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Study of the Acid-Base Properties of Heterogeneous Catalysts by Infrared Spectroscopy

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The quantitative assessment of the acid-base properties of the surface of heterogeneous catalysts by i.r. spectral studies of adsorbed molecules is discussed. The quantities through which the protonic (Brønsted), aprotic (Lewis), acidic and basic centres of the surface can be most easily characterised are analysed. Reported methods of determining the number and strength of the surface centres are described. 135 references.

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I. INTRODUCTION

Solid acids and bases are widely used to catalyse various reactions at the solid-gas or solid-liquid interface. In order to understand the mechanism of their catalytic action and to predict their activity and selectivity we need quantitative information on the number and strength of the acid or basic centres on their surface[1-3]. In the 1950's the indicator method of determining the strength of the acid centres[4] and the indicator titration method of determining their number[5] were proposed: both these methods were based on a study of the interaction of indicator molecules (probes) with the surface. More recently similar methods have been used to characterise basic centres[6,7].

The physicochemical foundation of these methods of quantitative assessment was the postulate that the interaction between the acid centres on the surface and bases from the external phase is analogous to acid-base equilibria in solutions. However, some differences in principle between solid acids (or bases) and acids or bases in solution were subsequently discovered. On a surface we find, at the same time, fixed, non-interacting acid centres (aprotic, L, and protonic, OH) and basic centres (B_S), of different strengths. This gives rise to independent, parallel reactions, seldom reaching equilibrium, between the added (probe) molecules and the surface centres. Under these conditions the above methods[4-7] cannot give the true characteristics of the acid–base properties of specified surface centres.

Some attempts[2,8] to develop more realistic methods of studying the acid-base properties of surfaces proved unsuccessful. However, they led to the formulation of the following list of requirements to be met by a successful quantitative method: 1) the interactions between the probe molecules and the protonic, aprotic, and basic centres should be

Table 1. Acidic and basic surface centres, and requirements on the probe molecules used to study them by i.r. spectroscopy.

Type of centre	Lewis (L) centres	Brønsted (OH) centres		Basic (B_S) centres
Type of complex with probe	donor-acceptor complex	H-bond	ion pair	H-bond
Spectral criterion of complex formation	change in frequency of the characteristic vibrations of B molecules ($\Delta\nu_B$)	change in ν_{OH}	disappearance of ν_{OH}, appearance of ν_{BH^+} and $\delta^{as}_{BH^+}$	change in ν_{HX}
Most exact method of determining the strength of the centres	from the change in frequency of the characteristic vibrations ($\Delta\nu_B = \nu_B - \nu_B^{gas}$) expressed in a scale of heat of adsorption; $Q = 10.5 + 0.5\nu_{CO}$ for CO	from ν_{OH}, in a proton affinity scale; $PA^{OH} = 1390 - \frac{\lg(\Delta\nu_{OH}/\Delta\nu_{OH}^{SiOH})}{0.00226}$	from the heats of formation of ion pairs	from $\Delta\nu_{HX}$ in the PA scale; $PA^{B_S} = \frac{3.54 + \lg\Delta\nu}{0.0057}$ CD for $CDCl_3$
Method of calculating the concentration of the centres	from the intensity of the characteristic bands of the B molecules	from the intensity of the ν_{OH} band	from the intensity of the most characteristic bands of the spectrum	from the intensity of the ν_{HX} band
Required physicochemical properties of the probes	to characterise the centres fully we must cover a range of dipole moment (μ) and of functional groups giving a $\Delta\nu_B$ shift on complex formation greater than the line width of ν_B (usually CN, CO)	absence of OH groups	the ν_{BH^+} band should not overlap the ν_B, H-complex, or M^{n+}:B bands	the ν_{HX} band should not overlap the ν_{OH} or ν_{CH} bands
Most widely used probes	acetone, pyridine, ammonia, acetonitrile, benzonitrile, carbon monoxide	nitromethane, acetonitrile, benzonitrile, acetone, dioxan, diethyl ether, tetrahydrofuran, pyridine and substituted pyridines, aniline, amines	ammonia, pyridine, and its derivatives	deuteriated chloroform

* A change in the number and position of the absorption bands of the B molecules may be observed under these conditions.

reliably identified and differentiated; 2) the strength of the individual centres should be determinable numerically, on a defined scale; 3) the concentration of each type of surface centre should be independently determinable.

These requirements are most easily met by spectroscopic methods, in particular the i.r. spectroscopy of adsorbed molecules. Unfortunately, very few studies of acidic or basic centres are mentioned in recent reviews[2,8,9] of advances in i.r. spectroscopy. The aim of the present review is to fill this gap.

The most basic application of i.r. spectroscopy to the study of the acid–base properties of surfaces is the spectral probe method, in which the properties of adsorption centres are characterised through the absorption spectra of molecules adsorbed on them and through the change in intensity of the bands associated with functional groups of the surface. The main features of this method as applied to the study of different types of centre are outlined in Table 1, which shows the types of complex formed by probe molecules with OH, L, and B_S centres, defines the vibrations used to measure the strength and number of surface centres, lists the most important physicochemical and spectral properties of the probe molecule, and names the probes most widely used as bases (B) to study acidic centres and as acids (HX) to study basic centres. Table 1 can be used as a starting point in the search for new probes and in the selection of a suitable method of characterising the acid–base properties of a particular catalyst. Let us examine each method in turn.

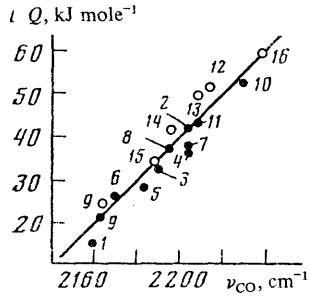


Figure 1. Correlation between νCO and the heat of adsorption Q of carbon monoxide on different surfaces: *1*) MgO, *2*) and *3*) γ-Al_2O_3, *4*) and *5*) ZrO_2, *6*) Ga_2O_3, *7*) and *8*) BeO, *9*) NaY, *10*) H-erionite, *11*) TiO_2, *12*) ZnY, *13*) MnY, *15*) CaY, *16*) Al_2O_3. The data *1–11* are taken from Ref.14, *9*, *12*, and *15* from Ref.15, *16* from Ref.16. The filled circles denote i.r. spectral data, the open circles calorimetric data. Points *2* and *3*, *4* and *5*, and *7* and *8* are for different complexes of the probe on the same adsorbent.

II. STUDY OF APROTIC CENTRES

1. Physicochemical Foundations of the Method

The strength of an aprotic centre is most correctly characterised by the free energy (ΔG) and the enthalpy (ΔH) of its interaction with a base[10]:

$$L + B \rightarrow L{:}B \qquad (I)$$

Since both protonic and aprotic centres are present simultaneously on the surface those quantities cannot be determined directly from measurements of the heat of reaction, as most probes react with both L and OH centres. It has therefore been suggested[11] that the strength of the L centres could be conveniently characterised by the quantity $\Delta\nu_B = \nu_B^{ads} - \nu_B^{gas}$, where ν_B^{ads} is the shifted absorption band in the spectrum of the adsorbed probe, on the assumption that $\Delta\nu_B$ is proportional to the extent of interaction of L and B in the donor–acceptor (D–A) complex. The main problem in using this assumption is that the formation of a D–A complex usually causes a rearrangement of both the electronic and the geometric structure of the probe molecule, both of which are reflected by the change in ν_B in the vibrational spectrum.

In specific cases this assumption has been confirmed both experimentally[12] and theoretically[13]. We have reported[14] an i.r. spectroscopic study of the correlation between the heat of adsorption of carbon monoxide and $\Delta\nu_{CO}$ on the metal cations for a series of silicate and oxide systems. The correlation (Fig.1) for the transition metal cations, and also Zr^{4+}, Zn^{2+}, and Mn^{2+}, can be described analytically as

$$Q, \text{ kJ mole}^{-1} = 10.5 + 0.5\,\Delta\nu_{CO} \qquad (1)$$

where $\Delta\nu_{CO} = \nu_{CO}^{ads} - 2143$ (cm^{-1}). By using this equation the strength of the aprotic centres can be determined (on the heat of adsorption scale) from the measured shift $\Delta\nu CO$ of the adsorbed carbon monoxide molecule.

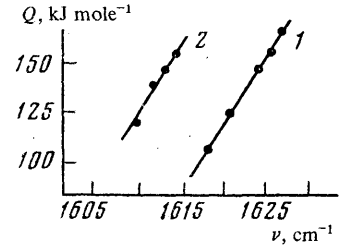


Figure 2. Relationship between the isosteric heat of adsorption of pyridine and the ν_{8a} frequency on aluminium oxide and zeolite (*1*) and on zirconium oxide (*2*).[17]

We have studied[17] the correlation between the heat of adsorption of pyridine on aluminium and zirconium oxides and the frequency of the absorption band for the pyridine ring which is most sensitive to co-ordination[18] ($\nu_{8a}^0 = 1580$ cm^{-1}). For the complexes with aprotic centres formed by the cations of one metal we found that ν_{8a} varies linearly with the heat of adsorption. For example, for Al^{III} (curve *1* of Fig.2) the correlation is

$$Q, \text{ kJ mole}^{-1} = 6.55 \cdot (\nu_{8a} - 1580) - 86 \qquad (2a)$$

whereas for the Zr^{4+} cation the correlation (curve *2* of Fig.2) is

$$Q, \text{ kJ mole}^{-1} = 7 \cdot (\nu_{8a} - 1580) - 26 \qquad (2b)$$

This means that in the case of pyridine the position of the ν_{8a} band in the D–A complex with an aprotic centre can be used as a measure of the strength of the centre if only one metal cation is present.

Thus it is essential to establish the correlation between $\Delta\nu_B$ and Q before using a compound as a spectroscopic probe to measure the strength of aprotic centres.

Table 2. Properties of probe molecules used to study surface Lewis-acid centres.

No.	Probe	μ, D	Interaction with Lewis-acid centres: Complex	Interaction with Lewis-acid centres: Frequency used to measure strength of centres	Interaction with Lewis-acid centres: Frequency used to measure concentration of centres	Possible complications from interaction with Brønsted centres	Remarks
1	Acetone	2.82	M^{n+} : O=C(CH$_3$)$_2$	ν_{CO} (ν^0_{CO} = 1720 cm^{-1}) decreases; $\Delta\nu \leqslant 150$ cm^{-1}	no data	H-complex is formed; ν_{CO} decreases by 20–40 cm^{-1}	easily oxidised
2	Ammonia	1.48	M^{n+} : NH$_3$	δNH_3 ($\delta^0_{NH_3}$ = 968 cm^{-1}) increases; $\Delta\nu \leqslant 300$ cm^{-1}	from δ_{NH} intensity, δ^0 = 1620–1640 cm^{-1}	H-complex is formed, with $\delta NH_3 \cong$ 1620–1640 cm^{-1}	unsuitable because of partial amination of surface
3	Pyridine	2.20	M^{n+} : C$_5$H$_5$N	$\nu_{CC(N)} = \nu_{8a}$ (ν^0_{8a} = 1583 cm^{-1}); increases, $\Delta\nu \leqslant 40$ cm^{-1}	from intensity of $\nu_{CC(N)}$ = 1583 cm^{-1}, $\nu_{CC(N)}$ = 1445 cm^{-1}	H-complex is formed, $\nu_{CC(N)}$ = 1445–1450 cm^{-1}; ion pair gives overlapping bands, $\nu_{CC(N)}$ = 1610–1640 cm^{-1}	correlation between $\Delta\nu_B$ and ΔH for complexes with same cation
				$\nu_{CC(N)}$ ($\nu^0_{CC(N)}$ = 1445 cm^{-1}) increases, $\Delta\nu \leqslant 20$ cm^{-1}			
4	Acetonitrile	3.94	M^{n+} : N≡C–CH$_3$	ν_{CN} (ν^0_{CN} = 2275 cm^{-1}) increases, $\Delta\nu \leqslant 60$ cm^{-1}	from intensity of ν_{CN}	H-complex formed, $\Delta\nu_{CN} \cong$ 5–10 cm^{-1}	deutero-acetonitrile is better, because the ν_{CN} band shows Fermi resonance with $\nu_{CC} + \delta_{CH_3}$ = 2290 cm^{-1}
5	Benzonitrile	4.39	M^{n+} : N≡C–Ph	ν_{CN} (ν^0_{CN} = 2229 cm^{-1}) increases, $\Delta\nu \leqslant 65$ cm^{-1}	from intensity of ν_{CN}	H-complex formed, $\Delta\nu_{CN} \cong$ 5–10 cm^{-1}	convenient because of high intensity of ν_{CN}
6	Carbon	0.1	M^{n+} : C≡O	ν_{CO} (ν^0_{CO} = 2143 cm^{-1}) increases, $\Delta\nu \leqslant 100$ cm^{-1}	from intensity of ν_{CO}	H-complex formed, $\Delta\nu_{CO} \cong$ 30 cm^{-1}	very unstable complexes; low-temperature adsorption essential

* Allowing for Fermi resonance.

Though the series of aprotic acids (in order of strength) is not usually the same for solutions of different bases, we can define two classes of bases which give similar aprotic acids: the "hard" bases, usually with a large dipole moment (μ), and the "soft" bases, which have no dipole moment but are easily polarised[19]. It is reasonable to expect a similar behaviour when the bases form surface complexes. Some properties of soft and of hard bases which can be used to measure the strength of surface centres are listed in Table 2.

It is clear from published data[14,16,20,21,22] that even on a single catalyst the $\Delta\nu_{CO}$ values for a metal cation in different co-ordinations can be very different: for example, for Al^{3+} and ν_{CO} frequency varies from 2190 to 2240 cm^{-1}. Even in simple oxides several types of complex between CO and the L centres are observed[14,16]. Therefore this probe molecule, being a soft base, can be used to identify the different states of the cation of a given metal in different co-ordinations.

A different situation is observed when "hard" bases are used as probes. It is found[23] that the ν_B frequencies for pyridine, benzonitrile, and acetonitrile (the probes most often used to study electron-acceptor centres) are almost constant for the cation of a given metal in different catalysts (oxides, amorphous or crystalline alumina–silicas, phosphates, germanates, molybdates, and antimonates). Therefore the position of the ν_B band is determined by the nature of the cation. The quantity γ_r^{n+} can be used to characterise the cation: it is defined as the ratio I^{n+}/r, where I^{n+} is the appropriate value of the ionisation potential of the metal cation (in eV) and r is its orbital radius (in Å).[24] Physically the quantity γ_r^{n+} is closely related to e/r, but it allows for differences between metal cations formally in the same state of oxidation[24]. Fig.3 shows a plot of ν_{CN} in the spectrum of benzonitrile adsorbed on different substances[23,25] against the γ_r^{n+} value of the appropriate metal cation. The plot is fitted by the equation

$$\nu_{CN} = 2228\,(\pm 3) + 5{,}18\,(\pm 0{,}37)(\gamma_r^{n+})^{1/2} \qquad (3)$$

with a correlation coefficient $|R| = 0.97$ and a standard deviation of the ν_{CN} values of 5 cm^{-1}.

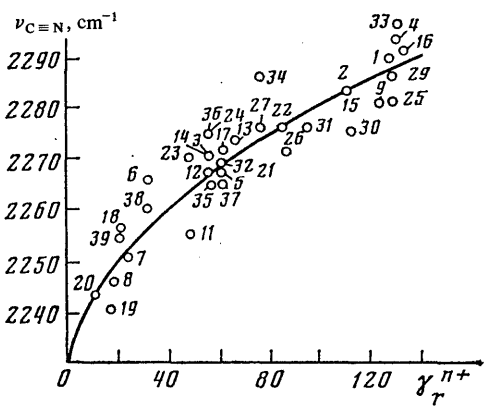


Figure 3. Dependence of ν_{CN} for benzonitrile adsorbed on catalysts upon γ_r^{n+}: *1*) Al_2O_3–SiO_2, *2*) Ga_2O_3–SiO_2, *3*) ZrO_2–SiO_2, *4*) BeO–SiO_2, *5*) MgO–SiO_2, *6*) Y_2O_3–SiO_2, *7*) La_2O_3–SiO_2, *8*) NaY, *9*) HNaY, *11*) CoNaY, *12*) NiNaY, *13*) CuNaY, *14*) ZrO_2–GeO_2, *15*) Ga_2O_3–GeO_2, *16*) BeO–GeO_2, *17*) MgO–P_2O_5, *18*) CaO–P_2O_5, *19*) SrO–P_2O_5, *20*) BaO–P_2O_5, *21*) Fe_2O_3–P_2O_5, *22*) Fe_2O_3–MoO_3, *23*) CoO–MoO_3, *24*) NiO–MoO_3, *25*) Al_2O_3–Sb_2O_5, *26*) Fe_2O_3–Sb_2O_5, *27*) Ga_2O_3–Sb_2O_5, *29*) γ-Al_2O_3, *30*) Ga_2O_3, *31*) TiO_2, *32*) ZnO, *33*) BeO, *34*) Cr_2O_3, *35*) ZrO_2, *36*) NiO, *37*) MgO, *38*) ThO_2, *39*) CaO. *1*)–*29*) from Ref.23, *30*)–*39*) from Ref.25.

Eqn.(3) can be used to study electron-acceptor centres in complex oxide systems containing various additives. Let us examine, for example, iron antimonate[26]. Taking tabulated values of γ_r^{n+} for all the cations which may be present on the surface (Fe^{3+}, Sb^{3+}, Sb^{5+}), and calculating the ν_{CN} frequencies by Eqn.(3), we obtain the ν_{calc} values 2276, 2255, and 2291 cm^{-1} respectively. By comparing them with

ν_{exper} (2270 and 2247 cm^{-1}) we conclude that the aprotic centres most likely to be present in iron antimonate are the iron and the antimony(III) cations.

No satisfactory explanation has yet been proposed for the low sensitivity of the position of the ν_B band to changes in the electronic state of the metal cation coupled with a high sensitivity to the nature of the metal cation. Some tentative suggestions appear in Ref.23.

It follows that in order to characterise fully an electron-acceptor centre on a catalyst surface we must use at least one hard and one soft base as probes (see Tables 1 and 2). The hard probe identifies the metal cations which form electron-acceptor centres, and the soft probe detects differences in the properties of a given cation in different environments.

2. Determination of the Concentration of L Centres

The surface concentrations are measured by assuming that the Beer–Lambert law is applicable to the bonds of adsorbed molecules. The most convenient form of this law is

$$A = 10^{-3} \cdot A_0 c_s \rho \qquad (4)$$

where A is the observed integral absorption for the analytical band in cm^{-1} (an analogous expression can be written for the optical density D), A_0 is the integral intensity of the band for a concentration of 10^{-6} mole $litre^{-1}$, c_S is the concentration of surface centres (expressed as μmole g^{-1} of catalysts), and ρ is the amount of catalyst (in mg) exposed to 1 cm^2 of the cross-section of the light beam. The product $10^{-3} c_S \rho$ gives the number of μmole of adsorbate in 1 cm^2 of the cross-section of the light beam. To find c_S we need to know A_0 (or the extinction coefficient ε if the optical density D is used). When overlapping bands (due to different forms of adsorption) are present, as is often the case since surface centres tend to be inhomogeneous, the complex band must be resolved into its individual components.

Unfortunately the A_0 coefficient has been obtained only in a few cases. The values of A_0 for the complexes of CO with Zn^{2+} are given in Ref.22. A_0 values for carbon monoxide forming D–A complpxes with a series of transition metal cations have also been reported[27]. A_0 has also been determined for the complexes of pyridine with aluminium cations[28], and the A_0 values have been studied[29] for some absorption bands of pyridine and of 2,6-dimethylpyridine interacting with NaY zeolite.

Thus it is clear that the absolute values of c_S for L centres can be measured only in a few cases from the i.r. absorption spectra of adsorbed molecules, and that the determination of the A_0 coefficients for the absorption bands of a wide range of individual probe molecules has become an urgent problem.

In studies of a series of chemically similar catalysts we can detect changes in the concentration of surface centres without knowing the A_0 coefficient. If the Beer-Lambert law is obeyed the parameter A for any of the ν_B bands is proportional to the concentration of the corresponding centres, and therefore the changes in A (normalised for $\rho = 1$) reflect the changes in the concentration of surface centres. This approach has been used[30–32] to reveal the nature of the catalytically active centres in a number of zeolites and zeolite-containing catalysts.

It is important in this connection to define the conditions under which the Beer–Lambert law is obeyed. Published data[14,22,28,33–35] suggest that this law is not infringed if two conditions are satisfied simultaneously: 1) the position of ν_B is unaffected by changes in surface coverage, and 2) the coverage of the adsorbent surface by adsorbate molecules is much less than a monolayer. Recommended values of ν_B for the most commonly used probes are given in Table 2. We should also bear in mind that the concentration of adsorption centres is not always equal to the number of adsorbed molecules per unit surface area. Adsorption should be carried out under conditions which ensure 100% filling of the centres of interest (or, at least, the same fractional filling in different experiments).

Thus the surface concentration of aprotic centres can be determined quantitatively by i.r. spectroscopy at three distinct levels of complexity and reliability. The first is suitable for qualitative studies of the changes in concentration of the centres in series of closely similar catalysts. We merely measure the change in intensity of the ν_B band, referred to 1 g of the catalyst. These experiments can be carried out in the simplest apparatus, using standard conditions for the adsorption of the probe. The second level of complexity is the determination of the concentration of surface centres by using published values of A_0. In this case the adsorption of the probe must be controlled to give almost 100% filling of the centres: this can be achieved by using a high relative pressure of adsorbate vapour or a low adsorption temperature. Usually under these conditions the probe is adsorbed in more than one form, and therefore the combined overlapping absorption bands must be resolved into the individual components before determining c_S. The third level of measurement complexity is reached when the concentration of acid centres on the surface has to be determined with a probe for which the A_0 value is not known. In this type of work the adsorption apparatus and the i.r. cell must be designed to allow simultaneous determinations of the adsorption and spectral measurements over a wide range of temperature and pressure. With this exception the third level does not differ from the second: it is potentially the most useful of the three levels, and it is attracting increasing interest.

We must now examine in detail the experimental methods of determining A_0. In order to find A_0 we need to know the surface concentration of the probe molecules, corresponding to the observed intensity of the experimental ν_B band. Some workers[36–40] have evaluated surface concentrations in parallel adsorption measurements, but as Little[41] has pointed out this can lead to serious errors because of the difficulty of reproducing exactly the conditions in adsorption experiments and i.r. spectral experiments.

An attempt[35] to make these conditions identical as far as possible by using pressed samples and by heating the adsorption sample to 50 °C (to simulate the heating of the spectral sample by i.r. radiation) was inconclusive, since no evidence was obtained that exactly equal amounts of pyridine were adsorbed on the same type of centre in the two pressed samples.

Undoubtedly the best approach is to determine the surface concentration of B centres and the parameter A for the ν_B band on a single sample in the same experiment. Two basic methods are available: the volumetric and the gravimetric method.

Volumetric method. The volumetric method often takes the form of a titration. Known amounts of adsorbate are added successively to the cell, and the spectrum is recorded after each addition. This approach has been used[28] to measure A_0 for the ν_B bands of pyridine and piperidine sorbed on decationated Y zeolite, aluminium oxide, and amorphous alumina–silica.

The use of the volumetric method is complicated in some cases by the adsorption of the probe molecules on the unheated parts of the cell. Quantitative corrections for the

adsorption on the cell walls are difficult to apply. In order to eliminate the effect provisions for heating the whole cell must be made, and the adsorption must be carried out at pressures well below the saturated vapour pressure of the probe at the temperature of the cell wall. The volumetric method can be used, without a correction for the adsorption on the cell wall and without heating the cell, to study the adsorption of carbon monoxide[14], ammonia ($T_b = 239.6$ K), acetone ($T_b = 329.6$ K), and acetonitrile ($T_b = 353.2$ K) at pressures up to 10 mmHg. With pyridine ($T_b = 388.4$ K) the adsorption on the cell wall at 300 K is negligible at pressures below 10^{-1} mmHg. For benzonitrile ($T_b = 463.8$ K) the volumetric method is probably inapplicable, since its vapour pressure at 300 K is 0.1 mmHg.

Gravimetric method. The gravimetric method consists in measuring the weight of the sample before and after admitting the adsorbate into the cell. Since the pressed samples used to measure the i.r. spectra are small, and the average concentration of acidic centres is also small, the precision of the measurement of sample weight should be at least 10^{-7} N.[42-44] As a result, a fairly complicated cell design is needed for simultaneous gravimetric and i.r. spectral measurements. For a detailed description of different types of these cells the reader is referred to recent monographs[18,41]. The apparatus must also include a system for introducing the adsorbate and means for measuring pressure.

The gravimetric method of measuring the amount of B molecules on the surface seems to be preferable to the volumetric method in two circumstances:

1) with weakly adsorbed gases (for example, alkenes[42]), when the precision of the volumetric method is inadequate. A comparison of the results obtained by both methods for the adsorption of unsaturated hydrocarbons is given in Refs.42 and 45.

2) for the adsorption of high-boiling probe substances, when the adsorption of B molecules on the cold wall of the cell is significant.

The gravimetric method should be chosen when pyridine is used as the adsorbate[35] (and probably also benzonitrile). A more detailed description of the properties of the probes listed in Table 2 and of their special features in use can be found in Refs.3, 11, 14–16, 18, 23, 24, 30–32, 42, and 46–54.

Evidently these difficulties in the determination of the surface concentrations of adsorbed substances from their i.r. spectra are not confined to the aprotic centres. Studies of protonic or basic centres present similar problems, which can be overcome in similar ways. Therefore we shall limit our discussion of the determination of the concentration of the latter types of centre to a few specific cases.

III. STUDY OF PROTONIC ACID CENTRES

1. The Concepts of "Acid Strength" and "Acidity", and their Measurement Units

The theory of acids and bases is most fully developed for aqueous solutions[55], but it includes a group of concepts which can be used in the qualitative and quantitative description of the properties of any solution. Three of these concepts are especially relevant to the present discussion: the acid (or base) strength, the acidity of the solution, and the solvation effect. According to Hammett[56] the acid or base strength denotes the extent to which the acid is converted into an anion (or the base into its conjugated acid) under standard conditions. These degrees of conversion are characterised by the appropriate equilibrium constants, or in pK_a units.

Thus the "acid strength" is a thermodynamic quantity which describes the properties of substances in relation to a chosen standard medium. The second concept ("acidity of the solution") describes the tendency of the solution as a whole to donate a proton to a base. This tendency increases with the concentration of the acid. In dilute aqueous solutions it is measured by the pH, or by the more universal acidity function H_0 (which is less dependent on the solvent)[56]. If the tendency of the acid to transfer a proton to the base is characterised by the protolytic base indicator equilibrium

$$HInd^+ \rightleftarrows Ind + H^+ \qquad (II)$$

for which we can write

$$K_a = \frac{a_{H^+} a_{Ind}}{a_{HInd^+}} \quad \text{or} \quad pK_a^{Ind} = -\lg \frac{a_{H^+} f_{Ind}}{f_{HInd^+}} + \lg \frac{[HInd^+]}{[Ind]}$$

where a is the activity and f the activity coefficient in the given medium, the acidity function is given by the expression

$$H_0 = pK_a^{Ind} - \lg \frac{[HInd^+]}{[Ind]} \qquad (5)$$

The quantity $H_0 = -\lg a_{H^+} f_{Ind}/f_{HInd^+}$ is a measure of the acidity of the medium. It is important to note that the scale of H_0 characterises the acidity of the solution but not the acid strength, since it depends on the concentration of the acid. It is applicable when: 1) the protonation of the base [described by Eqn.(II)] has reached equilibrium, and 2) the properties of the uncharged Ind molecules allow the ratio f_{Ind}/f_{HInd^+} in the given medium to be constant for any indicator. For equal concentrations of the protonated and of the initial base the H_0 value is equal to the pK_a of the indicator.

The indicator method was later extended by Walling[4] to solid acids by postulating that the ability of a surface to convert a base into a protonated acid can be characterised in the H_0 scale. The surface is treated as a medium with a high dielectric constant, and H_0 as a measure of the acid strength (determined from the pK_a value for the weakest of the protonated base indicators adsorbed from non-polar solvents). The second term of Eqn.(5) was ignored. Thus a confusion in the use of the "acid strength" concept arose at that early stage in the development of the study of the acidity of solids.

The need to quantify the strength of solid acids arose during the development of heterogeneous acid-base catalysis. However, in catalytic reactions the base is in the gas phase, and therefore it is more correct to examine the tendency of the catalyst surface to protonate the base after it has been adsorbed from the gas phase. In other words, whereas the acid strength in an aqueous solution is characterised by the equilibrium constant for the dissociation

$$AH \overset{K_a}{\rightleftarrows} A^- + H^+ \qquad (III)$$

no such dissociation takes place on the surface, and the protonation of the base cannot be described by the simple equation (II).

The mechanism of the interaction of a molecule of a gaseous base B with a protonic acid centre on a solid surface can be described[57] by the scheme

$$\underset{A}{|-OH} + B^{gas} \rightarrow \underset{H\text{-complex}}{|-O-H \ldots B} \rightarrow \underset{IP}{|-O^- \ldots {}^+HB} \qquad (IV)$$

where A is the initial state of the system, H-complex is a complex in which B is hydrogen-bonded to an acidic OH group, and IP is an ion pair. A similar mechanism applies to the interaction between an acid and a base in non-polar

solvents[58]. According to this scheme the tendency of protonic acid centres to interact with the base B can be determined by studying the reaction between A and the H-complex or between A and IP. In the following sub-sections we shall examine both these approaches, which have been called respectively the "hydrogen bond method" and the "ion pair method".

Recent work[59–74] has established that the strength of a Brønsted acid or base in the gas phase is more correctly defined through the "proton affinity" (PA). In the case of acids the PA is determined by the enthalpy (ΔH) of the reaction

$$AH \rightarrow A^- + H^+ \qquad (V)$$

and the PA of bases by the enthalpy of the reaction

$$HB^+ \rightarrow H^+ + B \qquad (VI)$$

Both reactions are assumed to take place in the gas phase.

Table 3. Probes used to study Brønsted acid centres.

No.	Probe	pK_a [75—78]	PA, kJ mole^{-1} (Ref. 59,60, 68–74)	**$\Delta\nu_{OH}$, cm^{-1}	
				SiO_2	HNaY
1	Argon	—	377	8	34
2	Oxygen	—	423	12	37
3	Krypton	—	435	16	60
4	Xenon	—	477	19	—
5	Nitrogen	—	477	24	91
6	Cyclohexane	—	586	45	—
7	Carbon monoxide	—	598	90	250
8	Chloromethane	—	670	110	—
9	Nitromethane	11.93	753	160	550
10	Acetaldehyde	—	774	290	—
11	Ethyl methyl ketone	−7.2	774	330	—
12	Dioxan	−3.22	799	390	1000
13	Acetone	−7.2	816	340	900
14	Tetrahydrofuran	−2.02	820	470	1000
15	Diethyl ether	−2.42	824	460	1000
16	Acetophenone	−6.15	833	320	—
17	Methyl acetate	—	816	270	—
18	Dimethylsulphoxide	0	870	550	1050
19	Benzonitrile	−10.43	—	300	750
20	Acetonitrile	−10.13	783	300	750
21	Ammonia	9.25	846	750	—
22	Tripropylamine	11.0	940	990	—
23	Aniline	4.81	874	500	—
24	Methylimidazole	6.95	—	830	—
25	Diethylamine	10.7	929	930	—
26	Trimethylamine	9.67	929	990	—
27	Piperidine	11.22	933	980	—
28	Triethylamine	11.02	958	990	—
29	Perchloropyridine	−8	—	270	850
30	2,5-Dibromopyridine	−3	—	450	1000
31	2-Bromopyridine	0.8	891	580	1150
32	3-Chloropyridine	3.6	891	630	—
33	Pyridine	5.21	912	750	1250
34	2-Methoxypyridine	3.28	912	550	—
35	2-Methylpyridine	5.97	925	750	—
36	Hydrogen sulphide	—	714	150	—
37	Dimethyl sulphide	−5.25	824	370	—

Criterion for the formation of an ion pair (IP):
- 1–8: not formed *
- 9–20: »
- 21: $\delta_{NH_4^+} = 1400—1450$ cm^{-1}
- 22–28: —
- 29: $\nu_{NH} = 3250$ cm^{-1}
- 30: $\nu_{CC(N)} = 1520$ cm^{-1}
- 31: $\nu_{CC(N)} = 1530$ cm^{-1}
- 32: —
- 33: $\nu_{CC(N)} = 1540$ cm^{-1}
- 34–37: —

Notes. The bases in this Table are classified into groups as follows: Nos.1–8 do not show basic properties in aqueous solutions, Nos.9–18 are oxygen-containing bases, Nos.19–28 are nitrogen-containing bases, Nos.29–35 are pyridine and its derivatives, Nos.36 and 37 are sulphur-containing bases. The dash denotes the absence of suitable data. Probes No.1–5 were adsorbed at low temperature, No.13 is difficult to use (readily oxidised), No.21 tends to aminate the surface. With probes No.21–28 the donor–acceptor complexes are difficult to distinguish from protonated molecules, Nos.29–31 have a low vapour pressure.

* Ion pairs are not formed on protonic centres with PA > 1200 kJ mole^{-1}.

** Data taken from Refs.41, 91–93, 96–98.

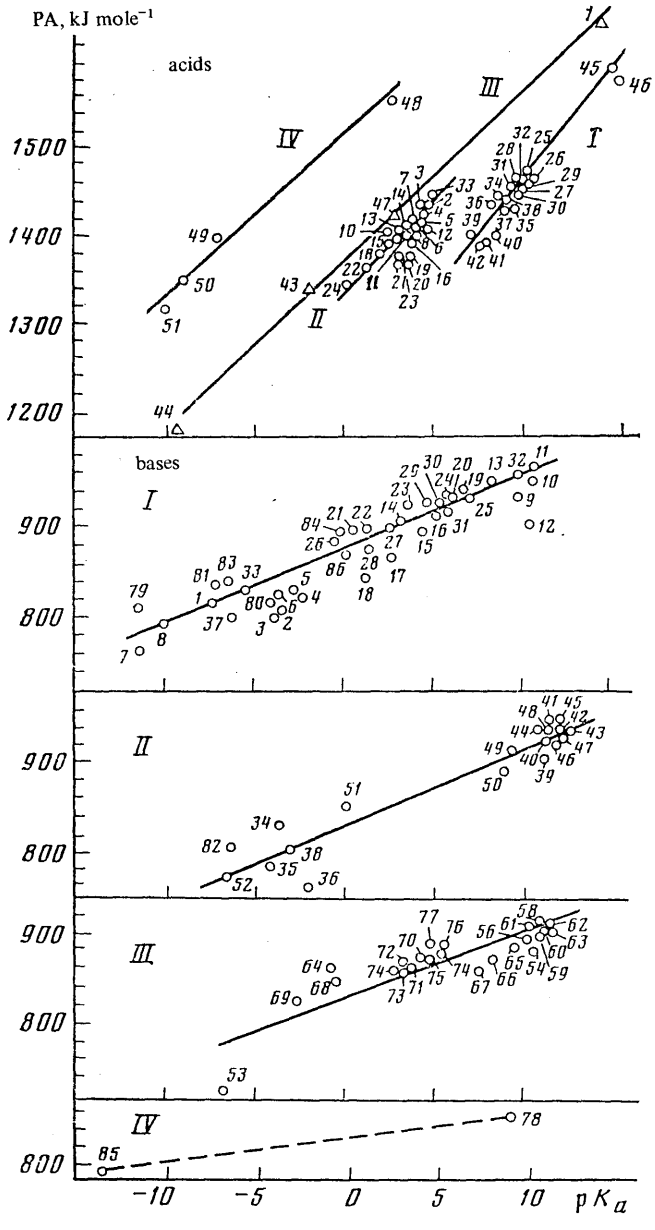


Figure 4. Correlation between PA and pK_a for different types of acid and base. Bases: (*I*) no protons on the proton-acceptor atom, (*II*) one proton, (*III*) two protons, (*IV*) three protons. Acids: (*I*) alcohols and phenols, (*II*) carboxylic acids, (*III*) inorganic oxygen-containing acids, (*IV*) hydrogen halide acids. Bases: *1*) acetone, *2*) dioxan, *3*) dimethyl ether, *4*) tetrahydrofuran, *5*) tetrahydropyran, *6*) diethyl ether, *7*) nitromethane, *8*) acetonitrile, *9*) trimethylamine, *10*) triethylamine, *11*) tri-n-propylamine, *12*) methylcyclobutylamine, *13*) triallylamine, *14*) tripropylamine, *15*) 2,2,2-trifluoroethylamine, *16*) pyridine, *17*) 4-trifluoromethylpyridine, *18*) 4-nitropyridine, *19*) 4-methoxypyridine, *20*) 4-methylpyridine, *21*) 2-chloropyridine, *22*) 2-bromopyridine, *23*) 2-methoxypyridine, *24*) 2-methylpyridine, *25*) 2-aminopyridine, *26*) 2-fluoropyridine, *27*) 3-chloropyridine, *28*) 3-cyanopyridine, *29*) 3-methoxypyridine, *30*) 3-methylpyridine, *31*) 3-aminopyridine, *32*) 4-aminopyridine, *33*) dimethyl sulphide, *34*) t-butanol, *35*) n-butanol, *36*) methanol, *37*) acetic acid, *38*) isopropanol,

39) dimethylamine, *40*) diethylamine, *41*) di-n-propylamine, *42*) di-isopropylamine, *43*) di-n-butylamine, *44*) di-isobutylamine, *45*) di-s-butylamine, *46*) cyclopropylamine, *47*) cyclobutylamine, *48*) cyclopentylamine, *49*) diallylamine, *50*) dipropylamine, *51*) pyrrole, *52*) methyl sulphide, *53*) water, *54*) methylamine, *55*) ethylamine, *56*) n-propylamine, *57*) isopropylamine, *58*) n-butylamine, *59*) isobutylamine, *60*) s-butylamine, *61*) t-butylamine, *62*) n-pentylamine, *63*) t-ethylamine, *64*) hydrazine, *65*) allylamine, *66*) propylamine, *67*) 2-isocyanoethylamine, *68*) acetamide, *69*) formamide, *70*) aniline, *71*) 3-fluoroaniline, *72*) 3-chloroaniline, *73*) 4-chloroaniline, *74*) 3-methylaniline, *75*) 4-methylaniline, *76*) 3-methoxyaniline, *77*) 4-methoxyaniline, *78*) ammonia, *79*) benzonitrile, *80*) ethyl methyl ether, *81*) benzaldehyde, *82*) phenol, *83*) methyl phenyl ether, *84*) *N,N*-dimethylacetamide, *85*) phosphine, *86*) dimethylsulphoxide. Acids: *1*) water, *2*) acetic acid, *3*) 4-methylbenzoic acid, *4*) 2-methoxybenzoic acid, *5*) 3-methylbenzoic acid, *6*) benzoic acid, *7*) 3-methoxybenzoic acid, *8*) 2-methoxybenzoic acid, *9*) 2-methylbenzoic acid, *10*) fluoroacetic acid, *11*) 2-fluorobenzoic acid, *12*) 3-fluorobenzoic acid, *13*) 2-chlorobenzoic acid, *14*) 4-fluorobenzoic acid, *15*) chloroacetic acid, *16*) 4-chlorobenzoic acid, *17*) 3-chlorobenzoic acid, *18*) 2-nitrobenzoic acid, *19*) 3-nitrobenzoic acid, *20*) 2-cyanobenzoic acid, *21*) 3-cyanobenzoic acid, *22*) dichloroacetic acid, *23*) 4-nitrobenzoic acid, *24*) trifluoroacetic acid, *25*) 4-methylphenol, *27*) 3-methylphenol, *28*) phenol, *29*) 2-methylphenol, *30*) 2-methoxyphenol, *31*) 3-methoxyphenol, *32*) 4-fluorophenol, *33*) propionic acid, *34*) 2-fluorophenol, *35*) 3-fluorophenol, *36*) 2-chlorophenol, *37*) 4-chlorophenol, *38*) 3-chlorophenol, *39*) 2-nitrophenol, *40*) 3-cyanophenol, *41*) 3-nitrophenol, *42*) 4-cyanophenol, *43*) nitric acid, *44*) perchloric acid, *45*) methanol, *46*) ethanol, *47*) nitrous acid, *48*) hydrogen fluoride, *49*) hydrogen chloride, *50*) hydrogen bromide, *51*) hydrogen iodide. PA data taken from Refs.59, 60, 64, 65, 67 for acids and from Refs.60, 61, 68–71, 73, 74 for bases. Data on pK_a taken from Refs.71, 75–78.

Experimentally the parameter PA is found by studying the equilibrium gas-phase proton transfer reactions between the acid and the acid residue or between the protonated and the free base. The enthalpy of the reaction is determined in relation to a chosen standard: in particular, ammonia, whose PA [determined directly by reaction (VI)] is 846 kJ mole^{-1}.[69]

Thus we can use the PA to characterise the interaction of acidic OH groups of the surface with B molecules in the gas phase, and the problem reduces to finding the functional relationship between any measurable property of the system which reflects the extent of proton transfer and the quantities PA_{AH} and PA_B. Under these conditions PA_B is always known (see Table 3). However, in many current publications the acid–base properties of surfaces are measured in pK_a units, and therefore the reported PA values have to be compared with the properties of the solute in water, i.e. on the pK_a scale. Data on pK_a and on the PA can be found in many recent papers[59–78] and in their References. In general, an increase in the PA of bases from 710 to 960 kJ mole^{-1} is accompanied by an increase in pK_a from (−14)–(−11) to (11)–(12). However, we should note that often the pK_a values differ by 10 or more units for substances with almost identical PA, and conversely for substances with similar values of pK_a the PA can differ by 100–120 kJ mole^{-1} (see Table 3).

Since the pK_a value is largely determined by the state of solvation of the ionised base, we can use specific features of the solvation as a basis for classification. In particular, we can expect bases with different numbers of protons on the acceptor atom (for example, primary, secondary, and tertiary amines) to form different numbers of hydrogen bonds with water molecules, and therefore to show differences in solvation energy for the same basicity.

This criterion is used in Fig.4 to establish correlations between pK_a and PA values for compounds containing equal numbers of protons. In each group of bases we find an obvious proportionality between the two parameters: the mean scatter is ~40 kJ mole^{-1} for the PA and ~3 units for pK_a. Even closer correlations between pK_a and the PA are found in series of isostructural bases[68,72].

We can also compare the PA and pK_a values of acids by classifying the acids into several groups (see Fig.4). Group I includes alcohols and phenols, group II the carboxylic acids, group III oxygen-containing inorganic acids and water, while group IV is reserved for hydrogen halides. It is clear from these results that only bases or acids of a given type can be arranged in order of strength (in the gas phase) from pK_a data obtained for these substances in aqueous solutions: to a first (and rough) approximation we can use the classification suggested above.

It has recently been suggested[79–81] that the thermodynamic characterisation of the proton-donor properties of catalysts should be supplemented by a kinetic criterion: the activation energy (E_a^H) for the transfer of the proton from the surface to the adsorbed molecule. A spectroscopic method of calculating E_a^H from measurements of ν_{OH} for the surface before and after adsorption was developed, using the specially established correlation between $\Delta\nu_{OH}$ and E_a^H.

Let us now examine in detail each of the above methods of quantifying the proton-donating properties of solid acids.

2. The Hydrogen Bond (HB) Method

a) *Physicochemical basis.* Attempts to characterise the strength of acids or bases through the properties of the H-complex [see reaction (IV)] raise two important questions: can the influence of the acid or base strength on the properties of the complex be revealed explicitly, and what is the relationship between the various properties of the H-complex and the thermodynamics of the proton transfer reaction.

Detailed and precise studies of the enthalpy of formation of the H-bond (ΔH_H) and of the change in frequency of the stretching vibrations ($\Delta\nu_{HX}$, $\Delta\nu_{OH}$) for the formation of the complex in non-aqueous solutions have been reported[82]. An unambiguous correlation between these quantities was demonstrated[82–86]. Since $\Delta\nu_{HX}$ is directly measurable from the i.r. spectra we shall use only this parameter to characterise the H-complexes.

The answer to the first question is given in a comparison [87–89] of various characteristics of the H-bond (including $\Delta\nu_{HX}$) with the properties of the acid or based involved, which led to the formulation of the following "factor rule": any parameter used to characterise the H-bond can be expressed as a product of a function describing the dependence of the stated parameter of the complex on the nature of the i-th acid (P_i) and a function describing its dependence on the nature of the j-th base (E_j). It was shown[86–88] that the ratio of $\Delta\nu_{HX}$ for any acid interacting with the base B to $\Delta\nu_{OH}$ for phenol (chosen as a standard) interacting with the same B is the same for all bases B, and depends only on the nature of HX: $\Delta\nu^B_{HX}/\Delta\nu^B_{OH(PhOH)} = \text{const} = P_i$. This suggests that the nature of the base has the same influence on

the $\Delta\nu_{HX}$ value of any acid: thus, if the P_i values are calculated for a series of acids the dependence of $\Delta\nu_{HX}$ on the nature of the acid can be obtained to the precision of a constant factor.

Furthermore, the ratio of the shift of the ν_{HX} frequency for different acids (HX) interacting with the same base B to the $\Delta\nu_{HX}$ value of the same acids interacting with another base chosen as a standard (for example, diethyl ether[87]) is also constant, and depends only on the nature of B and on the chosen standard: $\Delta\nu^{B}_{HX}/\Delta\nu^{(C_2H_5)_2O}_{HX} = \text{const} = E_j$. Thus the change of E_j for a series of B is a function describing the dependence of $\Delta\nu_{HX}$ on the nature of the base B to a precision determined by the choice of the standard B.

The full form of the function describing the effect on $\Delta\nu_{HX}$ for any acid of the interaction with the base B (taking PhOH and $(C_2H_5)_2O$ as standards) is

$$\Delta\nu_{HX} = C\left(\frac{\Delta\nu^{B}_{HX}}{\Delta\nu^{B}_{OH(PhOH)}}\right)\cdot\left(\frac{\Delta\nu^{B}_{HX}}{\Delta\nu^{(C_2H_5)_2O}_{HX}}\right)$$

where the constant C reflects the properties of the chosen standards. It is easily shown, by putting HX = PhOH, that $C = \Delta\nu^{(C_2H_5)_2O}_{OH(PhOH)}$. According to Iogansen[87], in this case $C = 282$ cm^{-1}, and therefore

$$\Delta\nu_{HX} = 282 P_i \cdot E_j \qquad (6)$$

By using Eqn.(6) we can establish the dependence of P_i on the relevant property of the acid (or the dependence of E_j on the property of the base) from experimental $\Delta\nu_{HX}$ data. Direct correlations between $\Delta\nu_{OH}$ in the H-complexes and the K_p (or $\lg K_p$) value (which characterises thermodynamically the proton transfer from the acid to the base) have not so far been reported. However, in a series of different B with the same OH acid or in a series of different acids with the same base the dependence of $\Delta\nu_{OH}$ on K_p is equivalent (to the precision of a constant term) to the dependence of $\Delta\nu_{OH}$ on pK_a^{base} or on pK_a^{acid}, since $-\lg K_p = pK_a^{acid} - pK_a^{base}$. This dependence of $\Delta\nu_{OD}$ (for deutero-methanol) on the pK_a values of various bases was first demonstrated by Hammett[90], and the dependence on pK_b by Gordi and co-workers (see Ref.82). According to Arnett[77] the dependence of $\Delta\nu_{OH}$ on pK_a^{base} can be described by the correlation equation

$$\Delta\nu_{OH}/\nu^{0}_{OH} = a + b\,pK_a^{base} \qquad (7)$$

This equation was proposed[91,92] for a strong H bond, formed on Aerosil, phosphates, or HNaY zeolite. For example, for Aerosil $a = 0.145 \pm 0.004$ and $b = 0.0096 \pm 0.0007$.

The dependence of $\Delta\nu_{OH}$ on the pK_a of adsorbed bases for Aerosil, with additional results from Ref.93, is shown in Fig.5. For bases of group I the dependence on pK_a^{base} can be fitted more accurately to the following equation than to a linear equation:

$$\Delta\nu_{OH} = 530(\pm 14)\cdot 10^{0.026(\pm 0.0015)pK_a^{base}} \qquad (8)$$

According to this equation we can calculate pK_a^{base} to a precision better than ± 1.4 pK_a units if $pK_a > -12$ and $\Delta\nu_{OH} > 150$ cm^{-1}. The standard deviation of the $\Delta\nu_{OH}$ values is less than ± 20 cm^{-1}.

The few available data on the adsorption of bases in groups II–IV gave $\Delta\nu_{OH}$ values lower by 100–200 cm^{-1} than the $\Delta\nu_{OH}$ values for group I bases at the same pK_a. This is consistent with the above conclusion that the correlation between pK_a and the characteristics of the acids (or bases) applies only within a single group of compounds.

Eqn.(8) is physically analogous to (6), since the factor 530 cm^{-1} is determined by the strength of the Aerosil (or other acid) and is proportional to P_i, and the term $10^{0.026}\,pK_a^{base}$ is proportional to E_j.

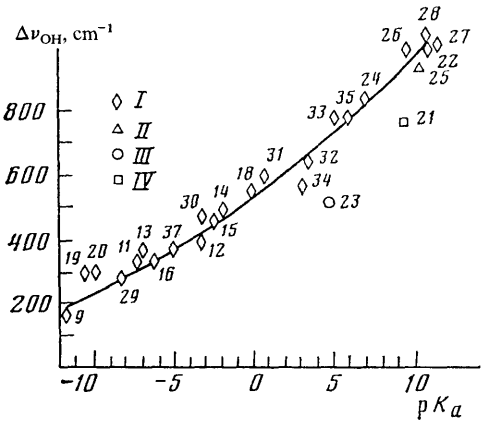


Figure 5. Dependence of $\Delta\nu_{OH}$ for the hydroxyl groups of Aerosil on the pK_a value of adsorbed bases: (*I*) bases from group I, (*II*) from group II, (*III*) from group III, (*IV*) ammonia. The numbering of the points corresponds to Table 3.

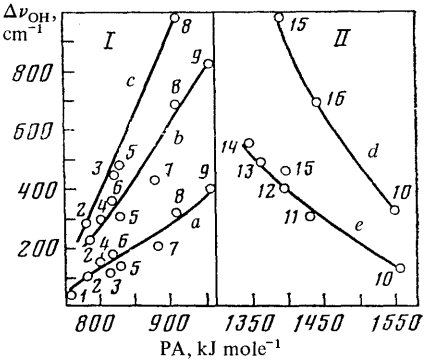


Figure 6. Dependence of $\Delta\nu_{OH}$ of the H-complexes on the PA of the bases (*I*) for t-butanol (*a*), 4-fluorophenol (*b*), and 4-nitrophenol (*c*), and on the PA of the acids (*II*) for acetone (*d*) and pyridine (*e*) in non-polar solvents. The numbering of the points denotes the base: *1*) nitromethane, *2*) acetonitrile, *3*) acetone, *4*) dioxan, *5*) diethyl ether, *6*) tetrahydrofuran, *7*) dimethylfluoramide, *8*) pyridine, *9*) triethylamine, *10*) t-butanol, *11*) acetic acid, *12*) chloroacetic acid, *13*) dichloroacetic acid, *14*) trifluoracetic acid, *15*) 4-nitrophenol, *16*) 4-fluorophenol. Data from Refs.88, 89, 99, and 100 were used.

Until recently there had been no attempt to find a correlation between $\Delta\nu_{OH}$ of the H-complex and the PA of acids or bases. Fig.6 shows the dependence of $\Delta\nu_{OH}$ for the H-complexes of some acids on the PA of bases (I), and for the complexes of some bases on the PA of acids (II) in non-polar

solvents, calculated from published data[89,90,99,100], with PA values taken from Refs.59–74. The dependences are practically linear, and the $\Delta\nu_{OH}$ values increase with the PA of the base, the slope of curves showing a marked increase as we change from the weak acid t-butanol (curve *a*) to the stronger acids 4-fluorophenol (curve *b*) and 4-nitrophenol (curve *c*). The $\Delta\nu_{OH}$ values decrease as the PA of the acid increases.

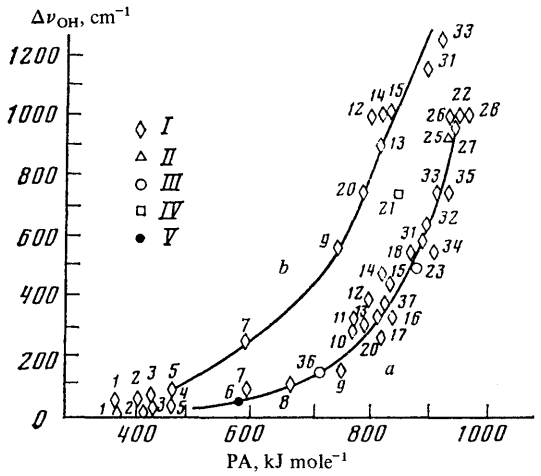


Figure 7. Dependence of $\Delta\nu_{OH}$ for H-complexes on the PA of adsorbed bases. Curve *a* refers to Aerosil, curve *b* to HNaY zeolite: (*I*) bases of group I, (*II*) group II, (*III*) group III, (*IV*) ammonia, (*V*) cyclohexane on Aerosil. The numbering of the points corresponds to Table 3.

We have observed[94] a correlation between $\Delta\nu_{OH}$ for the solid acids Aerosil and HNaY zeolite and the PA of adsorbed bases (Fig.7). For both acids, with $\Delta\nu_{OH} < 400$ cm^{-1} (weak hydrogen bond), the dependence is described by the equation

$$\Delta\nu_{OH} = \alpha' \cdot 10^{0.0036(\pm 0.0002)PA^{base}} \qquad (9)$$

where α' is a coefficient dependent on the properties of the acid. Changing from SiO_2 to a stronger acid (HNaY zeolite) causes α' to increase. Eqn.(9) also is similar to (6), with α' functionally related to P_i and the term $10^{0.0036}$ PAbase related to E_j. From Eqn.(9) we can find the PA of the base from the $\Delta\nu_{OH}$ values with a precision of ±20 kJ mole^{-1}.

For $\Delta\nu_{OH} > 400$ cm^{-1} we again find a clear correlation between $\Delta\nu_{OH}$ and PA^{base}. For bases with a PA between 850 and 960 kJ mole^{-1} the variation of $\Delta\nu_{OH}$ of Aerosil (say) with the PA of the base is accurately linear. With the exception of ammonia, all the bases (groups I–III) in Fig.7 accurately lie on the curves *a* or *b*. However, since the study of strong hydrogen bonds is often complicated by Fermi resonance[95], and since a base forming weak bonds can always be found for any solid acid (see Table 3), we shall confine our discussion to weak bonds.

Let us examine in detail the reported functional relationships between *b*, P_i (i.e. $\Delta\nu_{OH}$) and the pK_a or PA values of acids. The $\Delta\nu_{OH}$ values of silica gel, magnesium oxide, phosphoric acid, and B_2O_3 (on silica gel) have been measured[101] for the interaction with various aromatic compounds, CCl_4, and oxygen- or nitrogen-containing bases, and also $\Delta\nu_{OH(PhOH)}$ in a solution of CCl_4 in the presence of the same bases, in order to determine $\Delta\nu_{OH}^{sol}/\Delta\nu_{OH(PhOH)}$. At the same time the P_i values were obtained for non-aqueous solutions of the H-complexes of the acids and bases, and their dependence on the pK_a of the acids was analysed. Lastly, assuming that the same relationship is retained in heterophase systems, the pK_a values for the OH groups of Aerosil and magnesium oxide were obtained from the plot of P_i against pK_a and the $\Delta\nu_{OH}^{sol}/\Delta\nu_{OH(PhOH)}$ values. The results were +7 and +15.6 respectively.

A similar approach, with a wider range of P_i values for the acid solutions, has been used[102] to calculate the strength of the protonic centres in amorphous alumina-silicas. The pK_a value of the most acidic OH groups in this material was found to be $-(6 \pm 2)$.

It was also found[91,92] that in practice only the parameter *a* of Eqn.(7) depends on the strength of the acidic centre. This means that for a strong H bond the $\Delta\nu_{OH}$ value is determined (by an additive formula) by the strength of the acid and of the base. Since the relationship between *a* and pK_a^{acid} for a strong H bond in solution is not known, it may be described approximately by an expression analogous to Eqn.(7). Taking the value[101] of +7 for the pK_a of the OH groups in Aerosil we obtained[91,92] the following expression for calculating the strength of acidic surface OH groups on the pK_a scale to a precision of ±2.5 pK_a units:

$$\frac{\Delta\nu_{OH}}{\nu_{OH}^0} = 0.216 - 0.0096(\Delta pK_a) \qquad (10)$$

where $\Delta pK_a = pK_a^{acid} - pK_a^{base}$.

Table 4. Strength of the Brønsted acid centres, measured by different methods.

Method*	HNaY zeolite and alumina–silica	P_2O_5 on SiO_2 and on M_xO_y	SiO_2	MgO
Weak H-bond method, in pK_a units	−6	−0.4	+7	+15
Strong H-bond method, in pK_a units	−9	−5	+7	—
Weak H-bond method, on the PA scale (kJ mole^{-1})	1200	1300	1390	1560(±40)

* The methods are described in the text.

We have used Eqn.(10) to determined pK_a for the OH groups of HNaY zeolite and of metal phosphates (Table 4). We also studied[94] the correlation between the P_i values averaged over many bases in non-aqueous solutions and the PA for a series of acids (Fig.8). For oxygenated acids in $\lg P_i$—PA co-ordinates the dependence is accurately fitted by the straight line.

$$\lg P_i = \lg\beta + 0.00226(\pm 0.00016)\,PA^{acid} \qquad (11)$$

or, from the definition of P_i,

$$\Delta\nu_{OH}^{B} = \beta \cdot \Delta\nu_{OH(PhOH)}^{B} \cdot 10^{0.00226(\pm 0.00016)PA^{acid}} \qquad (12)$$

We note that the coefficient β, being the value of P_i at PA = 0, is independent of the strength of the base B. Eqn. (12) is valid for any B, but is assumes that $\Delta\nu_{OH}$ and

$\Delta\nu_{OH(PhOH)}$ have been measured for the interaction of the respective acids with the same base. By using this equation we can measure $\Delta\nu_{OH}$ and $\Delta\nu_{OH(PhOH)}$ in non-aqueous solutions and hence obtain the PA of the acid to a precision (defined as the standard deviation of P_i in Fig.8) better than ±25 kJ mole^{-1}. Eqn.(12) was assumed to be equally applicable to hetero-phase systems[94]. In other words, it was assumed that the points for which $P_i = \Delta\nu_{OH}^{sol}/\Delta\nu_{OH(PhOH)}$ could be included in the plot of Fig.8. By writing Eqn.(12) for SiOH(SiO_2) and for the solid acid OH†, and by dividing one expression by the other, we can eliminate the term $\beta.\Delta\nu_{OH(PhOH)}$, and solving for PA^{acid} we arrive at the following expression for PA:

$$PA^{OH} = PA^{SiOH} - \frac{1}{0.00226}\lg\frac{\Delta\nu_{OH}^{B}}{\Delta\nu_{OH(SiO_2)}^{B}} \qquad (13)$$

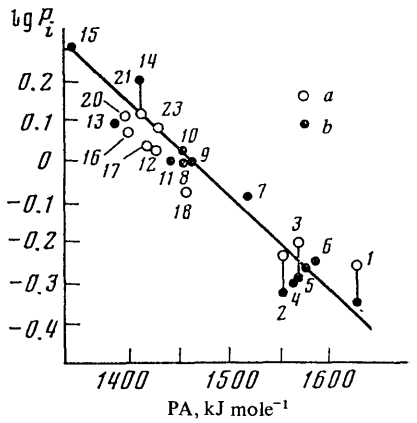


Figure 8. Correlation between lg P_i and the PA of the corresponding acids: *1*) water, *2*) t-butanol, *3*) isopropanol, *4*) n-propanol, *5*) ethanol, *6*) methanol, *7*) 2-trifluoroethanol, *8*) phenol, *9*) 4-methylphenol, *10*) 3-methylphenol, *11*) 4-fluorophenol, *12*) 4-chlorophenol, *13*) 4-nitrophenol, *14*) benzoic acid, *15*) trifluoroacetic acid, *16*) 4-nitrophenol, *17*) 3-chlorophenol, *18*) 4-methoxyphenol, *19*) acetic acid, *20*) chloroacetic acid, *21*) 3-methoxybenzoic acid. Points *a* from Ref.87, points *b* from Ref.102, PA values from Refs. 59, 66, and 73.

By changing to a new standard (Aerosil, with a PA of 1390 kJ mole^{-1} determined[102] according to Eqn.(11) (Fig.8) for $P_i = 1.2$)[102] we can not only avoid the need to calculate β and $\Delta\nu_{OH(PhOH)}$ when using different bases B, but also use a much wider range of bases. This is because phenol does not form stable H-complexes with some of the bases most commonly used to study solid acids, such as CO, probes No.1–6 in Table 3, etc.

To calculate the PA values of solid acids by Eqn.(13) we need to know $\Delta\nu_{OH}$ for the interaction of the base B on SiO_2 and on the solid acid under study. Like Eqn.(12), Eqn.(13) is valid only for oxygen acids. The precision of the determination of the PA by Eqn.(13) is ±25 kJ mole^{-1}. As the data in Fig.7 show, the choice of the base B cannot be arbitrary, since for $\Delta\nu_{OH} > 400$ cm^{-1} the logarithmic relationship between the PA and $\Delta\nu_{OH}$ ceases to apply. The study of the acidity of the OH groups on solids by using Eqn.(13) or the P_i–pK_a^{acid} correlation (which is limited in practice to the range of $\Delta\nu_{OH}$ values from 0 to 400 cm^{-1}) has been called the weak hydrogen bond method, whereas the study by Eqn.(10) is known as the strong hydrogen bond method.

By using Eqn.(13) we have shown[94] that the PA of the OH groups in decationated HNaY zeolite is 1200 kJ mole^{-1}. The difference in PA between Aerosil and zeolite is consistent with quantum-mechanical calculations[103].

Thus we can compare the different methods of determining the strength of acidic centres by listing their results for given systems (Table 4). On the whole all the methods yield similar sequences for the strength of the OH groups on different substances, but the last method [using Eqn.(13)] offers a higher relative precision in the determination of the parameter of interest.

It follows that the weak hydrogen bond method of determining the PA value can be recommended both from the point of view of the quantity used to characterise the protonic centres and of the precision obtainable. All three methods rely on doubtful assumptions, of which the least satisfactory are:

1) the assumed equality of the scales of "influence" of the pK_a values of acids and bases on $\Delta\nu_{OH}$ [91,92] in the strong hydrogen bond method, which seriously restricts the general validity of Eqn.(10), and

2) the need to define three groups of acids (I–III in Fig.4) in describing the dependence of pK_a on P_i. On the other hand the main assumption of the third method (which is made also in the second method) that the dependence of P_i on PA^{acid} is the same for P_i values obtained in non-aqueous solutions and in the adsorption of bases on solid acids appears to be confirmed, since the $\Delta\nu_{OH}$ values obtained in the gas phase are not very different from those obtained in solutions from ν_{OH}^{0} and ν_{OH}^{B} measurements in the same solvent.

b) *Determination of the concentration of protonic centres.* The concentration of protonic centres can be determined in various ways during the measurement of the strength of the centres by the hydrogen bond method. The simplest consists in measuring the integral intensity or the optical density of the ν_{OH} bands (in arbitrary units, normalised for $\rho = 1$) before interaction with the molecules of the base B. This approach has been used[30,31] to study the influence of the composition of zeolites on the concentration of hydroxyl groups: the result was that OH groups with $\nu_{OH} = 3640$ cm^{-1} are involved in the catalytic action of these materials. In a study of the acidic and catalytic properties (towards the formation of acrylonitrile) of TiO_2–Sb_2O_5 oxide catalysts the changes in the D/ρ ratio for the ν_{OH} bands showed that the concentration of acidic OH groups ($\nu_{OH} = 3730$ cm^{-1}) decreases as the concentration of Sb_2O_5 increases, and that the catalytic reaction on these centres is mainly in the direction of destructive oxidation of propene[52]. Thus even this very simple approach can yield important information on the nature of the catalytically active centres.

In some cases (for example, in amorphous alumino-silicate systems) OH groups of different strength have almost identical ν_{OH} values and the measured intensity of the band corresponds to the total number of centres. In this case the changes in concentration of the different centres can be monitored by measuring the intensity of the OH stretching vibration bands, which are shifted by the formation of an H bond with a B molecule (ν_{OH}^{B}). This type of analysis is reported in Ref.104.

† This term denotes the surface of any solid containing acidic OH groups.

The absolute concentration of OH groups can be determined when the integral molar absorption coefficients (A_0) of the ν_{OH} bands are known. Unfortunately, these coefficients are known only for a very few substances at present. Hughes and White[28] found that the A_0 value for the ν_{OH} 3640 cm^{-1} band of HNaY zeolite is 12.2 cm $\mu mole^{-1}$, whereas for the 3550 cm^{-1} band it is 19.5 cm $\mu mole^{-1}$. For Aerosil the value $A_0 = 9.8$ cm $\mu mole^{-1}$ has been reported[105].

The total number of OH groups can be deduced from the weight loss of the catalyst after heat treatment[18], but it may be difficult to distinguish the true surface OH groups from the co-ordinated or physisorbed water. The concentration of surface OH groups accessible to adsorbed molecules can be identified by specific chemical reactions for water: these methods are fully discussed in Ref.106. However, this approach only gives the total number of OH groups, and even if combined with a full analysis of the spectra it cannot yield the A_0 coefficients for the different classes of OH groups.

A determination of A_0 for the OH groups of zeolite by "titration" with pyridine and piperidine has been reported[28]. Unfortunately, when the strength of the protonic centres was insufficient to form the pyridinium ion, or if the centres were not accessible to the pyridine molecules, or in the presence of a large number of aprotic centres, the method was found to be inapplicable. Methods relying on H–D exchange can also be used. Knowing the total amount of deuterium in the cell, and the degree of exchange of H by D in the OH groups when the isotope exchange reaction comes to equilibrium, the concentration of OH groups can be calculated. A detailed account of these methods is given in Ref.107.

When the concentration of OH groups has to be inferred from the intensity of the stretching vibration bands of the hydroxyl groups (shifted by hydrogen bond formation) the dependence of A_0 on $\Delta\nu_{OH}^{B}$ must be known. There is substantial evidence[82,89,90,99,100,105] of the existence of a functional relationship between ΔA_0 (where $\Delta A_0 = A_0^{H\text{-bond}} - A_0$) and $\Delta\nu_{OH}^{B}$ for a wide range of acids and bases.

3. The Ion Pair Method

a) *Physicochemical basis of the method.* As was pointed out above, the ion pair method consists in studying the transfer of a proton to the adsorbed base with formation of an ion pair, which can be represented by reactions (V) and (VI) followed by association of the A^- and HB^+ ions. Therefore the heat of protonation of the base on the surface can be described by the expression

$$Q_{IP} = PA^{base} - PA^{acid} - \Delta H_{ass}. \qquad (14)$$

Using the adsorption of pyridine on HNaY zeolite as an example we shall examine the possible contributions of the various terms to the parameter Q_{IP} (according to the data in Ref.108, $Q_{IP} = 170$ kJ $mole^{-1}$). For pyridine PA = 912 kJ $mole^{-1}$ (Table 3), and for the acidic centres of the zeolite the PA found by the weak hydrogen bond method is 1200 kJ $mole^{-1}$. Hence Eqn.(14) gives $-\Delta H_{ass} = 460$ kJ $mole^{-1}$, which is comparable (in order of magnitude) to the PA of the base.

In a series of chemically similar catalysts interacting with the same base we can expect ΔH_{ass} to be almost constant. In this case the difference between the Q_{IP} values for two catalysts will be approximately equal to the difference between PA values of their OH groups.

An approach essentially similar to the above was first discussed in Refs.53 and 109. Direct measurements of Q_{IP} can be made calorimetrically[2], though the type of centre on which the probe molecules are adsorbed cannot be identified without spectroscopic control. We have suggested[108] a method of measuring Q_{IP} for pyridine by analysing the ν_{OH} bands of the surface OH groups (the IPT method). From the change in intensity of the stretching vibrations of the free OH groups the adsorption isobars of pyridine on HNaY zeolite and on zirconium phosphate were measured at 4 mmHg pressure and temperatures between 423 and 723 K. The heat of protonation of pyridine on zeolite was 170 ± 15 kJ $mole^{-1}$, and on zirconium phosphate 65 ± 10 kJ $mole^{-1}$.

Historically, however, the first method used to study the proton-donor properties of solid acids was the indicator method outlined above[4]. Since on a surface the protonated indicator consists of an ion pair with an oxygen anion (rather than, as in a solution, of an ion solvated by solvent molecules) we shall classify this method as one variant of the IP method. The basic propositions of the indicator method are fully described by Benesi[5,110], and his method of visually determining the protonation of the indicator from the change in colour of the system was used by later workers almost without change. We shall only refer to publications containing new view-points or results. Refs.111 and 112 appear to be the first report of an attempt to analyse quantitatively the relationship between the H_0 value of the OH groups on catalyst surfaces and the rate constants of heterogeneous chemical reactions.

At about the same time it was found[113,114] that in some systems (for example, zeolite cracking catalysts and alumina–silicas) the Hammett indicators cannot distinguish between protonic and aprotic centres and give the same colour for both. It was suggested that the acidity of proton-containing surface centres could be determined by using indicators which form carbonium ions on the surface, the strength of the centre being calculated by the function

$$H_R = -\lg a_{H^+} + \lg a_{H_2O} + \lg (f_{R^+}/f_{ROH}) \qquad (15)$$

Similar problems stimulated other workers[115,116] to improve the indicator method by abandoning the visual observation of colour changes, and replacing it by measurements of the diffuse reflectance spectra of the catalyst surface covered with an adsorbed base. The same workers[115,116] were the first to use an indicator adsorbed not from solution in a non-polar solvent but from the gas phase. A more detailed discussion of this approach is given in Ref.117. Both in that work, and in later work[118], the strength of the acid centres was determined from the minimum value of pK_a for the base being protonated, the second term in Eqn.(5) being either ignored without comment or assumed[118] to be close to unity. However, the assumption appears to be incorrect[117], and in general the $[BH^+]/[B]$ term in Eqn.(5) can be quite small, making the H_0 value determined as $H_0 = pK_a^{base}$ much too low and the acidity of the OH groups on the surface much too high. We should stress that equating pK_a for the acid to pK_a for the indicator is legitimate only when the number of molecules of the base B in the system is equal to the number of OH groups, and the latter are 50% ionised. In practice no attempt is made to check whether these conditions apply. The first attempt to allow for the concentration term in Eqn.(5) led to the conclusion[119] that the pK_a scale of the base is not a suitable basis for measuring the acidic properties of the surface.

We have recently described[120,121] the development of an i.r. spectroscopic method of identifying the formation of an ion pair. Its main advantage over methods in the u.v. and the visible region of the spectrum is that the formation of

ion pairs, their adsorption on aprotic centres, and the formation of a hydrogen bond by the B molecules are all readily distinguished by their i.r. spectra, so that in principle the concentrations of BH^+ and B can be measured by analysing the intensities of the ν_{OH} bands and the characteristics of the bands in the spectrum of BH^+. However, in practice the calculation of $[BH^+]/[B]$ from the i.r. spectra is complicated by the lack of reliable data on the extinction coefficients (or on A_0) for the characteristic bands of the various adsorbed forms of the base B.

We should stress that the principles of Benesi's method were not questioned in any of the investigations mentioned above (except Ref.119). Though many of the results obtained made the method appear incorrect (see references quoted by Deeba and Hall[122]) no attempt was made to analyse the discrepancies before the paper[122] drew attention to them. It should not be forgotten that the indicator method of measuring acidity postulates not only constancy of the ratio f_B/f_{BH^+} but also maintenance of the equilibrium $B_{ads} + H^+ \rightleftharpoons BH^+_{ads}$ at all times, and independence of H_0 on the concentration of B. Accurate quantitative work[122] showed that on a surface this equilibrium is not reached. Taking a strong base (n-butylamine) in an amount much smaller than the total number of OH groups on the surface we find that the molecules of the base do not distribute themselves over the surface so as to be protonated by the most acidic centres: they remain on the acidic centres (both strong, and weak) with which they first came into contact. Similar effects occur with other bases. Therefore the amount of base which is protonated depends (among other things) on the physical conditions of the experiment (temperature, flow rate and amount of B, size of pores on the surface, etc.). These effects explain the reported discrepancies[119], and they suggest that the alternative approach to the study of catalyst surfaces should be preferred[4,5,110].

It has been pointed out[122] that the strength of acidic centres could be measured from the heat of desorption of a base (E_d) previously adsorbed on the surface (the adsorption being irreversible at the given temperature). The concentration of centres having different strengths can be estimated from the amounts of irreversibly adsorbed molecules of base B of different basicity. This approach is a natural development of the calorimetric method proposed earlier (see Ref.123, and list of references in Forni's review[3]).

Thus the H_0 values of the acidic centres on the surface obtained by the ion pair method need critical scrutiny. They are unacceptable as a measure of the acid strength of a surface centre. At best they can give an indication of the relative acidity of the centre. Isolated examples[2,118,124] of the successful use of this method can be explained by the fortuitous similarity of the concentrations of acidic centres on the different catalysts, the use of compounds of a given class as probe molecules, and the constancy of the indicator adsorption conditions, the aim of the experiment in every case being not to produce reliable values of H_0 but to assign a given solid acid correctly within a series of similar compounds in order of increasing acid strength.

The shortcomings of the proposed[122] method of determining the acid strength and the number of centres of a given strength include the failure to distinguish between the different adsorption forms of the molecules of the bases B. If the base is adsorbed irreversibly also on the aprotic centres at ordinary temperatures, its desorption from those centres may invalidate the results of the measurement of the heat of desorption from the H-centres. Furthermore, E_d is not so universal a parameter as the PA.

We therefore consider the most promising approach to be a combination of measurements of heat of adsorption (or desorption) and of measurements by i.r. spectroscopy of the number and nature of different compounds formed by the B molecules with the surface centres. Since the relative precision of the measurement of Q by the IPT method is ±10% the method could advantageously be combined with more accurate, purely calorimetric measurements. The advantages of using i.r. spectral methods are even more evident in studies of reaction mechanisms for different bases on catalyst surfaces.

A convenient indication of the formation of ion pairs is obtained by using nitrogen bases (Nos.21-37 in Table 3), because protonated amines and pyridines are easily distinguished from the unprotonated bases by their i.r. spectra. On the other hand, since these bases can also form D–A complexes with L centres (which are invariably present on the surface), and since the i.r. spectra of these complexes[28] are often similar to those of protonated bases, the identification of the formation of ion pairs is only seldom unambiguous. Clear identifications have been made only by using ammonia, pyridine[18,23], and some derivatives of pyridine[121]. The use and the properties of some other probes are discussed in Refs.125–127.

b) *Determination of the concentration of protonic centres.* In studies of protonic centres by the IP method the concentration of the centres can be determined not only from the intensity of the ν_{OH} bands (as discussed above) but also from the intensity of the bands of the BH^+ ions. Hughes and White[28] have measured the A_0 coefficient for the 1540 cm^{-1} band, assigned to the pyridinium ion. By using A_0 values we can determine the concentration of proton centres on zeolites and zeolite-containing catalysts.

The integral absorption coefficients for some absorption bands of 2,6-lutidine adsorbed on protonic centres have been measured[29]. We should note that in practical studies of adsorption all the protonic centres should be filled (if the stoichiometry of the interaction is known). The possibility of departures from the stoichiometric OH : B ratio of 1 : 1 has been demonstrated[33]. In some cases the role of the protonic centres in catalytic reactions can be identified simply by studying the dependence of the intensity of the 1540 cm^{-1} band of adsorbed pyridine on the preparation conditions of catalysts of a given composition or of a series of catalysts of different composition but similar properties [30–32].

4. Method of Calculating the Strength of Protonic Centres on the Scale of the Activation Energy of the Proton Transfer Process

The method proposed[79–81,128] for determining the activation energy of the transfer of the proton (E_a^H) from the acidic centre to the base in the H-complex assumes that the dependence of the potential energy of the system on the O–H distance can be fitted by a Morse function, and that the distribution of vibrational levels can be described in the isolated diatomic molecule approximation. In this case the energy needed for complete removal of the hydrogen from oxygen (i.e. the dissociation energy) is given by the expression

$$D_0 = \frac{\omega_e}{4x} - \frac{\omega_\varepsilon}{2} \qquad (16)$$

where x is the anharmonicity coefficient [$x = (2\omega_{0\to1} - \omega_{0\to2})/2\omega_e$], ω_e is the harmonic frequency ($\omega_e = 3\omega_{0\to1} - \omega_{0\to2}$), and $\omega_{0\to1}$ and $\omega_{0\to2}$ are the observed frequencies of the fundamental i.r. transition and of the first overtone (in the symbols used in Ref.128). It is also assumed that these expressions can be used to determine the dissociation energy of the hydrogen in the -O-H...B complex ($D_{0,\mathrm{eff}}$), and that $D_{0,\mathrm{eff}}$ is the upper limit of E_a^H. The parameter $D_{0,\mathrm{eff}}$ was calculated for several H-complexes of Aerosil with different bases: with bases having PA < 700 kJ mole^{-1} ($\Delta\nu_{OH} \leqslant 70$ cm^{-1}) the perturbation of the O-H bond is slight and $D_{0,\mathrm{eff}}$ is independent of the strength of the base. At the same time with bases whose PA lies between 700 and 850 kJ mole^{-1} ($\Delta\nu_{OH} \cong$ 200-350 cm^{-1}) $D_{0,\mathrm{eff}}$ was found to decrease with increase of PA. It was shown that varying the base has little effect on ω_e, and it was suggested that ω_e should be treated as a constant, thus allowing $D_{0,\mathrm{eff}}$ to be calculated simply from the correlation between E_a^H and $\Delta\nu_{OH}$. By using the latter approximation the $D_{0,\mathrm{eff}}$ values were obtained for several H-complexes of bases with the OH groups of Aerosil (505 kJ mole^{-1}) and zeolite (545 kJ mole^{-1}), and compared with the activation energies of proton transfer calculated from catalysis data. The activation energy of the deuterium-hydrogen exchange on OH groups is 105-118 kJ mole^{-1}: the calculated value of E_a^H for this reaction is 126-146 kJ mole^{-1}.

Data on the adsorption of various amines and isobutanol have also been compared. In the adsorption of n-butylamine on Aerosil[120] $\Delta\nu_{OH}$ is 1050 cm^{-1} and in the adsorption of pyridine on HNaY zeolite[120] it is 1250 cm^{-1}. The interaction of the alcohol with zeolite[120] shifts ν_{OH} by 1000 cm^{-1}. The calculated values[79-81] of the three paramters lie in the range $E_a^H = 68$-78 kJ mole^{-1}, whereas the experimental values of the activation energy of proton transfer from zeolite are $\leqslant 8$ kJ mole^{-1} for pyridine and 88 kJ mole^{-1} for the alcohol[120]. n-Butylamine is not usually protonated on Aerosil.

Thus calculations by this method for both large ($\geqslant$1000 cm^{-1}) and small ($\leqslant$70 cm^{-1}) values of $\Delta\nu_{OH}$ are inconsistent with experiment. For large values of $\Delta\nu_{OH}$ this discrepancy may be due to the inadequacy of the diatomic molecule approximation when applied to strong H-complexes. In the intermediate range of $\Delta\nu_{OH}$ values the method gives reasonable values of E_a^H.

In conclusion we note that in spite of the useful information on the ability of a catalyst to interact with a stated substance implicit in a knowledge of E_a^H this quantity is largely determined by the properties of the adsorbate and cannot be used as an independent measure of the acidic properties of the surface. Of course, solid acids can be arranged in order of increasing proton-donating power in terms of their E_a^H values for the same base B. However, the data needed for this assignment are not available, and in any case such a sequence could make the base B a model compound for acids which (for various reasons) do not catalyse its reactions, thus depriving the criterion of its main advantage. Lastly, of course, the mechanism of the reaction must be known before E_a^H can be meaningfully used.

For these reasons we consider the thermodynamic methods to be the only acceptable approach to the solution of these problems, since they allow the acidic properties of the surface to be calculated in terms of a constant which characterises the substance. We believe this information to be an essential basis of any mechanism used to explain the effect of the composition and structure of catalysts on their surface properties. The kinetic approach can also be useful, but only at the stage of detailed study of the mechanism of a specified catalytic reaction.

IV. METHODS OF STUDYING BASIC CENTRES

1. General Formulation of the Problem

The interaction of acids with basic centres (like the interaction of bases with acidic centres) probably takes place in two steps:

$$HX + B_s \to B_s \ldots HX \to B_s H^+ \ldots \bar{X} \qquad \text{(VII)}$$

By analogy with the determination of the acidic properties, the basicity of a surface can be studied by the H-bond method and by the IP method. It is again convenient to characterise the strength of the centres through their PA, and to use the pK_a values only within defined groups of acids.

Thus all the statements made in the above discussion of acidic centres are equally valid (*mutatis mutandis*) in the study of the basicity of surfaces. A suitable choice of probe molecule is extremely important in the development of accurate methods of studying the base properties of catalyst surfaces. The use of carboxylic acids and phenols is complicated by a number of factors. Firstly, the acids and phenols have fairly well developed acceptor properties (pK_a between -7 and -4,[77] PA = 750-800 kJ mole^{-1} [59]) which allow them to form D-A complexes with aprotic centres. Secondly, the most commonly used adsorbents and catalysts have surface OH groups whose i.r. absorption bands overlap the ν_{OH} bands of the acids and phenols which are sensitive to the interaction with B_S. Thirdly, if strong protonic centres are present on the surface they can cause the formation of surface esters[129], with spectral characeristics similar to those of the surface complexes of B_S with acids or phenols.

The proton-acceptor properties of surfaces can be assessed by using NH acids (in particular, pyrrole[130]), which form hydrogen bonds with the basic centres on the surface. However, the high proton affinity of the pyrrole nitrogen can cause complications (interaction of the nitrogen with the OH groups).

We have shown[131] that CH acids (in particular, $CDCl_3$) can be used as probes. The method relies on the ability of $CDCl_3$ to form H-complexes with bases[82,132]. The main advantage of this method is that hydrocarbons and their halogen derivatives are weak bases, and their interaction with aprotic or protonic surface centres is negligible. Furthermore, the ν_{CH} (or ν_{CD}) bands do not overlap the bands of the surface OH groups, and therefore the complexes of the probes with the basic centres are easily indexed.

Thus only the H-bond method has been widely used so far, and mainly in experiments with $CDCl_3$. The ion pair method has not been developed towards the study of basic centres. On the whole the search for suitable probes and the development of new methods of investigation present more serious difficulties in the study of basic centres than for protonic or aprotic (acid) centres.

2. Physicochemical Basis of the Method

By using published data[133,134] we have established[131] a correlation between the pK_a values of bases and $\Delta\nu_{CD}$ for deutero-chloroform. The relationship has been used as a calibration plot to determine pK_a for basic surface centres, and it was found that the strength of basic centres in oxides increases in the series γ-$Al_2O_3 < MgO \cong BeO < CaO$. At least two types of centre were shown to be present on the surface of these oxides: weak basic centres, possibly consisting of OH groups, and strong centres, thought to be associated

with the presence of a bridging oxygen atom M–O–M. By using the pK_a scale the basic properties of Fe/Sb catalyst were investigated[26], and two types of centre were again identified.

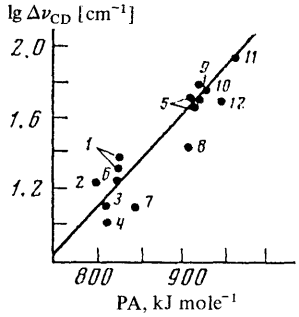


Figure 9. Dependence of lg $\Delta\nu_{CD}$ ($\Delta\nu_{CD} = \nu_{CD} - \nu_{CD}^{gas}$) for deutero-chloroform on the PA of bases forming a hydrogen bond to it. The data[60,70,71,133–135] are for: *1*) diethyl ether, *2*) dioxan, *3*) ethyl acetate, *4*) acetone, *5*) pyridine, *6*) tetrahydrofuran, *7*) ammonia, *8*) methylamine, *9*) dimethylamine, *10*) trimethylamine, *11*) triethylamine, *12*) 2,6-dimethylpyridine. The points *1*, *5*, and *9* are typical examples of the scatter of published $\Delta\nu_{CD}$ data.

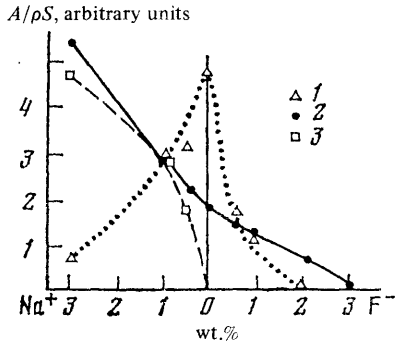


Figure 10. Variation of the relative concentrations ($A/\rho.S$) of basic centres on γ-Al_2O_3 samples modified by Na^+ or F^- ions for different PA values: *1*) 897, *2*) 810, *3*) 927 kJ mole^{-1}.

An attempt to extend the observed correlation[131] between the $\Delta\nu_{CD}$ values and the pK_a of the bases to $\Delta\nu_{CD}$ data from Ref.135 showed that methylamine and ammonia (i.e. bases from groups III and IV) cannot be included in the correlation. However, the data can all be included in a unified relationship if $\Delta\nu_{CD}$ is plotted against the PA of the base. The dependence (Fig.9) is described by the logarithmic equation

$$\lg \Delta\nu_{CD} = 0.0057\,PA - 3.54 \qquad (17)$$

which can be used to determine the PA of the basic centres. The deviation of the $\Delta\nu_{CD}$ values from the correlation curve is less than 15 cm^{-1}.

3. Determination of the Concentration of Basic Centres

Absolute integral intensity data for the $\Delta\nu_{CD}$ bands of adsorbed deutero-chloroform are not available. Therefore, by using the apparent integral intensity of the ν_{CD} band normalised to $\rho = 1$ we can only determine relative concentrations of basic centres of a given strength (i.e. centres having the same ν_{CD} frequency). This simple approach can be very useful, for example in studying the effect of treating Al_2O_3 catalysts with acids or alkalis. Plots of the intensity of the ν_{CD} bands in the spectrum of adsorbed $CDCl_3$ against the type of modifying additive are shown in Fig.10: we note that the addition of Na^+ increases the concentration of basic centres with a PA = 810 kJ mole^{-1}, while centres with PA = 897 kJ mole^{-1} disappear, and new centres with PA = 927 kJ mole^{-1} are created. The addition of F^- lowers the concentration of both strong and weak basic centres, though the effect on the former (PA = 897 kJ mole^{-1}) is more marked. No other method of obtaining this type of detailed information on the properties of basic centres exists.

V. CONCLUSIONS

The results discussed in this review show that the i.r. spectroscopy of adsorbed molecules is a revealing method of studying quantitatively the acidic and the basic properties of surfaces. By using the method with an appropriate choice of probe molecules, and by establishing the functional relationships between the normal vibration frequencies which are sensitive to the interaction with the surface centres and the thermodynamic characteristics of this interaction, we can determine the strength of the protonic, aprotic, and basic centres. The concentrations of acidic centres can be determined also by combined i.r. and adsorption measurements.

According to our experience, the following sequence of operations can be recommended for rating the acid–base properties of substances.

1) Carry out the adsorption of benzonitrile, and from the position of ν_{CN} in the absorption spectrum determine the number and type of cations acting as aprotic centres.

2) Carry out the low-temperature adsorption of CO, and measure the strength of the aprotic centres on a heat of adsorption scale. Using published data on A_0 for ν_{CO} calculate the number of aprotic centres.

3) Determine the number of different types of protonic centre from the i.r. absorption spectra of the OH groups on the surface of the sample.

4) Carry out the adsorption of a suitable weak base, and by using Eqn.(13) calculate the PA of the protonic centre. Carry out the adsorption of pyridine at different temperatures and from the intensity of the 1540 cm^{-1} band determine the number of H-centres (if PA $\leq$ 1300 kJ mole^{-1}). From the temperature dependence of the band intensity find the heat of absorption and the PA for the H-centres.

5) Carry out the adsorption of $CDCl_3$. Determine the number of types of basic centre, and calculate their PA values from $\Delta\nu_{CD}$. From the integral intensity of the ν_{CD} bands determine the relative numbers of different basic centres.

The further development of methods for the quantitative characterisation of the acid–base properties of surfaces should, in our view, proceed along the following directions: firstly, measuring the integral absorption coefficients for

the characteristic bands of the most commonly used probe molecules, and also for the individual stretching vibration bands of different types of OH group; secondly, extending the range of probe molecules which can be used to identify different types of centre; thirdly, establishing the correlations between the acid–base and the catalytic properties of catalyst surfaces (thus stimulating the practical application of these methods in heterogeneous catalysis).

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