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Acidity

A Unified pH Scale for All Phases**

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Arrhenius,[1] Brønsted,[2] and Lowry[3] defined acids as proton donors and bases as proton acceptors, a concept nowadays known as Brønsted acidity. It is used in all chemistry-related areas[4] including materials science[5] energy storage,[6] catalysis,[7,8] environmental science,[9] and molecular biology.[10] In aqueous solution Brønsted acidity is expressed quantitatively as the pH value (referred to here as "conventional pH value") that is $-\lg a(H^+,aq)$ with the activity of the hydrated proton $a(H^+,aq)$ given in $mol\,L^{-1}$.[11] Within one homogenous medium, pH differences are proportional to electrochemical potential differences and thus directly connected to thermodynamics.[11] The concept of pH [or $-\lg a(H^+,solv)$] for nonaqueous solutions is less common, but self-consistent pK_a scales of acidity and/or basicity exist in DMSO,[12] acetonitrile,[13] and other solvents. Importantly, the acidities determined in different solvents and expressed as conventional pH values in those solvents are not directly comparable.

To express the acidity of strongly acidic media—for example, pure mineral acids—the Hammett function and the H_0 value[14] were developed. For aqueous solutions of strong acids, the H_0 scale can be viewed as a continuation of the pH scale into the realm of negative conventional pH values. The H_0 value is currently the most common parameter for quantifying the acidity of superacidic media,[15] that is, Brønsted acids stronger than 100 % sulfuric acid.[16] However, although H_0 values are widely used, they do not represent a "thermodynamic" acidity scale, which one should be able to validate, for example, by electrochemical measurements or computations.[17] The first proposals for a unified acidity scale, which would make it possible to quantitatively compare acidity throughout different media, date back to the 1950s.[18] Approaches to thermodynamic acidity values were developed by Izmailov,[19] Alexandrov,[20] and Strehlow.[21] Although correct in their essence, the approaches have not found widespread application owing to experimental difficulties.

Herein we propose a unified Brønsted acidity scale on the basis of the absolute chemical potential of the proton in any medium. In this scale we define the reference state for maximum acidity as the absolute standard chemical potential $\mu_{abs}^{\ominus}(H^+,g)$ of the proton in the gas phase which is arbitrarily set to 0 $kJ\,mol^{-1}$. In fact, this standard state—the ideal proton gas at 1 bar and 298.15 K—is physically highly unstable, but it can be calculated very well and corresponds to the standard state of neutral gases. The acidity and hence the chemical potential of the gaseous proton $H^+(g)$ is lowered by the interaction with any type of medium, that is, by complexation of H^+ with molecules in the gas phase, solution, or in the solid state (Figure 1). Solid-state acidity is not discussed in detail here, but a concept to establish a thermodynamic acidity scale for ionic solids has been developed by Maier[22] and can be included in our concept without problems.

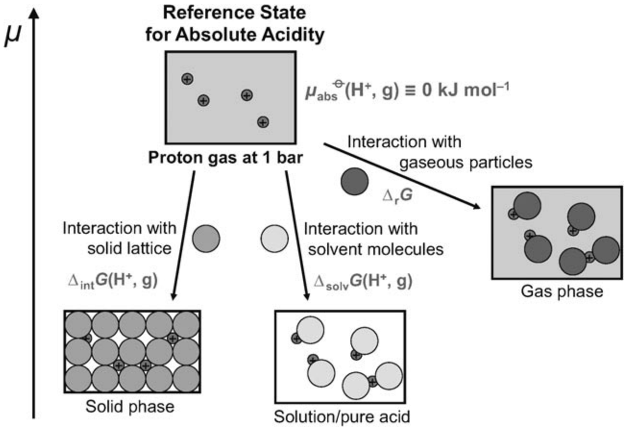

Figure 1. The reference state of maximum acidity for the unified Brønsted acidity scale and the quantitative thermodynamic relations to Brønsted acidity in all phases.

Initially we examine the acidity in the gas phase. If $H^+(g)$ reacts with a gas molecule $L(g)$, $HL^+(g)$ is formed and the lowering of the proton chemical potential under standard conditions can be expressed by the well-known gas-phase acidity (GA) of HL^+ according to Equation (1).[23]

$$H^+(g) + L^{(0,-)}(g) \xrightarrow{\Delta_r G^{\ominus} = -GA} HL^{(+,0)}(g) \qquad (1)$$

By definition, GA values are given only for standard conditions, yet the acidity of any given gaseous acid clearly depends on the partial pressure of the acid/protonated gas as well and usually also on its propensity for speciation, for example, formation of HL_2^+, HL_3^+, and $H_2L_3^{2+}$, etc. in the gas phase. In this context we explicitly investigated HCl gas as an example of a strong gaseous acid. Here, L in Equation (1) is

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Cl^-. Figure 2 summarizes the influence of pressure on the absolute chemical potential of the proton in HCl gas as a function of the total HCl pressure and speciation.

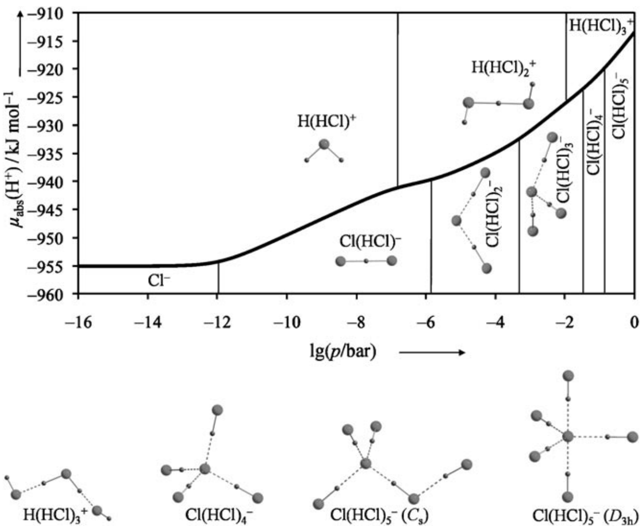

Figure 2. Pressure dependence of the absolute chemical potential $\mu_{abs}(H^+)$ of the proton in hydrogen chloride gas and Boltzmann weighted acidity-dominating gaseous ionic species. See the Supporting Information for the calculation of $\mu_{abs}[H^+$, in HCl(g)].

The acidity of gaseous HCl stretches over 42 kJ mol^{-1} of $\mu_{abs}[H^+$, in HCl(g)] in the given pressure range between 10^{-15} and 1.0 bar; this corresponds to 7 pH units. However, the range of $\mu_{abs}[H^+$, in HCl(g)] from −955 to −913 kJ mol^{-1} indicates much less stabilization of the proton in HCl(g) than one would expect from the GA value of HCl(g) of 1374 kJ mol^{-1}. This suggests that HCl(g) is only a mild acid, even weaker than, for example, an alcohol like $(F_3C)_3COH$ (GA = 1355 kJ mol^{-1}).[24] However, comparison of our $\mu_{abs}[H^+$, in HCl(g)] value to the situation for very strong pure acids or their solutions as given below [see Table 1, Figure 3, and Eq. (2)] clearly shows that gaseous HCl, but not aqueous HCl(aq), is superacidic. The chemical potential of the proton in HCl gas under standard conditions is 232 kJ mol^{-1} higher than that of water at pH 7; in other words H^+ is less stabilized by about 41 pH units [see Eqs. (2) and (3)]. The inclusion of the pressure dependence of the acidity in the gas phase and the formation of, for example, $H(HCl)_n{}^+$ and $Cl(HCl)_m{}^-$, represents a crucial advance of the unified acidity scale compared to the GA scale.

Let us now turn to $\mu_{abs}(H^+)$ in condensed phases: the lowering of the chemical standard potential of the gaseous proton in any solution is given by the Gibbs standard solvation energy $\Delta_{solv}G^\ominus(H^+,g)$, which corresponds to a proton transfer from the ideal proton gas at 1 bar to an ideal 1M solution of protons which means pH 0. Such a solution of protons can contain different protonated species, but their activities are all connected by equilibrium constants; the absolute chemical potential of the proton is determined by this ensemble of ions. These values can in part be extracted from the literature (see Table 1) but were mainly computed by using the rCCC model (for full details see the Supporting Information).

Table 1: Gibbs standard free energies of proton solvation $\Delta_{solv}G^\ominus(H^+)$ in different solvents. For comparison we also include the values for gaseous HCl in italics at three pressures.

Solvent L	$\Delta_{solv}G^\ominus(H^+)$ [kJ mol^{-1}] rCCC model	$\Delta_{solv}G^\ominus(H^+)$ [kJ mol^{-1}] assessed[a]
benzene	−816	–
CH_2Cl_2	−835	–
SO_2	−898	–
HF	−908[b]	–
HCl(g) (1.0 bar)	−913	–
HSO_3F	−924	–
HCl(g) (10^{-3} bar)	−931	–
HCl(g) (10^{-15} bar)	−955	–
H_2SO_4	−966	–
Et_2O	−998	–
H_3CCN	−1056	−1058;[c] −1052[d]
H_2O	−1107	**−1105 ± 8[25] reference value**
DMSO	−1120	−1124,[c] −1125[d] −1117,[27] −1124[28]

[a] See the Supporting Information for a detailed chapter. [b] Derived from its H_0 value (see the Supporting Information). [c] Derived from proton-transfer Gibbs energies $\Delta_tG^\ominus$ (see the Supporting Information). [d] Derived from the pK_a values of Me_3NH^+ in DMSO and H_3CCN (see the Supporting Information).

In brief, we developed and validated (see the Supporting Information) a method to calculate the Gibbs standard solvation free energy $\Delta_{solv}G^\ominus(H^+,g)$ of the proton in any solvent with an estimated 1σ error (standard uncertainty) of 10 kJ mol^{-1}. Note that standard conditions correspond to an activity of H^+(solv) of 1.0 mol L^{-1} at 298.15 K and 1 bar, which means pH 0. For the proton in water the magnitude of $\Delta_{solv}G^\ominus(H^+,H_2O)$ was determined[25] as −(1105±8) kJ mol^{-1}. This shows that the chemical potential of the gaseous proton H^+(g) under standard conditions is lowered in water of pH 0, and the absolute acidity of $H^+(H_2O)$ is −(1105±8) kJ mol^{-1}. Since the pH value also represents the protochemical potential and one pH unit difference amounts to a change of the chemical potential by 5.71 kJ mol^{-1},[26] one can now assign absolute acidities to H^+(solv) at all activities simply by subtracting pH × (5.71 kJ mol^{-1}) from $\Delta_{solv}G^\ominus(H^+)$ [Eq. (2)].

$$\mu_{abs}(H^+,\mathrm{solv}) = \Delta_{solv}G^\ominus(H^+) - [\mathrm{pH} \times (5.71\ \mathrm{kJ\,mol^{-1}})] \qquad (2)$$

Note that this relation is independent of the solvent used and one needs only $\Delta_{solv}G^\ominus(H^+)$ of the relevant solvent as an anchor point. To apply Equation (2) not only to water but also to other solvents/strong acids commonly used in chemistry, we assessed $\mu_{abs}{}^\ominus(H^+$, solv) = $\Delta_{solv}G^\ominus(H^+)$ of the solvents/pure acids listed in Table 1.

The $\Delta_{solv}G^\ominus(H^+)$ value of the solvent L in Table 1 reflects the lowering of the chemical potential of the gaseous proton H^+(g) on transfer to the solvent L under standard conditions giving $H^+(solv) = HL_n{}^+(solv)$ and a pH of 0 in the respective solvent L.[29] Using Equation (2) it is now possible to compare the absolute acidities of solutions. For example, an ether solution of $a(\mathrm{H^+,Et_2O})$ of $7\times10^{-11}\,\mathrm{mol\,L^{-1}}$ (conventional pH 10.2 in $\mathrm{Et_2O}$) has the same absolute acidity of $-1056\,\mathrm{kJ\,mol^{-1}}$ as a solution of protons in acetonitrile with $a(\mathrm{H^+,CH_3CN})$ of $1.0\,\mathrm{mol\,L^{-1}}$ (conventional pH 0 in $\mathrm{CH_3CN}$). Furthermore, the reference to the absolute chemical potential of the proton in the gas phase also allows assigning absolute (as opposed to conventional) $\mathrm{pH_{abs}}$ values simply by division by $-5.71\,\mathrm{kJ\,mol^{-1}}$ according to Equation (3).

$$\mathrm{pH_{abs}} = \frac{\mu_{\mathrm{abs}}(\mathrm{H^+,solv})}{-5.71\,\mathrm{kJ\,mol^{-1}}} \tag{3}$$

Note that now also for gaseous HCl a (pressure-dependent) $\mathrm{pH_{abs}}$ can be assigned. Using this relation, the conventional pH values in diethyl ether $[\mathrm{pH(Et_2O)}=10.2]$ and in acetonitrile $[\mathrm{pH(CH_3CN)}=0]$ can now be compared quantitatively and both have the same absolute $\mathrm{pH_{abs}}$ value of 184.9. These relations are shown in Figure 3 for all solvents/pure acids investigated as well as for gaseous HCl.

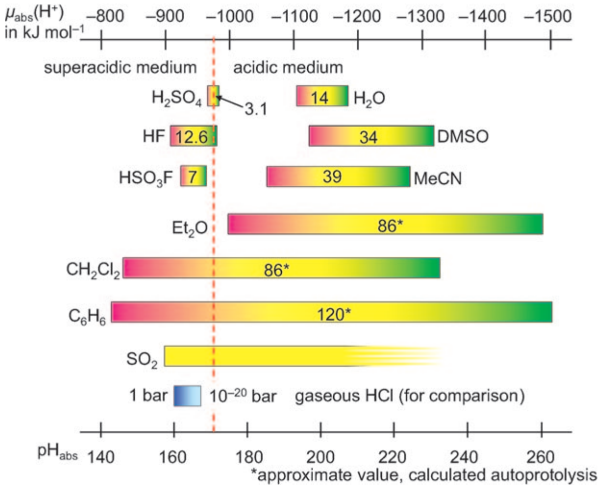

Figure 3. Comparison of the accessible absolute Brønsted acidities given by their $\Delta_{\mathrm{solv}}G^{\ominus}(\mathrm{H^+})$ [Eq. (2)] or $\mathrm{pH_{abs}}$ [Eq. (3)] values in different media as expressed by the width of their protochemical window ($=\mathrm{p}K_{\mathrm{AP}}$).

A word of caution is necessary here: From Figure 3 it might appear that of all the solvents presented, benzene is the ultimate solvent for maximum acidity. However, because of the very nonpolar character of this solvent, its capability to dissolve ionic compounds is very limited. A first guess would give the most acidic minimum pH that may be reached in benzene to be about 10 $[a(\mathrm{H^+,C_6H_6})=10^{-10}\,\mathrm{mol\,L^{-1}}]$; this corresponds to a maximal acidity $\mu_{\mathrm{abs}}(\mathrm{H^+,C_6H_6})$ of about $-873\,\mathrm{kJ\,mol^{-1}}$. Note that Debye–Hückel effects diminish the effective acidity level that may be reached in benzene only at concentrations higher than $10^{-6}\,\mathrm{mol\,L^{-1}}$ (see the Supporting Information for a discussion). This indicates that one can reach highly acidic conditions in benzene as a solvent, but it appears that in practice and given the normal strong acids available, the more polar solvents $\mathrm{CH_2Cl_2}$ or $\mathrm{SO_2}$ are better suited to achieve the desired acidity levels in solution.

Equations (2) and (3) can now be used to provide a sound thermodynamic definition of superacidity. We have calculated the absolute chemical potential of $\mathrm{H^+(H_2SO_4)}$ at standard conditions as $-966\,\mathrm{kJ\,mol^{-1}}$. Using the autoprotolysis relation [Eq. (4)] and the experimentally determined[30] autoprotolysis constant $\mathrm{p}K_{\mathrm{AP}}$ of $\mathrm{H_2SO_4}$, we calculated $\mu_{\mathrm{abs}}(\mathrm{H^+,100\,\%\,H_2SO_4})$.

$$\mathrm{H_2SO_4(H_2SO_4)} \rightleftharpoons \mathrm{H^+(H_2SO_4)} + \mathrm{HSO_4^-(H_2SO_4)} \tag{4}$$

At $\mathrm{p}K_{\mathrm{AP}}=3.1$, a proton activity of $\mathrm{H^+(H_2SO_4)}$ of $0.028\,\mathrm{mol\,L^{-1}}$ $(=\sqrt{K_{\mathrm{AP}}})$ or a $\mathrm{pH(H_2SO_4)}$ value of 1.55 is calculated for pure sulfuric acid. Employing Equations (2) and (3) gives $\mu_{\mathrm{abs}}(\mathrm{H^+,100\,\%\,H_2SO_4})=-975\,\mathrm{kJ\,mol^{-1}}$ and $\mathrm{pH_{abs}(100\,\%\ H_2SO_4)}=170.8$. Therefore, all solutions of acids/pure acids with $\mu_{\mathrm{abs}}(\mathrm{H^+,solv})>-975\,\mathrm{kJ\,mol^{-1}}$ or $\mathrm{pH_{abs}}<170.8$ can be considered as superacidic according to the definition:

“A Brønsted superacid is a medium, in which the chemical potential of the proton is higher than in pure sulfuric acid.”

In this respect HCl gas or solutions of strong acids in benzene[15b] can indeed be considered superacidic (see the pH 10 example above).

Using the absolute acidity scale we can now compare acidities in different solvents. The $\mathrm{p}K_{\mathrm{a}}$ values of acetic acid and 4-toluenesulfonic acid have been determined in water,[31] DMSO,[12] and $\mathrm{CH_3CN}$.[32] For example, using the rCCC $\Delta_{\mathrm{solv}}G^{\ominus}(\mathrm{H^+})$ values (Table 1), standard first-year chemistry knowledge,[33] and Equations (2) and (3), the absolute acidities of solutions of an activity of $0.1\,\mathrm{mol\,L^{-1}}$ acid in the given solvent can now be compared (Figure 4).

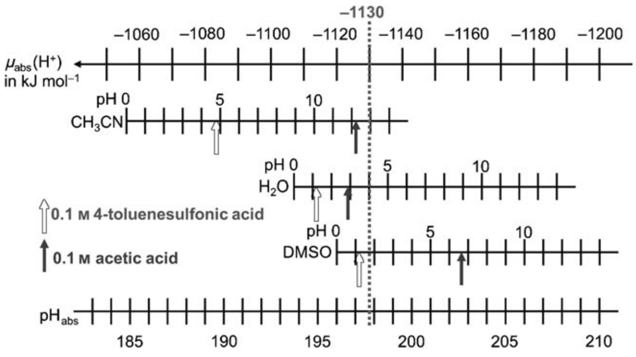

Figure 4. Comparison of the absolute Brønsted acidities of 0.1 M solutions of acetic acid and 4-toluenesulfonic acid in $\mathrm{CH_3CN}$, DMSO, and water. Conventional pH values for an absolute acidity of $-1130\,\mathrm{kJ\,mol^{-1}}$ or $\mathrm{pH_{abs}}$ of 197.9. rCCC $\Delta_{\mathrm{solv}}G^{\ominus}(\mathrm{H^+})$ values (Table 1) were used as anchor points.

Another example: An absolute acidity of $-1130\,\mathrm{kJ\,mol^{-1}}$ or ($\mathrm{pH_{abs}}$ 197.9; dotted line in Figure 4) is reached at a conventional pH of 13.0 (in $\mathrm{CH_3CN}$), 4.0 (in water), and 1.8 (in DMSO). Thus, application of the data collected in Table 1, Equations (2) and (3), and available $\mathrm{p}K_{\mathrm{a}}$ values of Brønsted acids in different solvents allows for a quantitative comparison of the level of acidity provided by the same acid in different solvents.

We have established a new unified Brønsted acidity scale by setting the absolute chemical standard potential $\mu_{abs}^{\ominus}(H^+,g)$ of the proton in the (ideal) gas phase at 1 bar and 298.15 K to 0 $kJ\,mol^{-1}$ and by using $\mu_{abs}(H^+,solv)$ [Eq. (2)] or pH_{abs} [Eq. (3)] of the proton $H^+(solv)$ in solution as an absolute measure for Brønsted acidity. This scale intrinsically also includes the well-established GA scale. However, it appears from our assessment of the gas-phase acidity of HCl(g) that since gas-phase speciation was previously neglected, the unified acidity scale is much better suited to investigate the acidity of gaseous media than a collection of GA values. Our investigations underline the importance of speciation and pressure dependence for the acidity in the gas phase.

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