

What is an Acid ?

GROUND CHALK?

LEMON
JUICE?

BORAX AND
WATER?

VINEGAR?

PURE
WATER?

ODA WATER?

SODIUM
BICARBONATE
AND WATER?

AMMONIUM
SULPHATE
AND WATER?

WATER?

← Acid ————— Neutral ————— Alkaline →



Pure water is a neutral substance because, on ionization it gives equal concentrations of hydrogen and hydroxide ions:
 $\text{H}_2\text{O}(\text{aq}) = \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$.
 The ionic product, $K_w = [\text{H}^+][\text{OH}^-]$, is constant both for pure water and for all aqueous solutions. It is equal to 10^{-14} at 25°C . Hence, in pure

water (HOH), $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$ g.ion litre $^{-1}$. The pH is defined as $-\log_{10}[\text{H}^+]$ so that in pure water $\text{pH} = -\log_{10} 10^{-7} = 7$. In alkaline solutions, the hydroxide ion concentration is greater than 10^{-7} g.ion litre $^{-1}$; since K_w is constant, it follows that the hydrogen concentration must fall below 10^{-7} g.ion

litre $^{-1}$. Hence, for alkaline solutions the pH is always greater than 7. Conversely, for acid solutions the pH value is always less than 7. It is important to note that the pH scale, based on the value of K_w , applies only to aqueous systems.

Part one

DEFINING AN ACID

The books in most libraries are divided into fiction and non-fiction. Then, within these main classifications, they may be further divided by subject matter, or date of publication, or alphabetically by the author's last name. By classification of this kind a reader can know what sort of book to expect to find on a particular shelf. Classification also plays an important part in chemistry. Earlier in the course we saw how the chemical elements could be classified under groups in the periodic table. Chemistry is often split into inorganic and organic chemistry. Substances can also be classified according to given properties which they have in common. Two of the most important of these chemical classifications are acids and bases.

The terms 'acid' and 'base' are very familiar, as are several acidic and basic substances, such as sulphuric acid, hydrochloric acid, sodium hydroxide, and many others of the most important industrial chemicals. What do the terms 'acid' or 'base' mean? What qualities does a substance have to have to be an acid or a base? We can start to answer these questions by listing the properties of acids we have noticed in our own experience with them. We know that they taste sour because the citric acid in lemon juice tastes sour as do lactic acid in sour milk and acetic acid in vinegar. Other acids should *not* be tasted because they burn the mouth.

We know also that acids change the colour of some plant dyes – for example, litmus from blue to red.

Many acids react with certain metals to liberate hydrogen.

These experimental facts provide us with our first answer to the question, 'What is an acid?' Any substances that have these properties might be classified as acids. We also know another important property of acids: when they react with bases, they lose their acidic properties. Our description of a



Litmus is made from lichens.
Acids change its colour from blue
to red. *K. L. Alvin.*

base might depend, then, on our description of an acid, and we may classify as bases those substances that make an acid lose its acidic properties.

Experimental descriptions of this kind provide a useful starting point. It was in this way that Robert Boyle classified acids as long ago as 1680. But can we be more exact than this? What makes acids and bases behave as they do? During the past 150 years, several explanations have been put forward – leading, in turn, to several different classifications. We shall be looking at some of these definitions and the corresponding classifications in this book. While reading about them, you might try to determine how useful each definition is; whether, in fact, it is so general as to include substances which are not usually thought of as acids or bases, for example substances that do not change the colour of litmus; or whether it is so narrow as to exclude substances generally thought of as acids or bases, for example substances that do change the colour of litmus. Is any definition so precise as to leave no doubt about whether a given substance is an acid or whether it is a base?

Oxygen versus hydrogen – Towards the end of the eighteenth century, chemists began to develop the means to analyse substances carefully so as to find out exactly what elements they contained. As a result of this work Lavoisier suggested that all acids contained the element oxygen. Oxygen had been discovered a few years before by Priestley in England and by Scheele in Sweden. But it was Lavoisier who called it ‘oxygen’ – from the Greek word meaning acid-former. Lavoisier’s suggestion was successful for acids such as sulphuric and nitric acids. But in 1811, when Davy came to analyse oxy-muriatic acid (the old name for hydrochloric acid), he found

no oxygen. If his analysis was correct, then either hydrochloric acid was not an acid, even though it showed all the properties of one, or the definition of an acid as an oxygen-containing substance had to be changed. Davy proposed that hydrogen, not oxygen, was the essential element in acidic substances. His idea met with considerable opposition from many of the famous scientists of his day, including Berzelius. It was eventually shown not to be sufficiently precise. Some years later Liebig redefined an acid as a compound containing hydrogen that could be replaced by a metal. The connection between hydrogen and acidic properties became generally accepted. It is still accepted in most present-day definitions.

The Arrhenius definition - Towards the end of the nineteenth century, the Swedish chemist Svante August Arrhenius (1859-1927) put forward his ionic theory about the behaviour of electrolytes in water. He was then twenty-four years old. According to his theory, when an electrolyte, a substance capable of conducting an electric current, is dissolved in water, some of the molecules of the substance dissociate into charged particles - anions and cations. The proportion of the molecules that ionize depends upon the nature of the electrolyte, the temperature, and the concentration. As the solution becomes more dilute, the proportion of ionized molecules increases. The ions are responsible not only for conducting electric current through the solution but also for the chemical properties of the solutions.

Almost all the acids and bases we commonly come across are solutions of ionized substances in water. From Arrhenius's theory, an acid could be defined as a compound which contained hydrogen and which ionized in water to give hydrogen ions (H^+). A base was any hydroxy compound which ionized

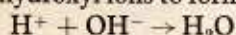


Justus von Liebig (1803-1873) proposed that the replacement of hydrogen by metals was characteristic of acids.

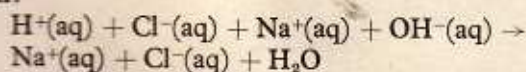
Svante August Arrhenius (1859-1927). *Swedish Institute.*



in water to give hydroxyl ions (OH^-). Water gave a substance its acidic or basic properties by causing it to ionize. Neutralization of acid by base, or base by acid, is a reaction of hydrogen ions with hydroxyl ions to form water:



For example, at ordinary temperatures, pure hydrogen chloride is a gas and does not behave like an acid. In water it forms a solution with acidic properties. It ionizes to give hydrogen ions (H^+) and chloride ions (Cl^-). By the Arrhenius definition, it is an acid. At ordinary temperatures sodium hydroxide is a white solid. In water, it forms a solution with basic properties: it gives sodium ions (Na^+) and hydroxyl ions (OH^-). By the Arrhenius definition, it is a base. An aqueous solution of hydrogen chloride reacts with an aqueous solution of sodium hydroxide to give sodium chloride (present as sodium and chloride ions) and water. This is the neutralization reaction:



The Arrhenius definition is a useful one as long as water is the solvent. It usually is. Some acids and bases are very much stronger than others. Nitric acid for example is much stronger than acetic acid. Strength depends on the proportion of molecules of the acid or base that ionize in the water. In other words, strength depends upon the concentration of the hydrogen ions or hydroxyl ions. This proportion, as mentioned in Arrhenius's ionic theory above, depends upon the interaction of the acid or base with water, the temperature of the solution, and the overall concentration. Nitric acid is much stronger than acetic acid because a much higher proportion of its molecules ionize in water. We can find out the hydrogen ion concentration of an aqueous solution by

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measuring the electrical conductivity of the solution or by observing the effect of the solution on coloured indicators. We express the hydrogen ion concentration in terms of a scale which you have already met, the pH scale. The pH of a solution is defined as minus the logarithm (to the base 10) of the hydrogen ion concentration. This is simpler than it may seem. The $\text{pH} = -\log_{10} [\text{H}^+]$ - where the square brackets [] indicate concentration. For example, if the hydrogen ion concentration of a solution is $0.010 \text{ moles litre}^{-1}$,

$$\text{the pH} = -\log_{10}[0.010] = -\log_{10}10^{-2} = -(-2) = 2$$

Or, if the $\text{pH} = 11.68$

$$-\log_{10} [\text{H}^+] = 11.68$$

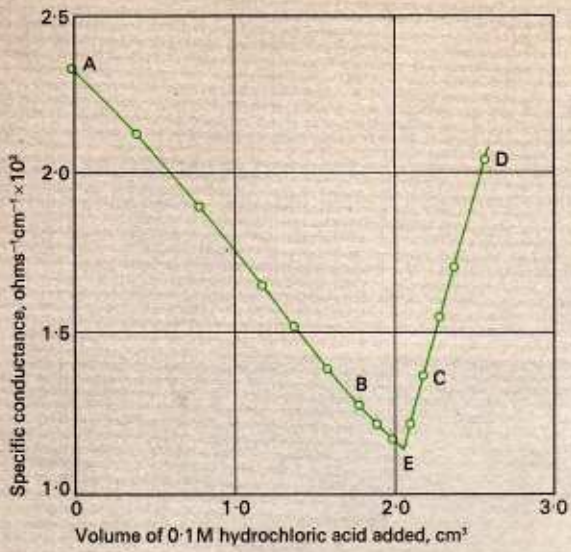
$$\log_{10} [\text{H}^+] = -11.68 = -12.00 + 0.32 = 12.32,$$

The antilog of this gives us the hydrogen ion concentration, i.e.

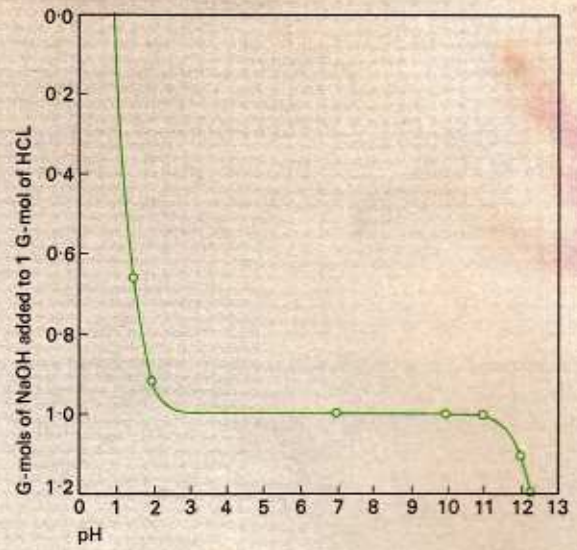
$$[\text{H}^+] = 2.1 \times 10^{-12} \text{ moles litre}^{-1}$$

From the definition, it follows that the higher the hydrogen ion concentration, the lower the pH and vice versa. It is found that the hydrogen ion concentration equals the hydroxyl ion concentration at pH7. Above pH7, the concentration of the hydroxyl ions exceeds that of the hydrogen ions and the solution is basic. Below pH7, the concentration of the hydrogen ions exceeds that of the hydroxyl ions and the solution is acidic.

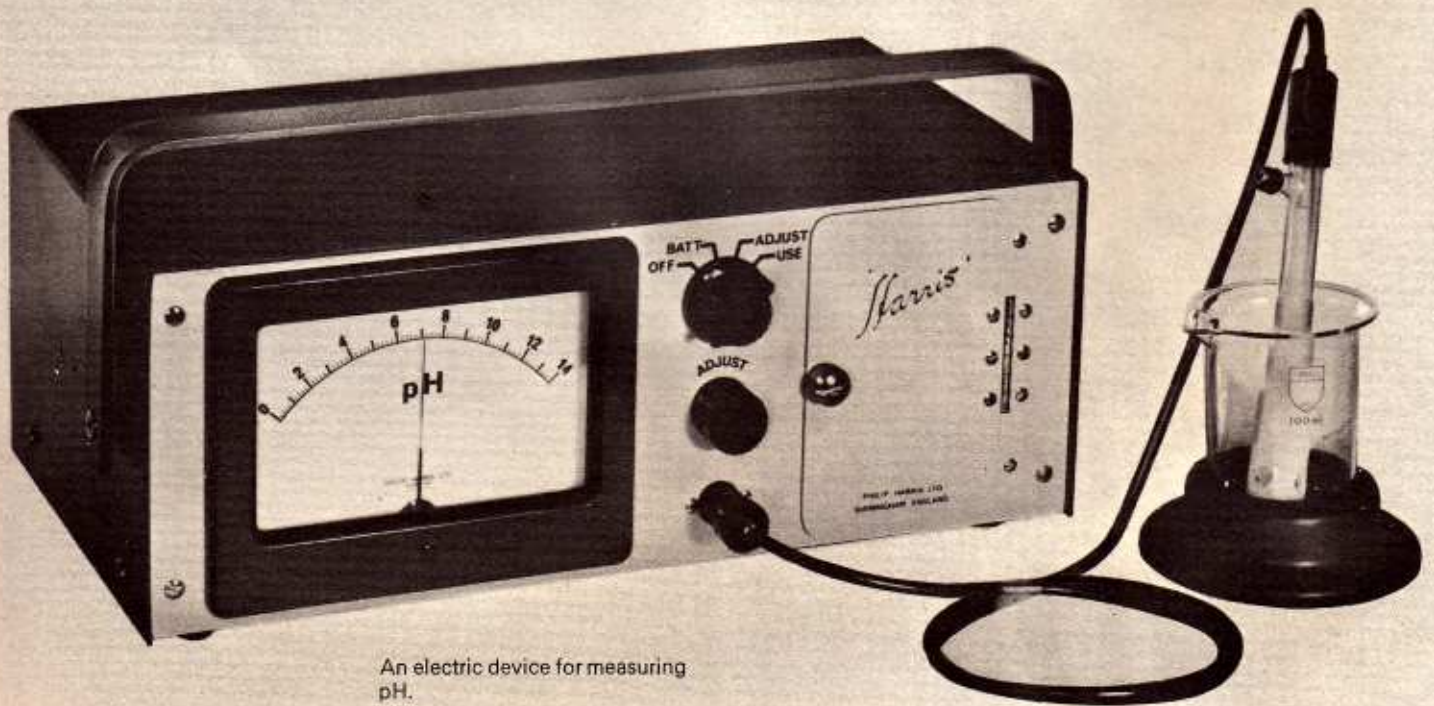
The fact that the Arrhenius definition provides for acid and base strengths to be measured and expressed quantitatively is a strong point in favour of the definition. Scientists generally try to express their findings quantitatively. By doing so, they can treat them mathematically, in a way that is far more exact than verbal description. Moreover the Arrhenius definition covers most of the acids and bases in common use in the laboratory. There are, however, some



Changes in electric conductance during the titration of NaOH by HCl.



Changes in pH in the titration of a solution of hydrochloric acid with sodium hydroxide.



An electric device for measuring pH.

Inter-relationship of pH, $[H_3O^+]$,
and $[OH^-]$.

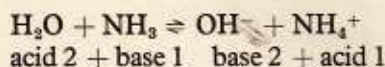
	pH	$[H_3O^+]$ (mole litre ⁻¹)	$[OH^-]$ (mole litre ⁻¹)
<i>Acid solutions</i>	-1	10	10^{-15}
	0	10^0 (or 1)	10^{-14}
	1	10^{-1}	10^{-13}
	2	10^{-2}	10^{-12}
	3	10^{-3}	10^{-11}
	4	10^{-4}	10^{-10}
	5	10^{-5}	10^{-9}
	6	10^{-6}	10^{-8}
<i>Neutral solutions</i>	7	10^{-7}	10^{-7}
<i>Basic solutions</i>	8	10^{-8}	10^{-6}
	9	10^{-9}	10^{-5}
	10	10^{-10}	10^{-4}
	11	10^{-11}	10^{-3}
	12	10^{-12}	10^{-2}
	13	10^{-13}	10^{-1}
	14	10^{-14}	10^0
	15	10^{-15}	10

objections to it; it is too narrow because it excludes all bases that are not hydroxy compounds.

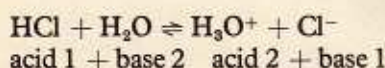
The Brønsted-Lowry definition – A more general definition of an acid and a base than Arrhenius definition was put forward independently in 1923 by the Danish chemist Johannes Nicolaus Brønsted and the British chemist T. M. Lowry.

In their definition, an acid is a substance which contains hydrogen and whose molecules or ions give up protons (hydrogen ions); a base is a substance whose molecules or ions are able to combine with protons. An acid is a proton donor; a base is a proton acceptor. Neutralization is a reaction in which protons are transferred from the molecules or ions of the acid to the molecules or ions of the base.

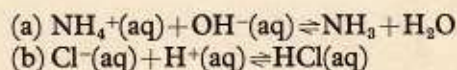
This definition resembles the Arrhenius definition, especially since it claims that acids contain hydrogen and give up hydrogen ions. But there are two important differences which meet the objections to the Arrhenius definition: there is no reference to a solvent; and a base is not restricted to a hydroxy compound. Furthermore, in the Arrhenius definition, the neutralization reaction results in the formation of a salt and water. But in the Brønsted-Lowry definition when a base accepts a proton in the neutralization reaction it becomes a substance that can, in turn, donate a proton. It becomes, in effect, an acid. Similarly by losing a proton an acid becomes a substance that can accept a proton: it becomes a base. For example,



In the reaction above, water behaves as an acid. Below it behaves as a base:

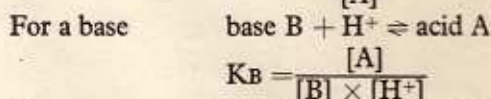
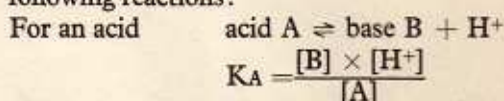


Acid and base reactions are essentially a competition for protons. Since the cation and anion of an electrolyte may differ in their proton donor and proton acceptor properties towards the water, for example, the result of the proton competition determines the acidity or alkalinity of a substance. When ammonium chloride (NH_4Cl) dissolves in water, there are two reactions we must consider.



The equilibrium lies more to the left in equation (b) than it does in equation (a). The result of this is that there is an excess of hydrogen ions in solution, and therefore the solution is acidic. (We would not call ammonium chloride an acid, although it gives a weakly acidic solution in water. The ammonium ion, which of course cannot exist as a substance of itself which we could put in a bottle, is, however, by this theory a weak acid.) By a similar argument, it can be shown that sodium carbonate (Na_2CO_3) dissolves in water to form a solution that is basic.

As we have seen, the pH scale of acid strength is based on the hydrogen ion concentration in water. In the Brønsted-Lowry definition, the strength of an acid is measured by the extent to which protons are released and the strength of a base by the extent to which protons are accepted. These strengths are given by the equilibrium constants (K) for the following reactions:



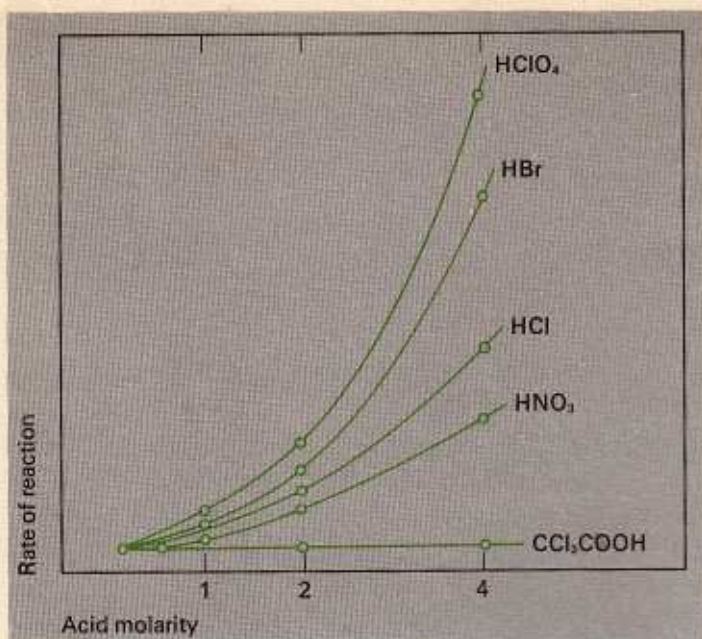
The accompanying table shows relative acid and base strength as represented by their equilibrium constants.

The Brønsted-Lowry definition covers almost all the common acid and base reactions and is the one most generally used. About the only objection to it is that it restricts acid and base reactions to those involving proton transfer but, except in specialized chemical studies, this is seldom an objection of any consequence.

Other definitions – The ‘solvents’ definition was first proposed in 1924. It is really an extension of the Arrhenius definition. It defines an acid as a substance that yields the cation of its solvent and a base is a substance that yields the anion of its solvent. Neutralization is the reaction between the cation and anion to give molecules of the solvent. For example, if ammonium chloride (NH_4Cl) is dissolved in pure liquid ammonia, the conductivity of the ammonia is increased, suggesting that the ammonium chloride has ionized to NH_4^+ and Cl^- . The solution affects the colours of indicators and gives off hydrogen when zinc is added. In other words, the

Relative strengths of acids in aqueous solution.

Acid	Conjugate Base	Dissociation constant	Temperature at which measured, °C
HClO ₄	ClO ₄ ⁻	?	..
HCl	Cl ⁻	~10 ⁻⁷	25
HNO ₃	NO ₃ ⁻	?	..
HSCN	SCN ⁻	?	..
H ₂ SO ₄	HSO ₄ ⁻	?	..
H ₃ O ⁺	H ₂ O	55.5	25
HIO ₃	IO ₃ ⁻	1.9 × 10 ⁻¹	25
H ₄ P ₂ O ₇	H ₃ P ₂ O ₇ ⁻	1.4 × 10 ⁻¹	25
H ₂ C ₂ O ₄	HC ₂ O ₄ ⁻	5.9 × 10 ⁻²	25
H ₃ PO ₃	H ₂ PO ₃ ⁻	5 × 10 ⁻²	25
HSO ₄ ⁻	SO ₄ ⁻²	2 × 10 ⁻²	18
H ₂ SO ₃	HSO ₃ ⁻	1.7 × 10 ⁻²	25
H ₃ PO ₂	H ₂ PO ₂ ⁻	1 × 10 ⁻²	25
H ₃ PO ₄	H ₂ PO ₄ ⁻	7.5 × 10 ⁻³	18
Fe (H ₂ O) _x ⁺³	Fe (H ₂ O) _{x-1} (OH) ⁺²	6.3 × 10 ⁻³	18
H ₃ AsO ₄	H ₂ AsO ₄ ⁻	4.8 × 10 ⁻³	25
H ₂ Te	HTe ⁻	2.3 × 10 ⁻³	25
HF	F ⁻	7.2 × 10 ⁻⁴	25
HNO ₂	NO ₂ ⁻	4.5 × 10 ⁻⁴	25
HCO ₂ H	HCO ₂ ⁻	1.8 × 10 ⁻⁴	18
H ₂ Se	HSe ⁻	1.7 × 10 ⁻⁴	25
HOCN	OCN ⁻	1.2 × 10 ⁻⁴	18
Cr (H ₂ O) _x ⁺³	Cr (H ₂ O) _{x-1} (OH) ⁺²	10 ⁻⁴	25
HC ₂ O ₄ ⁻	C ₂ O ₄ ⁻²	6.4 × 10 ⁻⁵	25
H ₂ PO ₃ ⁻	HPO ₃ ⁻²	2 × 10 ⁻⁵	25
HN ₃	N ₃ ⁻	1.9 × 10 ⁻⁵	25
HC ₂ H ₃ O ₃	C ₂ H ₃ O ₂ ⁻	1.9 × 10 ⁻⁵	25
Al (H ₂ O) _x ⁺³	Al (H ₂ O) _{x-1} (OH) ⁺²	1.3 × 10 ⁻⁶	18
HTe ⁻	Te ⁻²	1 × 10 ⁻⁶	25
H ₄ IO ₃ ⁻	H ₃ IO ₃ ⁻²	1 × 10 ⁻⁶	25
H ₂ CO ₃	HCO ₃ ⁻	3.5 × 10 ⁻⁷	25
H ₂ S	HS ⁻	9.1 × 10 ⁻⁸	18
HSO ₃ ⁻	SO ₃ ⁻²	6.24 × 10 ⁻⁸	25
H ₂ PO ₄ ⁻	HPO ₄ ⁻²	5.9 × 10 ⁻⁸	18
HOCl	OCl ⁻	3.7 × 10 ⁻⁸	18
HCN	CN ⁻	7.2 × 10 ⁻¹⁰	25
H ₃ BO ₃	H ₂ BO ₃ ⁻	5.8 × 10 ⁻¹⁰	25
NH ₄ ⁺	NH ₃	3.3 × 10 ⁻¹⁰	18
HSe ⁻	Se ⁻²	10 ⁻¹⁰	25
HCO ₃ ⁻	CO ₃ ⁻²	6 × 10 ⁻¹¹	25
HIO	IO ⁻	1 × 10 ⁻¹¹	25
H ₂ O ₂	HO ₂ ⁻	2.4 × 10 ⁻¹²	25
H ₂ AlO ₃	H ₂ AlO ₃ ⁻	6.3 × 10 ⁻¹³	25
HPO ₄ ⁻²	PO ₄ ⁻³	3.6 × 10 ⁻¹³	18
Ca (H ₂ O) _x ⁺²	Ca (H ₂ O) _{x-1} (OH)	10 ⁻¹³	25
HS ⁻	S ⁻²	1.2 × 10 ⁻¹⁵	18
H ₂ O	OH ⁻	1.07 × 10 ⁻¹⁶	18
OH ⁻	O ⁻²	<10 ⁻³⁶	25



Relative efficiencies of various acids in catalysing the conversion of sucrose to glucose, illustrating the relative acidities of their aqueous solutions.

solution has the properties of an acid. Furthermore, when potassium amide (KNH_2) is added to this solution of ammonium chloride in liquid ammonia, the solution loses these acid properties. It can be shown that the amide ion (NH_2^-) reacts with ammonium ion (NH_4^+) to produce molecules of the solvent ammonia:



This reaction, as you may have noticed, is similar to the reaction between hydrochloric acid and sodium hydroxide. Here, hydrogen ions react with hydroxyl ions to produce molecules of the solvent water. Both reactions are neutralization reactions leading to formation of the solvent.

Thus, in liquid ammonia, ammonium chloride is acidic because it yields the cation NH_4^+ and potassium amide is basic because it yields the anion NH_2^- . By a similar argument, hydrogen chloride in water is acidic and sodium hydroxide is basic.

As in the case of the Arrhenius definition, one of the chief objections against the 'solvents' definition is that it restricts acid and base reactions to solvents. A more serious objection may be that apart from water most of the solvents are of little practical importance. Except where reactions are being

studied in such unusual solvents as liquid ammonia or sulphur dioxide, the 'solvents' definition is usually ignored.

Another definition was put forward by the American chemist G. N. Lewis, it concerned the electron structure of acids and bases. An acid is an 'electron pair acceptor' and a base is an 'electron pair donor'. For example, neutralization is a reaction in which a bond is formed between atoms sharing an electron pair. This definition includes as acids and bases most of the substances that come under the definitions we have looked at, and other substances as well - in particular some acidic substances which do not contain hydrogen, for example, boron trifluoride, which is used as a catalyst in cracking petroleum. It is a useful definition in some specialized areas of study such as catalysis; but it classifies as acids and bases many substances which are not usefully thought of as such. In other words the definition is often too general to be useful.

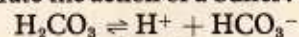
As stated at the beginning, each definition is to be evaluated by its usefulness. Each of the definitions we have looked at is derived from experimental observations of acid and base behaviour. From Arrhenius to Lewis, they include an increasingly larger number of acid and base reactions. The definition we favour is ultimately to be determined by the kind of work we are doing: if we are studying acid and base behaviour in water, then we probably use the Arrhenius definition; if we are concerned with proton transfer involving bases other than hydroxy compounds, we might use the Brønsted-Lowry definition; and if we are studying catalytic reaction, we might use the Lewis definition. In each case we apply the most useful definition, the one which provides the deepest insight into the reactions we are studying and helps us best to organize our findings.

ACIDS AND LIFE

The usefulness of these definitions in explaining inorganic reactions extends to organic reactions. In fact, a brief survey of some chemical reactions in living cells will indicate the usefulness of Brönsted-Lowry in this field of biochemistry as well.

The living cell requires an almost neutral internal environment for its immensely intricate chemical reactions. The pH of the protoplasm in living cells is about 6.9, while the extracellular fluids of vertebrates – blood and lymph – have a slightly alkaline pH of about 7.4. The cells produce acid continuously in the form of carbonic acid (CO_2 combined with water); but the production of CO_2 does not immediately affect the pH of either the cell or the extracellular fluid, stabilized by a system of buffers.

The carbonic acid-bicarbonate system may be taken as an example to illustrate the action of a buffer:



If hydrogen ions are added to the system, tending to cause a fall in pH, the equilibrium is pushed to the left, removing the extra H^+ ions as un-ionized carbonic acid. The pH is thus kept constant. If the H^+ ions decrease, bringing about a rise in pH, the equilibrium shifts to the right, and favours the dissociation of the acid to increase the H^+ ions and restore the pH to normal. In Brönsted-Lowry terms, buffers are conjugate pairs of strong bases with weak acids, so constituted that they respond to changes of pH in the neighbourhood of the neutral point by shifts of equilibrium tending to restore neutrality. The bases consist principally of bicarbonate, hydrogen phosphate, and protein.

However, buffers cannot maintain a constant pH indefinitely if too much CO_2 is added to the system. The unicellular animal loses excess CO_2 by diffusion through the cell mem-

brane into the surrounding water or air. Multicellular animals have a proportionately smaller amount of surface; as animals increase in size, there has to be an increase of diffusing surface in some way. In insects air is brought to all the tissues by fine *tracheal tubes*. This diffusion system suffices only for relatively small creatures. In the larger animals, there is an enormous diffusing surface in gills or lungs and a system of extracellular fluids and circulating blood to carry the buffered carbonic acid to them and to carry oxygen to the tissues. As the blood passes through the lungs, the carbonic acid is rapidly converted to CO_2 and water by the enzyme carbonic anhydrase. The CO_2 diffuses from the blood into the air inside the lungs, and is then removed in the expired air.

Animals also produce strong acids that cannot be excreted in gaseous form. The most important of these is sulphuric acid, formed by oxidation of the sulphur in the proteins of the food. In vertebrates, acids of this kind are secreted by the kidney into the urine. Urine may be as acid as pH4. Additional acids can be excreted as ammonium salts, since the kidney forms ammonium ions (NH_4^+) from the H^+ ions and ammonia (NH_3) in amino acids.

Amino acids are the units that are polymerized to give proteins. In spite of their name amino acids are both acid and base, and they act as buffers. The simplest amino acid, glycine (α -amino acid, $\text{CH}_2\text{NH}_2\text{COOH}$), can ionize in an acid environment as $\text{CH}_2\text{NH}_3^+\text{COOH}$, and in alkaline environment as $\text{CH}_2\text{NH}_2\text{COO}^-$. Glycine buffers are often used for experimental purposes. The proteins – themselves buffers – are broken down into amino acids during digestion, and some of the amino acids are used for synthesis of new proteins and other compounds. The amino acids, which are

not required as building materials lose the amino group. This occurs mainly in the liver. The ammonia thus produced exists in equilibrium with ammonium ion: $\text{NH}_3 + \text{H}^+ = \text{NH}_4^+$; but at the pH of the cell, equilibrium is well over to the left, and ammonia in more than trace amounts is a tissue poison. It is involved in the liver in a cycle of reactions (the 'ornithine' cycle), from which it emerges in combination with CO_2 as the neutral soluble compound urea, $\text{OC} \begin{matrix} \text{NH}_2 \\ \text{NH}_2 \end{matrix}$ to be carried by the blood to the kidney for excretion.

The amino acid residues are metabolized, along with carbohydrates and fats, in a way common to practically all cells: two-carbon fragments from the tissue fuels combine with four-carbon carrier molecules, and undergo a series of reactions in which their energy is transferred to energy-rich phosphates, while their hydrogen is oxidized to water and their carbon is set free as CO_2 .

The neutrality of the body fluids is further guarded by a centre in the brain. When CO_2 accumulates in the blood above the normal level, as in active exercise, the respiratory rate is stepped up to increase the loss of CO_2 from the lungs. If the CO_2 level falls, as after forced breathing for a minute or two, the brain centre retards the rate of respiration until the CO_2 level in the blood has risen to normal. Any condition that alters the pH of the blood beyond what can be readily compensated causes illness.

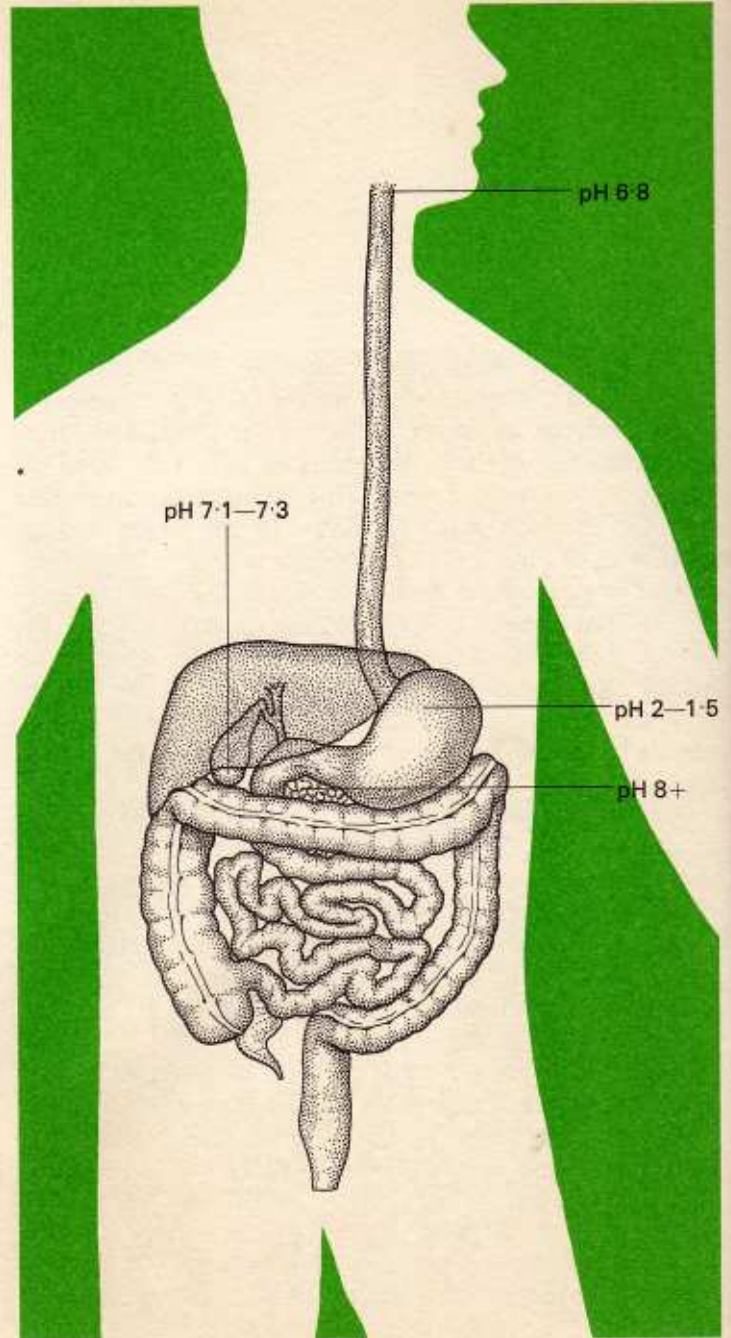
Although the internal environment is maintained at a nearly neutral pH, organisms can produce acids where required. For example, higher animals' stomachs secrete a fluid containing free hydrochloric acid. Human gastric juice may have a pH as low as 2 or 1.5; the gastric juice of dogs can dissolve bones. This acid solution provides the right condi-

tions for the stomach enzymes to act on food. The acid is neutralized by the food in the process of digestion, and is further neutralized, after leaving the stomach, by the pancreatic juice (pH up to 8.0). Indeed biochemically speaking, the stomach is outside the body, for the digestive canal is open to the external world at both ends, and the digested material has to traverse the cells that line the canal in order to enter the body.

Other examples of biochemical acids may be given. Some bacteria obtain energy from carbohydrates by a partial breakdown that does not require oxygen. This produces such acids as the lactic and butyric acids of sour milk. If the bacteria are supplied with oxygen, the acids may be further metabolized. Citric acid is manufactured commercially from molasses or sucrose by taking advantage of the activities of the mould *Aspergillus niger*. The highly aerobic bacterium *Acetobacter* uses atmospheric oxygen to oxidize alcohol to acetic acid, turning wine to vinegar. The acids formed by these microorganisms are by-products of their modes of obtaining energy; the acids accumulate in the media outside the cells, and may prove lethal to them in unbuffered conditions.

Green plants do not have the same need as the animal for protection against acids of internal origin. The plant's oxidative metabolism, and consequently its CO_2 production, is much slower, and the CO_2 in daylight is re-used for the manufacture of carbohydrate in photosynthesis. Similarly, the plant synthesizes its own amino acids for proteins, and does not have the animal's problem of excess ammonia arising from the metabolism of foreign proteins. The plant, therefore, has no need for an excretory system for either CO_2 or ammonia. It has, however, been suggested that some of the nitrogenous substances found in plants, such as the chemically complex and pharmaceutically active alkaloids (morphine, strychnine, quinine, etc.), which have no known function in the plant, may serve as a means of storing away excess nitrogen.

The main buffers in the plant cell are the same as in the animal, except that a more important part is played by organic acids, such as citric and malic acids, in equilibrium with their salts. The fluid or sap in the vacuoles that exist in many plant cells is less buffered than the living material, and is often more acid - pH 6.5 to 5.5, or even, in citrus fruits, as low as 2.4.



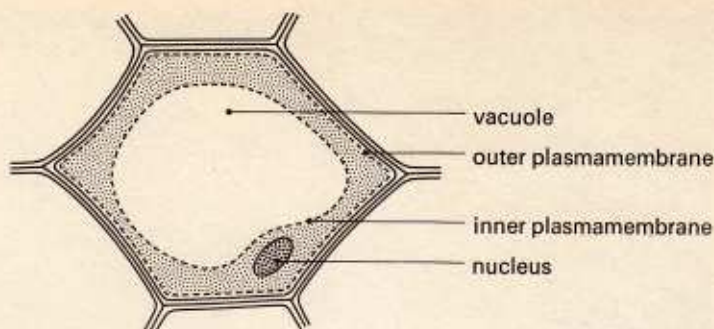
The variations of the pH of the secretions in the human digestive system. Reaction with food reduces the high acidity of the stomach fluids. The pH of the contents of the intestines varies to some extent according to what one has eaten.

Quinine, used in treating malaria, is made from the bark of the cinchona plant; it is one of the numerous examples of naturally occurring alkaloids. *Pfizer. (Below.)*



Oranges contain citric acid, one of the numerous examples of naturally occurring acids. *Israel Government Tourist Office.*

A plant cell showing a vacuole, a space within a cell that separates certain materials from the area of chemical reaction, preventing them from interfering in the cell's functioning. In some cases vacuoles may be storehouses of nutrients, or they may remove excess water.



The practice of liming the soil is a very old method of controlling soil acidity.
Farmers' Weekly.

The chief acid problem of the plant is external, in the soil from which it must draw its supply of mineral salts and nitrogen (as ammonium or nitrate ions). The pH of soil ranges from 10 or 11 in alkali deserts to 3.5 at the most acid. Extremes can be tolerated only by specially adapted plants. The outer ranges of normality in soil pH (8.0 to 4.5) can be recognized by the different flora characterizing the alkaline chalk and limestone soils on the one hand, and the acid peaty soils on the other. Liming soils to raise the pH is a common agricultural operation.

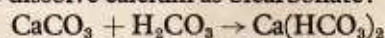
Besides varying in pH, soils vary in buffering power. Sand contains little buffer, and readily becomes too acid or too alkaline except for specialized plants, while a fertile soil full of decaying organic material is heavily buffered, both by the organic material and by the reactive aluminosilicate particles of clay, which are able to retain ions from the soil water.

The cells of plant root-hairs absorb ions from the soil by an active and selective process. It is active, since it occurs against a concentration gradient, and is accomplished with energy from oxidation; and it is selective, since the different ions absorbed need not be in the same relative proportions as in the soil. The absorption of ions by root-hairs may change the external pH. Thus absorption of nitrate (NO_3^-) ions from a solution, accompanied and balanced by H^+ ions from water or carbonic acid, leaves the solution more alkaline, because it contains more OH^- or HCO_3^- . In the case of absorption of K^+ ions, accompanied and balanced by OH^- or HCO_3^- , the solution is left more acid because of increased H^+ .

Plants must cope not only with acids in the soil, but also with those in the atmosphere. When flashes of lightning pass through the atmosphere, they cause the nitrogen and the oxygen of the air to combine. This nitric oxide eventually



falls to the earth as nitric acid in rainwater. The CO_2 emitted by organisms, and by the combustion of fuels, serves as source of carbon for plants, but also dissolves in rain water to form carbonic acid. As the water percolates through limestone or chalk, the carbonic acid reacts with the calcium carbonate to dissolve calcium as bicarbonate:



so making the water 'hard'. In the neighbourhood of towns, the air also contains sulphur dioxide, derived from the burning of the sulphur compounds in coal and oil; dissolved in rain, this gas gives sulphurous acid, H_2SO_3 , and may be partly oxidized to sulphuric acid, H_2SO_4 . These acids are particularly noticeable in city fogs, and are notorious for irritating the lungs of animals, corroding metal and stonework, and stunting or killing plants.

We can see that any definition of acids has to encompass a vast number of reactions, and, in the case of organic chemistry, some very complex ones. Biochemistry is the most rapidly advancing part of present-day chemistry. As new facts are brought to light, definitions of acids will doubtless have to be modified to account for them.

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WASHING
SODA AND
WATER?

LIME WATER?

BENCH
HYDROCHLORIC
ACID?

FRESH
COW'S MILK?

BENCH
CAUSTIC
SODA?

ORDINARY
DISTILLED

SO