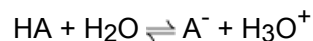


Acid dissociation constant

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An **acid dissociation constant**, denoted by K_a , is an equilibrium constant for the dissociation of a **weak acid**. According to the Brønsted-Lowry theory of acids and bases, an acid is a proton donor (HA, where H represents an acidic hydrogen atom), and a base is a proton acceptor. In aqueous solution, water can function as a base, as in the following general example.



Acid dissociation constants are also known as the **acidity constant** or the **acid-ionization constant**. The term is also used for $\text{p}K_a$, which is equal to minus the decimal logarithm of K_a (cologarithm of K_a).

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Definitions

Monoprotic acids

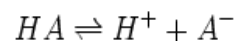
When an acid, HA, dissolves in water, some molecules of the acid 'dissociate' to form hydronium ions and the conjugate base, (A^-), of the

Concepts in Chemical Equilibria

Acid dissociation constant

Binding constant
Chemical equilibrium
Chemical stability
Dissociation constant
Distribution coefficient
Distribution ratio
Equilibrium constant
Equilibrium unfolding
Equilibrium stage
Liquid-liquid extraction
Phase diagram
Phase rule
Reaction quotient
Relative volatility
Solubility equilibrium
Stability constant
Thermodynamic equilibrium
Theoretical plate
Vapor-liquid equilibrium

acid.



It is understood that H^+

stands for the hydronium ion and that each species in this equilibrium may solvate to a greater or lesser extent. The acid dissociation constant is defined as

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

where the square brackets are usually taken to signify concentration. H_2O

is omitted from these expressions because in dilute solution the concentration of water may be assumed to be constant. Values of K_a vary over many orders of magnitude, so it is common to take the logarithm to base ten of the value.

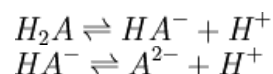
$$pK_a = -\log_{10} K_a$$

It is easier to compare the strengths of different acids by comparing pK_a values as they vary over a much smaller range.

Polyprotic acids

A polyprotic acid is one that has more than one proton to dissociate. Typical examples are malonic acid, which has two ionizable protons, and phosphoric acid, which has three. The constant for dissociation of the first proton may be denoted as pK_{a1} and the constants for dissociation of successive protons as pK_{a2} , etc.

It is generally true that successive pK values increase (Pauling's first rule).^[1] For example, for a diprotic acid, H_2A , the two equilibria are



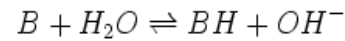
it can be seen that the second proton is removed from a negatively charged species. Since the proton carries a positive charge extra work is needed to remove it. Therefore $pK_{a2} > pK_{a1}$. There are a few exceptions to this rule which occur when there is a major structural change such as in the sequence

$VO_2^+(aq) \rightleftharpoons H_3VO_4 + H^+$	$pK_{a1} = 4.2$
$H_3VO_4 \rightleftharpoons H_2VO_4^- + H^+$	$pK_{a2} = 2.60$
$H_2VO_4^- \rightleftharpoons HVO_4^{2-} + H^+$	$pK_{a3} = 7.92$
$HVO_4^{2-} \rightleftharpoons VO_4^{3-} + H^+$	$pK_{a4} = 13.27$

The pKs of vanadic acid, H_3VO_4 , follow Pauling's rule just like phosphoric acid (values below). All species in this series are tetrahedral, but $VO_2(H_2O)_4^+$ is octahedral and $pK_{a2} < pK_{a1}$.^[2]

Bases

Historically the equilibrium constant K_b for a base was defined as the dissociation constant of BH , the acid conjugate to the base, B . Ionic charges on B and/or BH are omitted here because the base may be a neutral species such as ammonia or a charged species such as the ethanoate ion (acetate).



Using similar reasoning to that used before

$$K_b = \frac{[BH][OH^-]}{[B]}$$

$$pK_b = -\log_{10} K_b$$

Now, the concentration of the hydroxide ion is related to the concentration of the hydronium by $K_w = [H^+][OH^-]$, therefore

$$[OH^-] = \frac{K_w}{[H^+]}$$

K_w is the constant for the self-ionization of water. Substituting the expression for $[OH^-]$ into the expression for K_b

$$K_b = K_w \frac{[BH]}{[B][H^+]} = \frac{K_w}{K_a}$$

It follows that

$$pK_b = pK_w - pK_a$$

In water at 25 °C pK_w is 14 so then $pK_b = 14 - pK_a$.

In effect there is no need to define pK_b separately from pK_a , but it is done because pK_b values can be found in literature.

Protonation constants

The protonation constant for a substance S , is given by

$$S + H^+ \rightleftharpoons SH$$

$$K_{assoc} = \frac{[SH]}{[S][H^+]}$$

Again, ionic charges are omitted from S and SH . K_{assoc} is an association constant.

- For any substance $\log_{10}(K_{assoc}) = pK_a$

Temperature dependence

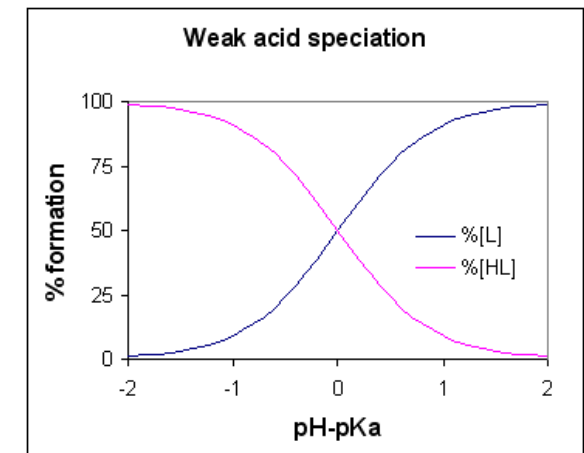
All equilibrium constants vary with temperature according the van 't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta H_m^\ominus}{RT^2}.$$

Thus, for exothermic reactions, (ΔH is negative) K decreases with temperature, but for endothermic reactions (ΔH is positive) K increases with temperature.

Usage

The pH of a solution of **weak acid**



can be expressed in terms of the extent of dissociation. After rearranging the expression defining the dissociation constant, and putting $\text{pH} = -\log_{10}[\text{H}^+]$, one obtains

$$\text{pH} = \text{p}K_a - \log \frac{[HA]}{[A^-]}$$

This is a form of the Henderson-Hasselbalch equation. It can be deduced from this expression that

- when the acid is 1% dissociated, that is, when $\frac{[HA]}{[A^-]} = 100$, $\text{pH} = \text{p}K_a - 2$
- when the acid is 50% dissociated, that is, when $\frac{[HA]}{[A^-]} = 1$, $\text{pH} = \text{p}K_a$

- when the acid is 99% dissociated, that is, when $\frac{[HA]}{[A^-]} = 0.01$, $pH = pK_a + 2$

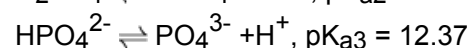
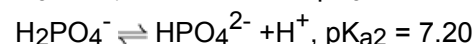
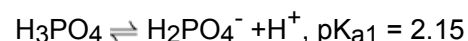
It follows that the range of pH within which there is partial dissociation of the acid is about $pK_a \pm 2$. This is shown graphically at the right.

A **weak acid** may be **defined** as an acid with pK_a greater than about -2. An acid with $pK_a = -2$ would be 99% dissociated at pH 0, that is, in a 1M HCl solution. Any acid with a pK_a less than about -2 is said to be a **strong acid**. Strong acids are said to be fully dissociated. There is no precise pK_a value that distinguishes between strong and weak acids because strong acids, such as sulfuric acid, are associated in very concentrated solution.

On the pK_a scale of acid strength, a large value indicates a very weak acid, and a small value indicates a not so weak one.

The pH of a solution of a weak acid can be easily calculated when the analytical concentration of the acid is known. See ICE table for details.

Some polyprotic acids can be treated as a set of individual acids. This is possible when successive pK values differ by 4 or more. For example with phosphoric acid



Both the hydrogenphosphate and dihydrogenphosphate ions can be treated as acids in their own right. On the other hand, the two pKs for malonic acid are 2.51 and 5.05, so there are pH values at which both malonic acid and the hydrogenmalonate ion co-exist. More elaborate calculations are needed to calculate the composition of solutions of malonic acid.

Factors that determine the relative strengths of acids

Being an equilibrium constant, the acid dissociation constant K_a is determined by the standard free energy difference ΔG^\ominus between the reactants and products, specifically, between the protonated (HA) and deprotonated (A^-) forms of the substance.

Pauling's second rule^[1] states that the value of the first pK for acids of the formula $XO_m(OH)_n$ is approximately independent of n and X and is approximately 8 for m=0, 2 for m=1, -3 for m=2 and <-10 for m=3. This correlates with the oxidation state of the central atom, X: the higher the oxidation state the stronger the oxyacid. For example, pK_a for HClO is 7.2, for HClO₂ is 2.0, for HClO₃ is -1 and HClO₄ is a strong acid.

With organic acids inductive effects and mesomeric effects affect the pKs. The effects are summarised in the Hammett equation and subsequent extensions.

Structural effects can also be important. The difference between fumaric acid and maleic acid is a classic example. Fumaric acid is (E)-1,4-but-2-enedioic acid, a *trans* isomer, whereas maleic acid is the corresponding *cis* isomer, i.e. (Z)-1,4-but-2-enedioic acid (see cis-trans isomerism). Fumaric acid has pK_a s of approximately 3.5 and 4.5. By contrast, maleic acid has pK_a s of approximately 1.5 and 6.5. The reason for this large difference is that when one proton is removed from the *cis*- isomer (maleic acid) a strong intramolecular hydrogen bond is formed with the nearby remaining carboxyl group. This favors the formation of the maleate H^+ , and it opposes

the removal of the second proton from that species. In the *trans* isomer, the two carboxyl groups are always far apart, so hydrogen bonding is not observed.

Importance of pK_a values

The pK_a value(s) of a compound influence many characteristics of the compound such as its reactivity, and spectral properties (colour). In biochemistry the pK_a values of proteins and amino acid side chains are of major importance for the activity of enzymes and the stability of proteins. This property is of general importance in chemistry because ionization of a compound alters its physical behavior and macro properties such as solubility and lipophilicity. For example ionization of any compound will increase the solubility in water, but decrease the lipophilicity. This can be exploited in drug development to increase the concentration of a compound in the blood by adjusting the pK_a of an ionizable group. This must be done with caution, however, since an ionized compound will pass less easily through cell membranes.

Further information: Protein pKa calculations

Acidity in nonaqueous solutions

Three properties of a solvent strongly affect acids and bases.

1. A Protic solvent can form hydrogen bonds and will promote ionisation.
2. A solvent with a high donor number is a strong Lewis base.
3. A solvent with a high dielectric constant (Relative permittivity) will promote ionisation.

	Donor number	dielectric constant
Acetonitrile	14.1	37.5
Dimethyl sulfoxide	29.8	45
Ethanol	31.5	24.3
Pyridine	33.1	12.3
Water	18	81.7

For a given acid, pK_a values will vary depending on solvent. The degree of dissociation of any acid increases with the increasing basicity of the solvent. On the other hand, dissociation is relatively less for solvents of low dielectric constant. An acidic solvent will also suppress dissociation of an acid. For example, hydrogen chloride is a weak acid, i.e. poorly ionised, when dissolved in the acidic solvent acetic acid.

Acidity scales have been developed for solvents aside from water, notably for dimethyl sulfoxide and acetonitrile.^[3] It can be seen in the table above that DMSO is more basic than water, but its dielectric constant is less. DMSO is widely used as an alternative to water in evaluating acids and bases.

In solvents of low dielectric constant, ions tend to associate, which complicates the interpretation of pK_a s. In particular, in aprotic solvents the process of homoconjugation occurs when the conjugate base forms a hydrogen bond with the parent acid as in the following equilibrium



Typically HA_2^- would have the structure $\text{A} \cdots \text{H} \cdots \text{A}$. This process does not occur in water because H_2O molecules are strong hydrogen bond donors and acceptors.

In acetonitrile solution, para-toluenesulfonic acid has a homoconjugation constant pK^{f} , of -2.9.^[4]

This indicates that the toluenesulfonate anion has a strong tendency to form a hydrogen bond with the parent acid. Homoconjugation has the effect of enhancing the acidity of acids, lowering their effective pK_{a} s, by stabilizing the conjugate base. Due to homoconjugation, the proton-donating power of toluenesulfonic acid in acetonitrile solution is enhanced by a factor of nearly 800.

pK_{a} of some common substances

Measurements are at 25°C in water for those with a pK_{a} at or above -1.76:

- - 25.00: Fluoroantimonic acid
- - 15.00: Magic acid
- - 10.00: Fluorosulfuric acid
- - 10.00: Perchloric acid
- - 10.00: Hydroiodic acid
- - 9.00: Hydrobromic acid
- - 8.00: Hydrochloric acid
- - 3.00, 1.99: Sulfuric acid
- - 2.00: Nitric acid
- - 1.76: Hydronium ion
- 3.15: Hydrofluoric acid
- 3.60: Carbonic acid
- 3.75: Formic acid
- 4.04: Ascorbic acid (Vitamin C)
- 4.19: Succinic acid
- 4.20: Benzoic acid
- 4.63: Aniline*
- 4.76: Acetic acid
- 4.76: Dihydrogencitrate ion (Citrate)
- 5.21: Pyridine*
- 6.40: Monohydrogencitrate ion Citrate
- 6.99: Ethylenediamine*
- 7.00: Hydrogen sulfide, Imidazole* (as an acid)
- 7.50: Hypochlorous acid
- 9.25: Ammonia*
- 9.33: Benzylamine*
- 9.81: Trimethylamine*
- 9.99: Phenol
- 10.08: Ethylenediamine*
- 10.66: Methylamine*
- 10.73: Dimethylamine*
- 10.81: Ethylamine*
- 11.01: Triethylamine*
- 11.09: Diethylamine*
- 11.65: Hydrogen peroxide
- 12.50: Guanidine*
- 12.67: Monohydrogenphosphate ion (Phosphate)
- 14.58: Imidazole (as a base)
- 15.76: Water
- - 19.00 (pK_b) Sodium amide
- 37.00: Lithium diisopropylamide (LDA)
- 45.00: Propane
- 50.00: Ethane

* Listed values for ammonia and amines are the pK_{a} values for the corresponding ammonium ions.

Further reading

- Atkins, Peter, and Loretta Jones. *Chemical Principles: The Quest for Insight*. 3rd ed. New York: W. H. Freeman and Company, 2005

- Housecroft, Catherine and Sharpe, Alan, *Inorganic Chemistry*, Prentice Hall, 2nd. edition, 2004. (Non-aqueous solvents)

See also

- Hammett equation
- QSAR
- Dissociation constant
- Henderson-Hasselbalch equation

References

1. [^] ^{*a*} ^{*b*} Greenwood, N. N.; Earnshaw, A. (1997). *Chemistry of the Elements*, 2nd Edition, Oxford:Butterworth-Heinemann. ISBN 0-7506-3365-4. p. 50
2. [^] Greenwood, N. N.; Earnshaw, A. (1997). *Chemistry of the Elements*, 2nd Edition, Oxford:Butterworth-Heinemann. ISBN 0-7506-3365-4. Chapter 22
3. [^] March, J. "Advanced Organic Chemistry" 4th Ed. J. Wiley and Sons, 1992: New York. ISBN 0-471-60180-2.
4. [^] Coetzee, J. F. and Padmanabhan, G. R., "Proton Acceptor Power and Homoconjugation of Mono- and Diamines", J. Amer. Chem. Soc., 1965, **87**, 5005-5010.

External links

- Bordwell pKa Table in DMSO (<http://www.chem.wisc.edu/areas/reich/pkatable/>)
- Shodor.org Acid-Base Chemistry (<http://www.shodor.org/unchem/basic/ab/>)
- Factors that Affect the Relative Strengths of Acids and Bases (<http://library.thinkquest.org/C006669/data/Chem/acidsbases/factors.html>)
- Purdue Chemistry (http://chemed.chem.purdue.edu/genchem/topicreview/bp/3organic/3org_frame.html)
- Distribution diagrams of acids and bases (http://www2.iq.usp.br/docente/gutz/Curtipot_.html) (generation from pK_a values with free spreadsheet)
- SPARC Physical/Chemical property calculator (<http://sparc.chem.uga.edu>)
- List of Aqueous-Equilibrium Constants (<http://www.jesuitnola.org/upload/clark/Refs/aqueous.htm>)
- Free guide to pKa & logP interpretation and measurement (<http://www.raell.demon.co.uk/chem/logp/logppka.htm>)

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Categories: Acids | Analytical chemistry | Thermodynamics

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