

NEW ACID-BASE TERMINOLOGY

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The last twenty years have seen a rather amazing change in the meaning of the terms acid and base for those who try to keep up with new developments. The following summary of the more important proposals will show that the meaning of the terms become more and more inclusive.

- a) Arrhenius 1887—Hydrogen ion donor in water.
- b) Brönsted 1923—Proton (H^+ ion) donor in general.
- c) Germann 1925—Solvent-cation donor.
- d) Lewis 1923 and 1938—Electron-pair acceptor.
- e) Sidgwick 1927—"Acceptor" for same idea as Lewis.
- f) Usanovich 1939—More inclusive—electrophile.

The Journal of Chemical Education has published many articles concerning the new ideas and has recently reprinted a very valuable selection of them in book form.¹ To me the ideas of G. N. Lewis² seem most reasonable. Usanovich's acids include almost everything, Lewis' acids, oxidizing agents and other substances while the Brönsted theory is forced to omit some real acids like SO_2 and $SnCl_4$. Lewis defines an acid as "a molecule, ion, or radical capable of accepting a pair of electrons furnished by some other element or group. Conversely, a base is a structure which can furnish such an electron pair."

Many felt at first that the new ideas were all right if only new names were applied. Sidgwick,³ for example, calls the Lewis acids "acceptors" and the bases "donors." Lewis, however is rapidly gaining support and the logic of his position is asserting itself.

When one considers the classical connotation of the word "base," it is hard to see how it could be the foundation of anything but the new usage makes it the base or foundation of an acid. The word "acid" means sour and that is generally true of Lewis' "acids." All the classical

acid radicals as well as some other entities are called bases by the new system. Thus the acetate ion is the base of $HC_2H_3O_2$. Acids or bases may be cations, neutral molecules, or anions as the following examples will show:

ACIDS (Electron-pair Acceptors)

Cations	Molecules	Anions
H_3O^+	HCl	$H_2PO_4^-$
NH_4^+	$HC_2H_3O_2$	HPO_4^{2-}
Zn^{++}	$SnCl_4$	$HC_2O_4^-$
Ag^+	H_2O	HSO_4^-
Fe^{+++}	H_3PO_4	
Al^{+++}	SO_2	
Mg^{++}	$HAIO_2$	
Cr^{+++}	SO_3	

BASES (Electron-pair Donors)

Cations	Molecules	Anions
$Zn(OH)^+$	H_2O	OH^-
$Al(OH)^{++}$	NH_3	PO_4^{3-}
AlO^+	$Al(OH)_3$	HPO_4^{2-}
$Fe(OH)^{++}$	NH_2OH	$H_2PO_4^-$
$Fe(OH)^+_2$		CN^-
FeO^+		$C_2H_3O_2^-$
		SO_4^{2-}
		HSO_4^-
		O^{--}

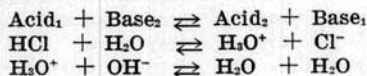
Those which occur in both lists would be called amphiprotic (since the words amphoteric and ampholytic are now obsolete). Perhaps the most striking contrast is in the classical use of the word "bases" in Soil Chemistry and qualitative analysis for cations and "acids" for anions. The new theory makes most of these same cations "acids" and the anions "bases." Thus Zn^{++} , Al^{+++} , Fe^{+++} have long been called bases but their solutions taste sour, turn litmus red and have other characteristics of acids, alum even being substituted for the acid in cheap baking powder. Modern ideas are therefore more realistic.

Again, solutions containing such ions as CN^- , $C_2H_3O_2^-$, SiO_3^{2-} , S^{2-} , SH^- , CO_3^{2-} and OH^- have a distinct basic reaction, yet some older books, especially qualitative texts, call them acids, including even OH^- by courtesy.

It would seem then, that at least for cations and anions, the new ideas are more logical than the classical. There is a feeling among many that somehow it is the Na^+ in NaOH that makes it a base. The new theory would say it is the OH^- which is the base and that the Na^+ is such a weak acid that it has practically no neutralizing effect upon the OH^- . Classical defenders will at once argue that NaOH is strong while $\text{Zn}(\text{OH})_2$ is weak. They will say that this proves that the cation is what makes a base. The answer is that the cation is important but not in the way they thought. The Zn^{++} is a stronger acid than the practically neutral Na^+ , and so partly neutralizes or minimizes the effect of the OH^- . This attitude, anyway, is no doubt a hangover from the confusion of a free element with its ion. While sodium is a very active element, the sodium ion is quite inactive, and it is this inactivity which allows the other ions of sodium compounds to exhibit their unhampered effects.

Now the Cl^- is a very weak base and practically neutral, while $\text{C}_2\text{H}_3\text{O}_2^-$ is a strong base. The molecule acid, HCl , is strong because Cl^- has little or no neutralizing effect upon the acid. $\text{HC}_2\text{H}_3\text{O}_2$ is weak because $\text{C}_2\text{H}_3\text{O}_2^-$ has a strong basic reaction and so reduces the acidity of the molecule.

The reaction between an acid and a base is not necessarily neutralization but can usually be fitted into the following scheme or a modification of it.

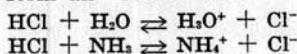


The word salt is restricted to a substance which has an ionic lattice in the solid form and is completely ionized when fused or dissolved. Thus, Na^+Cl^- , Na^+OH^- , and $\text{H}_3\text{O}^+\text{Cl}^-$ are all salts but As_2S_3 , HgCl_2 and CdCl_2 are excluded since the latter are practically un-ionized.

A classical "neutral salt" like Na^+Cl^- is a salt which contains the practically neutral weak acid Na^+ and the practically neutral weak base Cl^- . A classical "base" like Na^+OH^- is a salt which contains the weak acid Na^+ and the very strong base OH^- . $\text{H}_3\text{O}^+\text{Cl}^-$ is a salt which contains

the strong acid, H_3O^+ and the practically neutral base Cl^- .

It is unreasonable to call Na^+OH^- a base and not a salt and refuse a similar classification to Na^+CN^- , Na^+CO_3^- , Na^+SH^- , Na^+S^{--} , $\text{Na}^+\text{C}_2\text{H}_3\text{O}_2^-$, $\text{Na}^+\text{SiO}_3^-$, etc., which are in some cases almost as basic in reaction. Furthermore, the dry, fused classical "salts" and "bases" will carry an electric current while pure classical "acids" in the liquid state will not carry a current unless an ionizing solvent is added. This shows that there is no fundamental difference between the first two classes which are now to be classed simply as salts, containing more or less active bases. The term "base" is thus released for a more fundamental meaning. Classical "acids" do not become salts, however, until they have reacted with an ionizing solvent. Thus HCl must react with H_2O , NH_3 or similar ionizing solvent to form an "onium" salt.



Types of Lewis Salts

Classical Salts	"Onium" Salts
Na^+Cl^-	NH_4^+Cl^-
K^+NO_3^-	$\text{H}_3\text{O}^+\text{Cl}^-$
$\text{Ca}^{++}\text{SO}_4^{--}$	NH_4^+OH^-
$\text{Fe}^{+++}\text{Cl}_3^-$	$\text{H}_3\text{O}^+\text{HSO}_4^-$
Classical Bases	Not Salts
Na^+OH^-	As_2S_3
K^+OH^-	CdCl_2
Li^+OH^-	HgCl_2
$\text{Mg}^{++}(\text{OH})_2^-$	$\text{Hg}(\text{CN})_2$

The more we consider these points, the more reasonable the new ideas become but one could wish that more texts and teachers had the daring to use them consistently. I look forward to the time when some department somewhere will start a generation of students right and use the new ideas entirely. I am afraid, however, that they would still have to be somewhat familiar with the classical ideas in order to be able to converse with the "barbarians" elsewhere.

REFERENCES

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3. Sidgwick, "Electron theory of valency" Oxford Press, 1927.