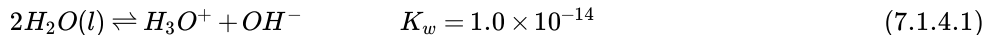


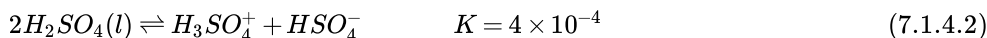
## 7.1.4: Autoionization and Solvent Leveling

### Solvent Autoionization

The Brønsted-Lowry concept allows for an understanding of hydrogen ion transfer chemistry in amphoteric protic solvents. Amphoteric protic solvents are those which can both accept and receive hydrogen ions. From the viewpoint of the Brønsted-Lowry concept the acid-base chemistry in these solvents is governed by autoionization equilibria analogous to water autoionization.

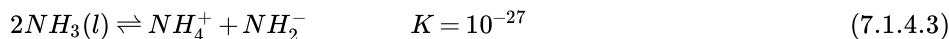


For example, sulfuric acid ionizes according to the equation:



The magnitude of the solvent autoionization constant in a given amphoteric solvent determines the amount of protonated and deprotonated\* solvent present. Since sulfuric acid's autoionization constant is much larger than that of water  $K_w = 10^{-14}$  the concentration of  $H_3SO_4^+$  and  $HSO_4^-$  present in pure sulfuric acid is  $\sim 0.02\text{ M}$ , much greater than the  $10^{-7}\text{ M}$   $H^+$  and  $OH^-$  present in pure water.

In contrast, ammonia's autoionization constant is much less than that of water and only  $\sim 10^{-27}\text{ M}$   $NH_4^+$  and  $NH_2^-$  are present in pure ammonia.



### Solvent Leveling Effect

The solvent leveling effect limits the strongest acid or base that can exist in acidic, basic, and amphoteric solvents. The conjugate acid and base of the solvent are the strongest Brønsted acid and bases that can exist in that solvent. To see why this is the case for acids consider the reaction between a Brønsted acid (HA) and solvent (S):



This equilibrium will favor dissociation of whichever is a stronger acid - HA or  $HS^+$ . If the acid is stronger it will mostly dissociate to give  $HS^+$ , while if the solvent's conjugate acid is stronger the acid will be mostly un-ionized and remain as HA.

Any acid significantly stronger than  $HS^+$  will act as a strong acid and effectively dissociate completely to give the solvent's conjugate acid  $HS^+$ . This also means that the relative acidity of acids stronger than  $HS^+$  cannot be distinguished in solvent S. This is called the leveling effect since the solvent "levels" the behavior of acids much stronger acids than it to that of complete dissociation. For example, there is no way to distinguish the acidity of strong acids like  $HClO_4$  and  $HCl$  in water since they both completely dissociate. However, it is possible to distinguish their relative acidities in solvents that are more weakly basic than the conjugate base of the strongest acid since then the acids will dissociate to different extents. Such solvents are called differentiating solvents. For example, acetonitrile (MeCN) acts as a differentiating solvent for  $HClO_4$  and  $HCl$ . Both  $HClO_4$  and  $HCl$  partially dissociate in MeCN, with the stronger acid  $HClO_4$  dissociating to a greater extent than  $HCl$ .

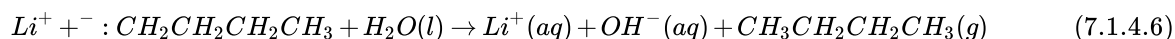
The leveling effect can also occur in basic solutions. The strongest Brønsted base, B, that can exist in a solvent is determined by the relative acidity of the solvent and the base's conjugate acid,  $BH^+$ , determines whether the base will remain unprotonated and able to act as a base in that solvent. If the solvent is represented this time as HS then the relevant equilibrium is:



The position of this equilibrium depends on whether B or  $S^-$  is the stronger base. If the solvent's conjugate base,  $S^-$ , is stronger then the base will remain unprotonated and available to act as a base. However, if B is a stronger base than  $S^-$  it will deprotonate the solvent to give  $BH^+$  and  $S^-$ . In this way the strongest base that can exist in a given solvent is the solvent's conjugate base. The relative strength of Brønsted bases can only be determined in solvents that are more weakly acidic than  $BH^+$ ; otherwise the bases will all be leveled to  $S^-$ .

It is important to consider the levelling effect of protic solvents when performing syntheses that require the use of basic reagents. For instance, hydride and carbanion reagents (Lithium aluminum hydride, Grignard reagents, alkylolithium reagents, etc.) cannot be used as nucleophiles in protic solvents like water, alcohols, or enolizable aldehydes and ketones. Since carbanions are stronger bases than these solvent's conjugate bases they will instead act as Brønsted bases and deprotonate the solvent. For example if one

adds n-butyllithium to water the result (along with much heat and possibly a fire) butane and a solution of lithium hydroxide will be obtained:



Since hydride and carbanion reagents cannot be used as nucleophiles in protic solvents like water or methanol they are commonly sold as solutions in solvents such as hexanes (for alkylolithium reagents) or tetrahydrofuran (for Grignard reagents and  $LiAlH_4$ ).

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2. (a) Gutmann, V. *Allg. Prakt. Chem.* 1970, 21, 116. (b) Gutmann, V. *Fortschr. Chem. Forsch.* 1972, 27, 59.
3. Burgess, J. *Metal Ions in Solution* Ellis Horwood, 1978, pg. 268.

## Contributors and Attributions

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