBr, %	H_0
0.1	+1.9	10	−0.35	37	−2.28
0.2	+1.6	12	−0.49	40	−2.26
0.3	+1.39	14	−0.64	42	−2.86
0.5	+1.22	16	−0.86	45	−3.24
0.8	+1.0	18	−0.89	47	−3.50
1.0	+0.90	20	−1.0	50	−3.95
1.5	+0.72	22	−1.13	52	−4.25
2.0	+0.56	25	−1.33	55	−4.76
3.0	+0.38	27	−1.47	56	−4.85
4.0	+0.23	30	−1.71	56.52	−4.90
6.0	−0.02	32	−1.83		
8.0	−0.20	35	−2.09		

* In calculating H_0, Vinnik and coworkers[30] used the values of the pK_{BH^+} for indicators given by Hammett and Paul[27]. In compiling this table, the pK_{BH^+} were calculated by comparing the values of $\log(C_B/C_{BH^+})$ for two indicators in the same solution. The pK_{BH^+} of *p*-nitroaniline were calculated by the formula:

$$pK_{BH^+} = -\log(C_B/C_{BH^+}) - \log m_{H_3O^+}$$

for the range of HBr concentrations 3.34×10^{-2}–0.158 m.

for *o*-nitroaniline for the same acid concentrations do not agree. According to Hammett and Paul the pK_{BH^+} of *o*-nitroaniline is more negative by 0.1 unit and the pK_{BH^+} of *p*-chloronitroaniline by 0.05 unit. Possibly this disagreement is connected with measurement errors. The results of Bonner and Lockhart and of Yates and Wai on the ionisation of these indicators agree satisfactorily. To obtain reliable values of pK_{BH^+} for the indicators it is necessary to assume information about the ionisation of strong bases which ionise in solutions where $H_0 = \log m_{H_3O^+}$. For this purpose *p*-nitroaniline can be used. The ionisation of this indicator has been measured[1] in rather concentrated solutions of perchloric acid ($C_{BH^+}/C_B > 10$). Unfortunately this indicator was not employed in the last investigations. Hammett and Deyrup[1] used a colorimeter and the other investigators[31,32] spectrophotometers, so that the results of the later works should be preferred. Table 9 gives the values of the acidity functions of aqueous solutions of perchloric acid.

e. Nitric Acid

In dilute aqueous solutions, nitric, phosphoric, methanesulphonic, and hydrofluoric acids are weak acids. However, concentrated solutions of these acids exhibit considerable catalytic activity in acid–base processes. An appreciable rise in the acidity of the medium is also observed in such solutions.

The acidity function for dilute and moderately concentrated solutions of nitric acid (up to 37.5% HNO_3) was measured by Hammett and Paul[27], using *p*-nitroaniline, *o*-nitroaniline, and 4-chloro-2-nitroaniline. Dawber and Wyatt[17] measured the acidity over a wide range of concentrations from 0.12 to 99.4% HNO_3. In measuring the acidity of concentrated aqueous solutions of nitric acid, difficulties arose over the choice of indicators, owing to their instability in such media. For example, in acid solutions with >65% HNO_3, 2,4-dinitroaniline, *N*-methyl-2,4-dinitroaniline, 4-methyl-2,6-dinitroaniline, 4-chloro-2,6-dinitroaniline, 4-dinitrodiphenylamine, and 2,4-dinitrodiphenylamine react with the acid. In solutions with >37% HNO_3, they used 2,6-dichloro-4-nitroaniline, 2,4-dichloro-6-nitroaniline, *NN*-dimethyl-2,4,6-trinitroaniline, and 4,4′-dinitrodiphenylamine. The value of pK_{BH^+} of *p*-nitroaniline was determined by the equation

$$pK_{BH^+} = \log \frac{C_{BH^+}}{C_B} - \log m_{H_3^+O},$$

pK_{BH^+} for the other indicators, except *NN*-dimethyl-2,4,6-trinitroaniline, being determined as usual. The difference in $\log (C_B/C_{BH^+})$ for two indicators in the interval of their overlap agrees with a satisfactory constancy. *NN*-Dimethyl-2,4,6-trinitroaniline ionises to an appreciable extent, starting from 71.2% HNO_3. In more dilute solutions 2,4-dichloro-6-nitroaniline was used for the measurements. However, it was used for acidity measurements only up to 64.5% HNO_3 and therefore it is impossible to determine the pK_{BH^+} of *NN*-dimethyl-2,4,6-trinitroaniline in the usual way. The authors[17] assumed that at the same value of $\log (C_B/C_{BH^+})$ there should be the same value of H_0 in aqueous solutions of sulphuric and nitric acids. The acidity for the range 64.5–83.7% HNO_3 was examined for comparison of C_B/C_{BH^+} for *NN*-dimethyl-2,4,6-trinitroaniline in solutions of nitric and sulphuric acids. As already mentioned the indicator ratio for this substance changes anomalously in sulphuric acid. When allowance is made for this, there are grounds for assuming, as the authors themselves did[17], that for solutions with >64.5% HNO_3 there are still no reliable values for H_0. In the range 83.7–99.4% HNO_3 4,4′-dinitrodiphenylamine was used. The change in H_0 can be calculated from the change in its $\log (C_B/C_{BH^+})$ (see Table 10). To determine its pK_{BH^+} it is necessary to find indicators with the aid of which H_0 can be determined in the range 60–90% HNO_3.

Table 11 gives the values of H_0 for the HNO_3–H_2O system.

f. Phosphoric Acid and Polyphosphoric Acids

Heilbronner and Weber[33] measured the acidity function at 20° of aqueous solutions of phosphoric acid containing 0.6–85.5% H_3PO_4. The acidity function of such solutions and of more concentrated solutions at 20° and higher temperatures have been measured[28,34]. Downing and Pearson[15] measured the acidity function of solutions of polyphosphoric acids. There were no experimental difficulties

TABLE 9*. Acidity function of aqueous solutions of $HClO_4$ at 25° from published data[31,32].

$HClO_4$, %	H_0	$HClO_4$, %	H_0	$HClO_4$, %	H_0
5	+0.02	27	−1.40	52	− 3.81
8	−0.21	30	−1.59	55	− 4.30
10	−0.34	32	−1.73	57	− 4.64
12	−0.47	35	−1.95	60	− 5.23
14	−0.60	37	−2.10	62	− 5.68
16	−0.72	40	−2.37	65	− 6.46
18	−0.85	42	−2.57	68	− 7.19
20	−0.97	45	−2.89	70	− 7.75
22	−1.09	47	−3.12	75	− 9.23
25	−1.27	50	−3.51	78	−10.13

* In compiling the table it was assumed that pK_{BH^+} for *o*-nitroaniline is −0.29.

TABLE 10. Ionisation of 4,4′-dinitrodiphenylamine in nitric acid[17] at 20°.

HNO_3, %	$\log \frac{C_{BH^+}}{C_B}$	HNO_3, %	$\log \frac{C_{BH^+}}{C_B}$
83.7	−1.29	94.1	−0.62
85.6	−1.72	95.4	−0.43
87.7	−0.84	97.5	−0.24
90.5	−0.72	98.9	−0.07
93.0	−0.66	99.4	−0.02

TABLE 11. Acidity function of solutions of nitric acid in water at 20°.

HNO_3, %	H_0	HNO_3, %	H_0	HNO_3, %	H_0
0.2	+1.50	8.0	−0.49	35	−2.09
0.4	+1.17	10	−0.65	37	−2.22
0.5	+0.99	12	−0.80	40	−2.36
0.7	+0.89	14	−0.92	42	−2.47
1.0	+0.71	16	−1.05	45	−2.63
1.5	+0.49	18	−1.18	47	−2.73
2.0	+0.33	20	−1.31	50	−2.90
2.5	+0.2	22	−1.43	52	−3.0
3.0	+0.05	25	−1.59	55	−3.16
4.0	−0.1	27	−1.69	57	−3.28
5.0	−0.22	30	−1.85	60	−3.45
6.0	−0.31	32	−1.94	62	−3.59
				65	−3.78

in using the indicator method for work with dilute solutions of phosphoric acid but they did arise in measuring the acidity of concentrated solutions of P_2O_5 in water and especially in polyphosphoric acids. As is known, solutions of P_2O_5 in orthophosphoric acid, and also aqueous solutions of phosphorus pentoxide in water, close in composition to H_3PO_4, consist of mixtures of orthophosphoric, pyrophosphoric, and polyphosphoric acids [35]. Possibly, owing to the slow establishment of equilibrium different investigators worked with the same specified content of P_2O_5 in water but differing in the composition of the individual components. This can explain much of the disagreement in the values of H_0. To measure the acidity function of the P_2O_5–H_2O system, *p*-nitroaniline, *o*-nitroaniline, 4-chloro-2-nitroaniline, 5-chloro-2-nitroaniline, *p*-nitrophenylamine, 2,4-dichloro-6-nitroaniline, 2,4-dinitroaniline, and 6-bromo-2,4-dinitroaniline were used. With 2,4-dinitroaniline there is a weak displacement of the absorption maximum [15], a shift which depends on the P_2O_5 concentration. While there is still no appreciable degree of ionisation in the solutions there is a significant change in the absorptivity of 2,4-dinitroaniline and because of this it is difficult to determine accurately the absorptivity of its un-ionised form. Table 12 gives the values of H_0 at 20° for solutions of P_2O_5 in water from published data [15,28,34]. The acidity function of solutions with from 43.45 to 72.85% P_2O_5 has been measured with 2,4-dichloro-6-nitroaniline colorimetrically [34] and with 2,4-dinitroaniline spectrophotometrically [15]. The results practically agree. The value of pK_{BH^+} for 2,4-dichloro-6-nitroaniline in phosphoric acid is -3.02 (in sulphuric acid pK_{BH^+} = -3.28; in hydrochloric acid, pK_{BH^+} = -3.33), and pK_{BH^+} of 2,4-dinitroaniline is -4.96 (in sulphuric acid pK_{BH^+} = -4.45; in hydrochloric acid pK_{BH^+} = -4.58). The reason for such a great difference in pK_{BH^+} is still difficult to explain.

g. Hydrofluoric Acid

The acidity function of solutions of hydrofluoric acid was measured by Bell and coworkers [36] from dilute solutions to 43% HF. The indicators used were: *p*-nitroaniline, *o*-nitroaniline, and 4-chloro-2-nitroaniline. The acidity function for more concentrated solutions (right up to 100% HF) was measured by Kilpatrick and coworkers [37], who worked with optical cells made from polyfluorochloroethylene with sapphire windows. The measurements were made with *p*-nitrodiphenylamine (39.6–48.7% HF), 4-methyl-2,6-dinitroaniline (55.3% HF), 6-bromo-2,4-dinitroaniline (61.4–71% HF), anthraquinone (80.9–100% HF), and 2,4,6-trinitroaniline (98.13–100% HF). Unfortunately in this work solutions were chosen which do not ensure an overlap of indicators with similar pK_{BH^+}. Therefore it is impossible to determine the pK_{BH^+} of the indicators in this particular medium. The authors of this work [37] used values of pK_{BH^+} for aqueous solutions of sulphuric acid and because of this the values they give are approximate. Judging from their results dilute solutions of water in liquid hydrogen fluoride have an acidity close to that of dilute solutions of water in sulphuric acid. This is evident from the values of C_B/C_{BH^+} for 2,4,6-trinitroaniline (see Table 13).

Table 14 gives values of H_0 for solutions of hydrogen fluoride in water over the range 2–42.7% HF, after Bell and coworkers [36].

h. Methanesulphonic Acid CH_3SO_3H

The acidity of aqueous solutions of methanesulphonic acid at 25° in the range 0–100% was measured by Bascombe and Bell [20]. No appreciable change in the ratio C_B/C_{BH^+} with wavelength is observed for the indicators listed below. The acidity was measured: from 3 to 13.9% acid with *p*-nitroaniline; from 17 to 21.9% with *o*-nitroaniline, from 25.5 to 54.5% acid with 4-chloro-2-nitroaniline, and from 61.5 to 80.6% acid with 2,4-dichloro-6-nitroaniline. The last range of acid concentrations partly overlaps with 4-methyl-2,6-dinitroaniline, the ionisation of which was measured in 74.9–85.2% acid. In 88.9–100% acid the C_B/C_{BH^+} ratio was measured for 6-bromo-2,4-dinitroaniline. To calculate H_0 the authors assumed that for *p*-nitroaniline, *o*-nitroaniline, and 4-chloro-2-nitroaniline, pK_{BH^+} in methanesulphonic acid is the same as in hydrochloric and sulphuric acids.

TABLE 12*. Values of H_0 for the P_2O_5–H_2O system at 22–26°.

H_3PO_4, %	P_2O_5, %	H_0	H_3PO_4, %	P_2O_5, %	H_0	P_2O_5, %	H_0
10	7.24	+0.65	57	41.3	−1.63	76	−5.12
12	8.7	+0.53	60	43.5	−1.83	77	−5.26
14	10.1	+0.44	62	44.9	−1.97	78	−5.42
16	11.6	+0.34	65	57.1	−2.19	79	−5.58
18	13.0	+0.25	70	50 7	−2.53	80	−5.72
20	14.5	+0.17	72	52.2	−2.69		
22	15.9	+0.09	75	54.3	−2.90		
24	17.4	0	78	55.5	−3.14		
26	18.8	−0.07	80	58	−3.30		
28	20.3	−0.16	82	59.4	−3.42		
30	21.7	−0.24	85	61.6	−3.62		
32	23.2	−0.33	87	63.1	−3.78		
35	25.4	−0.47	90	65.2	−4.01		
37	26.8	−0.55	92	66.7	−4.15		
40	29.0	−0 69	94	68.2	−4.29		
42	30.4	−0.78	96	69.6	−4.41		
45	32.6	−0.94	98	71.0	−4.52		
47	34.1	−1.05	99	71.7	−4.59		
50	36.2	−1.20	100	72.4	−4.66		
52	37.7	−1.32		73	−4.71		
55	39.9	−1.51		74	−4.85		
				75	−4.98		

* In compiling the table, pK_{BH^+} for *p*-nitroaniline was taken as +1.0; pK_{BH^+} for the other indicators were determined in the usual way.

TABLE 13. Ionisation of 2,4,6-trinitroaniline in hydrofluoric acid.

Concentration of H_2O in HF, M	$\log \frac{C_B}{C_{BH^+}}$	Concentration of H_2O in HF, M	$\log \frac{C_B}{C_{BH^+}}$
<0.001	−0.79	0.63	+0.07
<0.01	−0.55	0.83	+0.29
0.12	−0.18	0.87	+0.32
0.38	−0.06	0.89	+0.3
0.50	+0.1	1.03	+0.55

TABLE 14. Acidity function of aqueous solutions of hydrofluoric acid at 25°.

HF, %	H_0	HF, %	H_0
2	+1.33	20	−0.37
3	+1.09	22	−0.52
4	+0.98	25	−0.76
5	+0.87	30	−1.11
8	+0.57	32	−1.25
10	+0.37	35	−1.47
12	+0.21	37	−1.62
15	−0.01	40	−1.88
17	−0.15	42,7	−2.10

TABLE 15. Acidity function of aqueous solutions of methanesulphonic acid at 25°, after Bascombe and Bell[20].

CH_3SO_3H, %	H_0	CH_3SO_3H, %	H_0	CH_3SO_3H, %	H_0
3	+0.43	35	−1.19	70	−3.57
5	+0.17	40	−1.41	75	−4.04
10	−0.20	45	−1.67	80	−4.56
15	−0.43	50	−2.0	85	−5.37
20	−0.60	55	−2.34	90	−6.31
25	−0.76	60	−2.71	95	−7.11
30	−0.97	65	−3.11	100	−7.86

The values of pK_{BH^+} of 2,4-dichloro-6-nitroaniline and 6-bromo-2,4-dinitroaniline were calculated by extrapolation. It appeared that here pK_{BH^+} for these substances greatly differs from the values for sulphuric acid obtained by direct measurements. As pK_{BH^+} were not determined by overlap of the same ranges of acid concentrations for different indicators the values of H_0 for the methanesulphonic acid–water system (Table 15) must be considered only approximate. These results show that concentrated aqueous solutions of methanesulphonic acid exhibit strongly acid properties.

i. Solutions of DCl and D_2SO_4 in D_2O

In some kinetic investigations solutions of acids in deuterium oxide D_2O are used. It is therefore necessary to have information about the values of H_0 for such systems. Högfeldt and Bigeleisen[38] measured the acidity function for solutions of DCl in D_2O for the range 10^{-4}–1 M DCl and of D_2SO_4 in D_2O for the range 10^{-4}–12 M D_2SO_4 at 22° ± 2°. Fourteen indicators were used for the measurements. It appeared that at the same molarity of the acid the acidity function was the same (within the limits of error of the measurements) for solutions of HCl in H_2O and DCl in D_2O (from 10^{-4} to 1 M) and for solutions of H_2SO_4 in H_2O and of D_2SO_4 in D_2O (from 10^{-1} to 12 M). The acidity was not measured for more concentrated solutions of the acids in D_2O.

pK_{BH^+} for solutions in D_2O is greater than for solutions in H_2O. pK_{BH^+} in D_2O is greater than in water for aminoazobenzene, *m*-nitroaniline, 2,4-dichloroaniline, benzeneazodiphenylamine, *p*-nitroaniline, diphenylamine, *o*-nitroaniline, and 4-chloro-2-nitroaniline by 0.5–0.6 unit; for *p*-nitrodiphenylamine, by 0.27 unit; and for 2,4-dichloro-6-nitroaniline, 2,4-dinitroaniline, and 4-methyl-2,6-dinitroaniline by almost 0.4 unit.

4. ACCURACY OF MEASUREMENTS OF H_0

In the measurements of acidity function there are the following sources of error: (a) the determination of the concentration of the acid; (b) the determination of the indicator ratio C_B/C_{BH^+}; (c) the determination of the value of pK_{BH^+} for the indicator.

Usually, the concentration of aqueous solutions of strong acids is determined either by alkalimetric titration or by electrical conductivity. The electrical conductivity method[39] is used mainly for determining the concentration of sulphuric acid in solutions with >99% H_2SO_4. In alkalimetric titration the error does not exceed 0.1–0.05%. On altering the concentration of strong acids by 1% the acidity function changes by 0.1–0.15 unit in moderately concentrated and by 0.3 unit in extremely dilute solutions. Hence the error in measuring the acid concentration introduces 0.02–0.03 unit into the error in H_0. In measuring H_0 for sulphuric acid in the range 99.5–100% where H_0 changes by 0.3–0.5 unit per 0.1% acid, the error due to the inaccuracy in determining the H_2SO_4 concentration does not exceed 5×10^{-3}–0.01 unit. In this region the accuracy of determining the concentration by electrical conductivity is ±0.001%. In using spectrophotometry H_0 is frequently determined with an accuracy of ±0.01–0.02 unit[29]. However, in some instances an accuracy of ±0.003 is attained, when C_B/C_{BH^+} is determined at several wavelengths[9].

A more significant error is the measurement of the pK_{BH^+} of indicators. This quantity depends on the quantity of indicator used to measure H_0 of the solutions in which the indicator concerned ionises. The error in determining pK_{BH^+} of the first indicator (the strongest base) is made up of the errors in determining the concentration of the acid and $\log(C_B/C_{BH^+})$, since pK_{BH^+} is calculated by the equation:

$$(pK_{BH^+})_1 = -\log C_{H_3O^+} + \log \frac{C_B}{C_{BH^+}} .$$

The error $\Delta(pK_{BH^+})_1 = \pm(0.03-0.04)$ unit.

The quantity pK_{BH^+} of the second indicator, which is a rather weak base, is determined by the equation:

$$(pK_{BH^+})_2 = (pK_{BH^+})_1 + \log\left(\frac{C_B}{C_{BH^+}}\right)_2 - \log \frac{C_B}{(C_{BH^+})_1},$$

$$\Delta(pK_{BH^+})_2 = \Delta(pK_{BH^+})_1 + 2\Delta\log \frac{C_B}{C_{BH^+}} \simeq \pm(0.05-0.08) \text{ unit.}$$

For the third indicator:

$$\Delta(pK_{BH^+})_3 = \Delta(pK_{BH^+})_2 + 2\Delta\log\left(\frac{C_B}{C_{BH^+}}\right).$$

The error $(pK_{BH^+})_3$ amounts to ±(0.07–0.12) unit. The error in determining the pK_{BH^+} of subsequent indicators will be increased by ±(0.02–0.04) unit. The error in H_0 is the sum of the errors in pK_{BH^+}, $\log(C_B/C_{BH^+})$, and the acid concentration. When, for example, three indicators are needed to measure H_0 in a particular solution, then $\Delta H_0 = \pm(0.08-0.13)$ unit. When there are nine indicators, $\Delta H_0 = \pm(0.17-0.34)$ unit. This number of indicators is required in measuring the acidity of sulphuric acid from extremely dilute solutions to 100% H_2SO_4, where H_0 changes by 12–13 units. In practice in kinetic investigations narrower intervals are used, amounting to 3–5 units of the H_0 scale. In such an instance there is essentially no absolute error in the value of H_0 and the difference in the errors in measuring H_0 for the start and end of the interval. For the mentioned interval of 3–5 units, the error amounts to ±(0.08–0.13) unit), which is fully acceptable for kinetic investigations§. Table 1 does not give the errors in measurements for each indicator separately. The errors can be evaluated from what has been stated above. The stated experimental errors are also not given in the tables listing H_0 for acids. In dilute solutions the accuracy of these quantities is greater in dilute solutions than in concentrated. In each specific instance the error in H_0 is readily evaluated.

§ The errors in determining H_0 were calculated for instances when Hammett's hypothesis of an equality in the ratio of the coefficients for un-ionised and ionised forms of the substance is strictly obeyed.

5. PHYSICAL SIGNIFICANCE OF THE CONCEPT OF "ACIDITY OF THE MEDIUM"

The increase in the acidity of the medium $a_{H^+}(f_B/f_{BH^+})$ as the concentration of the acid in the solution is raised can be related to the change in the concentration of protons C_{H^+}, the activity coefficient of the protons f_{H^+}, and the ratio of the activity coefficients f_B/f_{BH^+} of the indicator. Since the energy of interaction of a proton with water is ~ 200 kcal $\times$ $\times$ mole^{-1}, the concentration of free protons in aqueous solutions of acids is vanishingly small; the protons are present as hydroxonium ions H_3O^+. It is therefore necessary to relate the acidity of aqueous solutions with the properties of H_3O^+ ions and with the f_B/f_{BH^+} ratio.

In aqueous solutions of acids, hydroxonium ions and molecules of the undissociated acids HA, which are in equilibrium with one another, can donate protons:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-. \qquad (8)$$

The ionisation of substance B can be expressed by the equations:

$$B + H_3O^+ \rightleftharpoons BH^+ + H_2O, \qquad (9)$$

$$B + HA \rightleftharpoons BH^+ + A^-. \qquad (10)$$

When the ionisation of B is represented by Eqns. (9) or (10) then the acidity is expressed thus:

$$h_0 = a_{H^+}\frac{f_B}{f_{BH^+}} = \frac{a_{H_3O^+}}{a_{H_2O}}\frac{f_B}{f_{BH^+}}; \qquad h_0 = \frac{1}{K_4}\frac{a_{HA}}{a_{A^-}}\frac{f_B}{f_{BH^+}},$$

where K_4 is the equilibrium constant for the ionisation of the acid by Eqn. (8):

$$K_4 = \frac{a_{HA}\,a_{H_2O}}{a_{A^-}\,a_{H_3O^+}}.$$

In non-aqueous solutions the ionisation of acids involves the transfer of a proton from the acid HA to the solvent molecule. In alcoholic solutions, alkoxonium ions ROH_2^+ are formed; in ethereal solutions, the ions $RR'O^+H$. In pure acids the ions are formed during autoprotolysis:

$$2HA \rightleftharpoons A^- + H_2A^+.$$

The acidity of the non-aqueous solutions should be related to the properties of the ions of type ROH_2^+, $RR'O^+H$, and H_2A^+ and to the ratio f_B/f_{BH^+} of the indicators used to measure H_0. It is well known that even highly concentrated aqueous solutions of hydrochloric acid [40,41] are completely dissociated. Perchloric acid [42,43] is also completely dissociated in aqueous solutions of moderate concentration (up to 6 M). The concentration of hydroxonium ions in such solutions equals the total concentration of the acid. In concentrated aqueous solutions of sulphuric [10,11] and nitric [44] acids there is incomplete dissociation. The concentration of H_3O^+ ions, anions, and undissociated HA molecules in such solutions can be determined from the Raman spectra, by infrared spectra, and by the NMR method. Acids such as phopshoric and hydrofluoric are weakly dissociated even in dilute aqueous solutions.

It is easy to conclude that the acidity of concentrated solutions increases much more strongly than the concentration of H_3O^+ ions. For solutions with completely dissociated acids with a range of concentrations of 1–10 M, $C_{H_3O^+}$ increases tenfold, and the acidity of the medium by a few orders of magnitude. Evidently the chief reason for the change in H_0 is not the change in $C_{H_3O^+}$, but the change in activity coefficients. The activity coefficients of individual ions, in principle, cannot be measured by thermodynamic methods. The acidity h_0 includes the activity coefficient of the un-ionised form of the indicator f_B, which can be measured indirectly.

The demonstration of the dependence of f_B for indicators on the acid concentration allows us to understand the physical significance of acidity h_0.

Until recently information about the dependence of f_B for indicators on the concentration of strong acids was limited solely to aqueous solutions of sulphuric acid. Figs. 2 and 3 show the dependence of f_B for certain indicators on sulphuric acid concentration from published data [45–47]. In dilute solutions the activity coefficients of the un-ionised form f_B are almost constant. On increasing the acid concentration the quantities f_B for various indicators change differently for different indicators. For *o*-nitroaniline, f_B remains constant almost up to 25% H_2SO_4, and then falls.

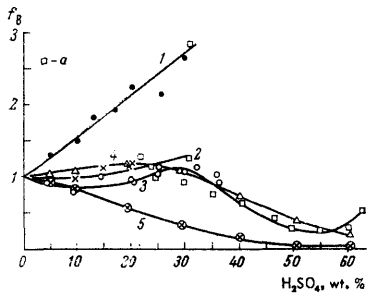


Fig. 2. Dependence of the activity coefficients f_B of the un-ionised form of the indicators on sulphuric acid concentration:
1) diphenylamine; 2) *p*-nitroaniline; 3) *o*-nitroaniline; 4) 2,6-dichloro-4-nitroaniline;
5) 2,4,6-trinitroaniline; □ experiments on the distribution of the substance between two phases; other experiments, by solubility.

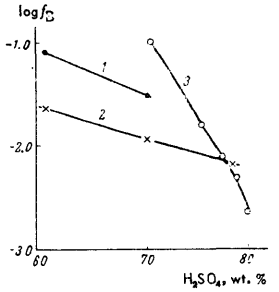


Fig. 3. Dependence of the activity coefficients f_B of the un-ionised form of the indicators on the sulphuric acid concentration:
1) 2,4-dinitroaniline; 2) 2,4,6-trinitroaniline; 3) *p*-benzoylbiphenyl. For *p*-benzoylbiphenyl instead of f_B we give the quantity $(1 + h_0/k_{BH^+})/S$ which is proportional to f_B. In this, S is the solubility of the substance in acid of the specified concentration.

For 2,4-dinitroaniline and 2,4,6-trinitroaniline there is only a decrease in f_B with increasing acid concentration, and the degrees of change of f_B are different. With *p*-nitroaniline, f_B remains constant at first and then rises slowly. With diphenylamine there is a rise in f_B, starting from dilute acid solutions. For these indicators Hammett's hypothesis of the equality of the ratios of activity coefficients of the ionised and un-ionised forms of the indicator is satisfied:

$$\frac{f_B}{f_{BH^+}} = \frac{f_C}{f_{CH^+}} = \frac{f_D}{f_{DH^+}}. \qquad (11)$$

In the general example this ratio should depend on the composition of the solution. Assume that on going from a dilute solution of sulphuric acid to solution N this ratio changes m times, and the coefficients f_B, f_C, and f_D change b, c, and d times respectively. Then:

$$f_{BH^+} = \frac{b}{m}; \quad f_{CH^+} = \frac{c}{m}; \quad f_{DH^+} = \frac{d}{m}.$$

Hammett's relationship is also observed during the ionisation of an already protonated base [48] and during the protonisation of anions, for example, of picric acid [50,51]:

$$\frac{f_B}{f_{BH^+}} = \frac{f_{BH^+}}{f_{BH_2^{2+}}} = \frac{f_{A^-}}{f_{AH}},$$

where f_{AH} and f_{A^-} are the activity coefficients of the acid and its anion. When in solution N we have $f_B = b$ and $f_{AH} = a$, then:

$$f_{BH_2^{2+}} = \frac{b}{m^2} \text{ and } f_{A^-} = ma.$$

Consequently, when the value of relationship (11) depends on the solution composition, then in comparison with the activity coefficient of the un-ionised form, the activity coefficient of the singly-charged positive ion changes $1/m$ times; that of a doubly-charged positive ion $1/m^2$ times, and that of a singly-charged negative ion, m times.

An activity coefficient characterises the change in free energy of the substance. When relationship (11) depends on the composition of the solvent, then it can be taken that the change in free energy of the ion is the sum of two parts. One part (ΔF_1) equals the change in free energy of the un-ionised species; the other part (ΔF_2) is determined solely by the charge of the ion and does not depend on its structure and chemical composition. The substances for which relationship (11) is observed are usually large polyatomic molecules. In solutions with a high concentration of ions they are polarised. The substances investigated for which Hammett's hypothesis is obeyed contain such functional groups as amino, nitro, carbonyl, etc. On the basis of what has been said above, it is to be expected that the addition of a proton to various functional groups has the same effect on the activity coefficient of the ionised molecule. Moreover, in substances with such functional groups there is a marked change in the activity coefficient f_B with change in the acid concentration. In this connection it can be assumed that these particular groups are mainly responsible for the change in the activity coefficient of the un-ionised molecules. Undoubtedly, the acquisition of a charge is reflected in the properties of all the molecules as a whole, and in particular of the atoms of the functional group bearing the charge. When the contribution of the charge to the free energy of the ionised molecule is large then it significantly changes the properties of all the atoms of the molecule and in particular the atoms of the charged functional group. Here it is difficult to suggest that the change in free energy represents the sum of two independent terms, as it should be were f_B/f_{BH^+} dependent on the solution composition. When the effect of the charge is small, then the change in free energy of the ion can be expressed as the sum ($\Delta F_1 + \Delta F_2$) and the contribution of the charge ΔF_2 to this sum can be neglected.

Hence we come to the conclusion [46] that the ratio f_B/f_{BH^+} is independent of the solvent composition and equals unity, as is assumed for dilute aqueous solutions.

The acidity of the medium equals the activity of the protons $h_0 = a_{H^+}$.

Rybkin and Shevchenko [52] measured the compensating effect of the cell for aqueous solutions of hydrogen chloride and of solutions of HCl in water saturated with surface-active acids (hexanoic and enanthic) and alcohols (heptyl and nonyl). The compensating effects of the cell of type:

$$H_2 \mid \underset{(I)}{\text{acid}} \mid \text{air} \mid \underset{(II)}{\text{acid}} \mid H_2,$$

depend considerably on the state of the surface of the investigated (I) and standard (II) solutions. The surface adsorption potential of hydrogen chloride in aqueous solutions is suppressed by additions of pentanol [49]. Surface-active substances are added to balance the surface properties of the solutions. Since their solubility is not high it can be considered that they do not change the acidity of the test solutions. In solutions saturated with surface-active alcohols there is satisfactory agreement of the measured values of $\log a_{H^+}$ with the acidity function H_0. These experiments also show the independence of f_B/f_{BH^+} on the concentration of a strong acid in aqueous solution. The view that the ratio f_B/f_{BH^+} is constant in aqueous solutions of strong acids was expressed by Gutbezahl and Grunwald [53] in 1953. It is evident that the equality of the acidity of the medium and the activity of the protons does not mean in the least that in all instances Hammett's relationship should be observed. An example of the non-observance of this relation was given on p. 806. Hammett's relation is also not observed in instances when the ionic and un-ionised forms differ significantly in their structure, as happens in the ionisation of cyanocarboxylic acids [50].

6. RELATION BETWEEN THE ACIDITY OF THE MEDIUM AND THE THERMODYNAMIC ACTIVITY OF WATER

In aqueous solutions in which strong acids are completely ionised, there are anions and water molecules in addition to the hydroxonium ions. In such systems the properties of the H_3O^+ ions are determined by the properties of water and the anions A^-. If the conclusion about the independence of the ratio f_B/f_{BH^+} and the acid concentration is correct, then:

$$h_0 = \frac{1}{K_4}\frac{a_{HA}}{a_{A^-}} = \frac{a_{HA}}{K_4 C_{A^-} f_{A^-}}, \qquad (12)$$

where C_{A^-} is the concentration of the anions and f_{A^-} the activity coefficient of the anions of the acid.

For hydrochloric, hydrobromic, perchloric, and nitric acids the standard state is chosen in such a way that the constant K_4 equals unity. For these acids:

$$h_0 = \frac{a_{HA}}{C_{A^-} f_{A^-}}. \qquad (13)$$

Hydrochloric [40,41] and perchloric [42] acids are completely dissociated even in highly concentrated aqueous solutions

and the concentration of the anions equals the total concentration of the acid. Apparently, hydrobromic acid is also completely dissociated in concentrated solutions. It is well known that a molecule of water combined with a proton is spectroscopically distinct from the remaining molecules of water in aqueous solution[54]. Molecules of water entering into the solvate sheaths of the anions and H_3O^+ ions apparently differ little from the remaining water molecules present in the solution. To the first approximation it can be assumed that the concentration of water molecules in an aqueous solution equals the difference between the stoichiometric concentration of water and the concentration of H_3O^+ ions. Therefore it is sensible to compare the values of f_A- for solutions with the same molality. The activity coefficients of the anions can be calculated by Eqn. (13).

To calculate the activity coefficient f_A- for solutions of nitric acid in water, allowance must be made for the degree of dissociation of the acid. The degree of dissociation of HNO_3 in water is taken from Young and coworkers[44]. In dilute solutions of sulphuric acid there are SO_4^{2-} and HSO_4^- anions. The standard state for solutions of H_2SO_4 in water is chosen in such a way that the activity coefficients of the H_3O^+ ions and SO_4^{2-} anions equal unity in extremely dilute solutions. In concentrated solutions of the acid the SO_4^{2-} concentration is low[10,11] and the ionised acid is present as HSO_4^- anions. Then the equilibrium constant K_4 does not equal unity. For sulphuric acid the product $K_4 f_A$- can be calculated. Table 16 gives the activity of the anions of aqueous solutions: from 0.1 m to 12 m for HCl and HBr, from 0.5 m to 12 m for $HClO_4$, from 0.1 m to 10 m for HNO_3, and the values of $K_4 f_{HSO_4^-}$ for sulphuric acid solutions in the range 0.5–12 m.

As Fig. 4 shows, in the range from 1 m to 9 m the change in the acidity function H_0 is almost the same for aqueous solutions of HCl, HBr, $HClO_4$, and H_2SO_4¶. Since the activities of the anions change differently in this range it can be concluded that the change in $h_0/C_{H_3O^+}$ is connected with a change in the solvation of the hydroxonium ion and not with a change in a_A-.

With a decrease in the number of water molecules adjacent to one hydroxonium ion, the acidity rises. The

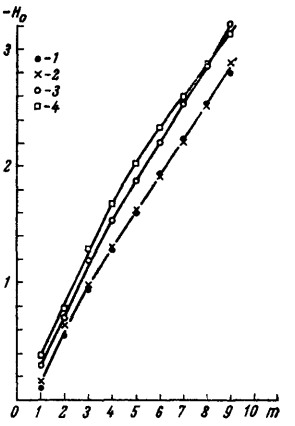


Fig. 4. Dependence of H_0 on the molar [presumably molal [Ed. of Translation)] concentration m of the strong acids: 1) HCl; 2) HBr; 3) $HClO_4$; 4) H_2SO_4.

activity of water in the solution is connected with the properties of the hydroxonium ion and the anion. In those instances where the activity of the anions change similarly for a change in the concentration of the acids it can be expected that at the same values of the activity of water a_{H_2O} the values of the acidity will be almost the same†. Table 17 gives the values of H_0 at the same activities of water. For solutions of sulphuric (from 11 to 57.8% H_2SO_4) and perchloric (from 11.3 to 54.6% $HClO_4$) acids, where the activity of water changes from 0.85 to 0.20, there are almost the same values of H_0 at the same activities of water.

Starting from solutions in which the activity of water < 0.45 the acidity of the medium for HCl, HBr, $HClO_4$, and H_2SO_4 is almost the same for the same values of a_{H_2O}. In such solutions the activities of the anions differ significantly. The activity coefficients of the ClO_4^- and HSO_4^- anions rise considerably and those of Cl^- and Br^- remain

¶ This first received attention from Bascombe and Bell[59].

† Wyatt[60] and Högfeldt[61] have compared values of H_0 and a_{H_2O} for various acids.

TABLE 16. Logarithms of the activity coefficients of the anions of hydrochloric, hydrobromic, perchloric, sulphuric, and nitric acids as a function of the concentration of the acid in aqueous solutions*.

Acid	Function	Molality of the acid												
		0.1	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11	12
HCl	$\log \frac{a_{HCl}}{h_0}$	−1.22	−0.62	−0.28	+0.06	+0.25	+0.40	+0.54	+0.64	+0.74	+0.93	+0.91	+0.97	+1.06	+1.07
	$\log f_{Cl^-}$	−0.22	−0.32	−0.26	−0.24	−0.24	−0.20	−0.16	−0.14	−0.1	−0.03	−0.04	−0.03	+0.02	−0.01
HBr	$\log \frac{a_{HBr}}{h_0}$	−1.19	−0.57	−0.03	+0.11	+0.42	+0.54	+0.66	+0.77	+0.83	+0.90	+0,96	+0.97	+1.06	+1.12
	$\log f_{Br^-}$	−0.19	−0.27	−0.27	−0.19	−0.06	−0.06	−0.04	−0.01	+0.01	0.0	0,0	−0.03	+0.02	+0.04
$HClO_4$	$\log \frac{a_{HClO_4}}{h_0}$	—	−0.8	−0.47	−0.15	+0.01	+0.31	+0.51	+0.71	+0.8	+1.08	+1.26	+1.42	+1.58	+1.75
	$\log f_{ClO_4^-}$	—	−0.5	−0.47	−0.45	−0.47	−0.29	−0.19	−0.07	−0.04	+0.18	+0.31	+0.42	+0.54	+0.67
H_2SO_4	$\log \frac{a_{H_2SO_4}}{h_0}$	—	−2.78	−2.41	−2.07	−1.81	−1.59	−1.39	−1.18	−0.96	−0.78	−0.68	−0.53	−0.43	−0.32
	$\log f_{HSO_4^-} k_4$	—	−2.48	−2.41	−2.37	−2.29	−2.19	−2.09	−1.96	−1.80	−1.68	−1.60	−1.53	−1.47	−1.40
HNO_3	$\log \frac{a_{HNO_3}}{h_0}$	−1.28	−0.84	−0.58	−0.36	−0.29	−0.12	−0.06	−0.03	+0.01	—	—	−0.22	—	—
	$\log f_{NO_3^-}$	−0.28	−0.54	−0.53	−0.66	−0.75	−0.69	−0.71	−0.73	−0.73	—	—	−0.60	—	—

* The activities of the acids were taken from published works: hydrochloric[55], hydrobromic[30], perchloric[56], sulphuric[57], nitric[58]. In calculating $f_{NO_3^-}$ the degree of dissociation of nitric acid[44] was taken into account.

TABLE 17*. Values of H_0 for aqueous solutions of sulphuric, hydrochloric, hydrobromic, nitric, and phosphoric acids having the same activity of water at 25°.

a_{H_2O}	H_0					
	H_2SO_4	HCl	HBr	$HClO_4$	HNO_3	H_3PO_4
0.95	−0.51	−0.35	—	−0.42	−0.51	—
0.9	−0.95	−0.68	—	−0.89	−0.96	—
0.85	−1.30	−1.0	—	−1.23	−1.27	—
0.8	−1.59	−1.30	—	−1.46	−1.52	—
0.75	−1.82	−1.56	—	−1.68	−1.76	—
0.7	−2.04	−1.71	—	−1.91	−1.92	—
0.65	−2.31	−1.97	—	−2.12	−2.08	—
0.60	−2.42	−2.15	—	−2.32	−2.33	—
0.55	−2.59	−2.36	—	−2.52	−2.45	—
0.50	−2.37	−2.58	—	−2.71	−2.58	−1.97
0.45	−2.99	−2.83	—	−2.93	−2.75	−2.17
0.40	−3.21	−3.21	—	−3.15	−2.91	−2.34
0.35	−3.40	−3.35	—	−3.37	−3.11	−2.53
0.3	−3.64	−3.63	−3.74	−3.63	−3.31	−2.71
0.25	−3.90	−3.91	−3.95	−3.89	−3.52	−2.90
0.2	−4.25	−4.27	−4.2	−4.19	−3.78	−3.13
0.15	−4.61	−4.66	−4.5			−2.34
0.1	−5.1	−4.9				−3.60

* The activities of water a_{H_2O} in acids were taken from published data: sulphuric acid[57]; hydrochloric acid[41]; hydrobromic acid[41]; perchloric acid[58]; nitric acid[58]; phosphoric acid[62].

almost constant. This suggests that in solutions with >8–9 m acid the change in the activity of the anion is weakly reflected in the change in the activity of water. On the other hand, even a slight decrease in the activity of water in concentrated solutions of acid is linked with a significant increase in the activity coefficient of the oxygen-containing anions ClO_4^- and HSO_4^-. On comparing solutions of strongly and weakly dissociated acids with the same activities of water, the acidity is much less for weak acids than for strong acids. For example, for solutions with a water activity of 0.2, the acidity function for strong acids is H_0 = -4.25, for nitric acid H_0 = -3.78, and for phosphoric acid H_0 = -3.13. This can be explained by the strong hydration of the undissociated molecules of a weak acid.

It is interesting to note that in the dissolution of anhydrous hydrogen chloride in concentrated phosphoric acid containing 80% H_3PO_4, the acidity of the medium rises as the concentration of water in the solution decreases. At the same time the activity of the Cl^- anion remains almost constant[63]. A slight change in the activity coefficients of Cl^- in aqueous solutions and in solutions in phosphoric acid and also of Br^- in aqueous solutions shows the slight solvating ability of these ions.

In sulphuric acid solutions with >94% H_2SO_4‡, there is a relation found by Brand[25]:

$$-\log\frac{C_{H_2SO_4}}{C_{HSO_4^-}} + \log k = H_0, \qquad (14)$$

where k is a constant.

‡ It has been assumed[25,64] that in sulphuric acid with > 90% H_2SO_4, all the water is present as H_3O^+:

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-.$$

The concentration of the undissociated H_2SO_4 molecules was calculated as the difference between the initial concentrations of acid and water. Then Eqn. (14) is correct in the range 90–99% H_2SO_4. However, from the spectroscopic data[11], it follows that in solutions where the acid concentration is < 94%, the concentration of HSO_4^- anions is less than the concentration of water in the initial acid.

In such solutions the change in activity of the sulphuric acid equals the change in the mole fraction of the undissociated molecules in solution. When the concentration of the anions in Eqn. (14) is expressed by mole fraction, then it is found that $f_{HSO_4^-}$ is constant in the range from 94 to 99% H_2SO_4. In solutions where the H_2SO_4 concentration <94%, considerable numbers of ion pairs are present in equilibrium with the H_2SO_4 molecules[11].

The chemical shifts of the NMR protons reflect the change in the acidity of the medium. The chemical shifts of the NMR protons depend on the nature and concentration of the acids[65]. The acidity function and also the value of $\log(h_0 a_{H_2O})$ for hydrochloric, perchloric, sulphuric, and nitric acids are linearly related to the chemical shift σ. However, the slope of the straight line in the coordinates: $[H_0; \sigma]$ or $[\log(h_0 a_{H_2O}); \sigma]$ depends on the nature of the anion. It changes in the following sequence: $HClO_4 > HCl > H_2SO_4 > HNO_3$.

As mentioned above, the change in the activity of the anion has little effect on the acidity h_0. The existence of a relation between proton shift and the nature of the anion at the same values of H_0 is evidence of the considerable effect of the anion on the screening of the proton in aqueous solutions.

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TAUTOMERIC TRANSFORMATIONS OF PHENOLS

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CONTENTS

1. Introduction 817
2. Tautomerism of phenols 818
3. Tautomerism of nitrosophenols 823
4. Tautomerism of azophenols 825
5. Equilibrium phenol–quinonoid transformations of *p*-substituted phenols 827

1. INTRODUCTION

Problems of the tautomerism of organic compounds are at present of interest to many research workers[1]. Even in the most familiar type of tautomerism (keto–enol tautomerism) there are little-studied relationships and phenomena, in particular the tautomerism of phenolic compounds. These transformations aroused the interest of research workers at an early date, but the systematic study of this interesting phenomenon was made possible only by the development of modern physical methods for studying organic compounds.

In keto–enol tautomeric transformations of organic compounds, the tautomerism of hydroxyaromatic compounds occupies a special place, since the phenomenon is accompanied by breakdown of the aromatic bond system. The present paper summarises results concerning the actual phenomenon of tautomerism in the phenol series, and also some reactions of substituted phenols (for example, salt formation), as a result of which equilibrium is established between the aromatic (phenolic) and quinonoid or quinolide†

† We apply the term "quinolide", as distinct from "quinonoid" in the description of bond systems, to cyclohexadienones in which the carbon atom in the *ortho*- or *para*-position relative to the carbonyl group is joined by ordinary (not double) bonds to two substituents.