

Acid-Base Strength

Chapter 6

Monday, November 2, 2015

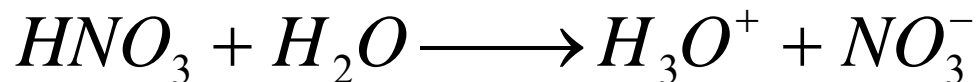
Acid-Base Strength

We've seen that the reactivity of acids and bases can be viewed through the HSAB Model or the EC Model.

- **Both of these models try to provide a conceptual framework to explain empirical observations about acid-base reactivity**
- **To determine the actual strength of an acid or of a base, different measurements can be made:**
 - **calorimetric measurements of reaction enthalpies (direct)**
 - **temperature dependence of K_{eq} (direct)**
 - **spectroscopic measurements (IR, NMR, UV-Vis) (indirect)**

Direct Thermodynamic Measurements

For reactions that go to completion, the enthalpy of the reaction can be determined directly from calorimetry

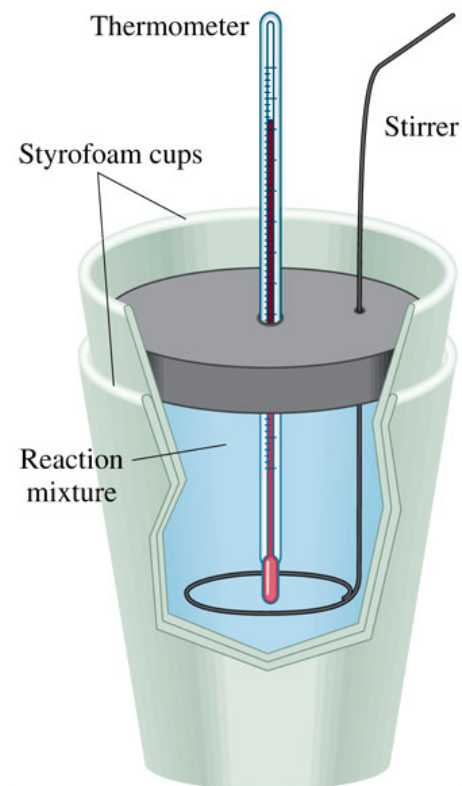


At constant pressure:

$$q_P = \Delta E + P\Delta V = \Delta H$$

Diagram illustrating the relationship between heat at constant pressure (q_P), change in internal energy (ΔE), change in volume (ΔV), and change in enthalpy (ΔH):

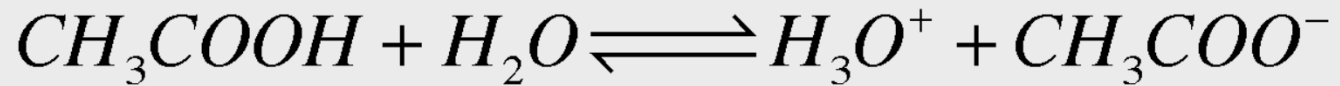
- q_P is equal to $\Delta E + P\Delta V$, which is equal to ΔH .
- $\Delta V \cong 0$ for liquid phase.
- Labels: internal energy, $\Delta V \cong 0$ for liquid phase, enthalpy.



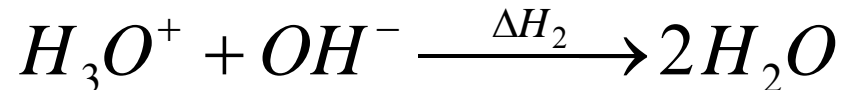
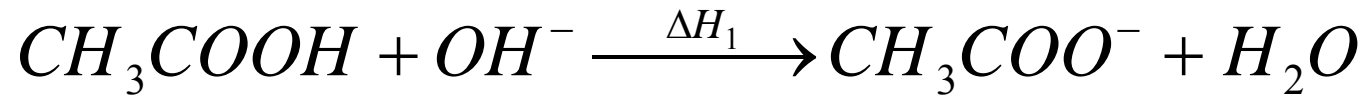
Constant Pressure Calorimeter

Direct Thermodynamic Measurements

If a reaction doesn't go to completion, the procedure is a little more complicated:

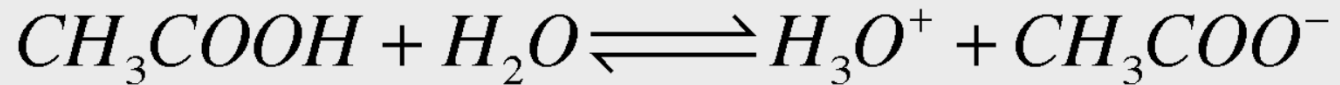


We can use Hess' Law and combine several different thermodynamic measurements to get the desired value:

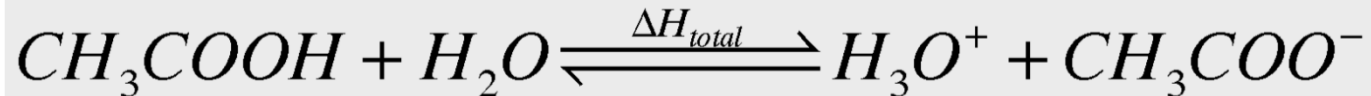
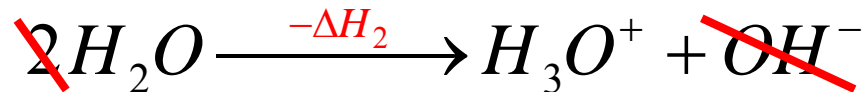
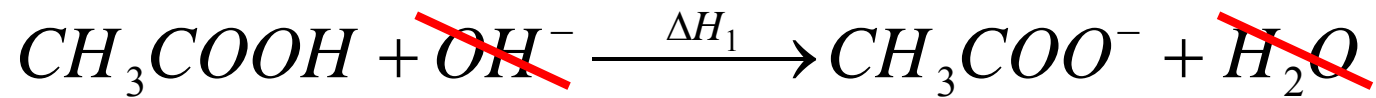


Direct Thermodynamic Measurements

If a reaction doesn't go to completion, the procedure is a little more complicated:



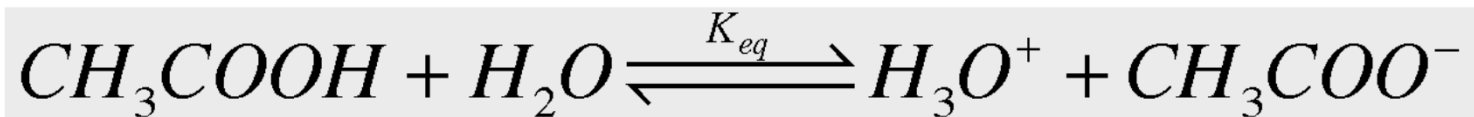
We can use Hess' Law and combine several different thermodynamic measurements to get the desired value:



$$\Delta H_{total} = \Delta H_1 - \Delta H_2$$

Direct Thermodynamic Measurements

If a reaction doesn't go to completion, the procedure is a little more complicated:



Another alternative is to measure the temperature dependence of K_{eq} ...

$$\Delta G_{total} = \Delta H_{total} - T \Delta S_{total} = -RT \ln K_{eq}$$

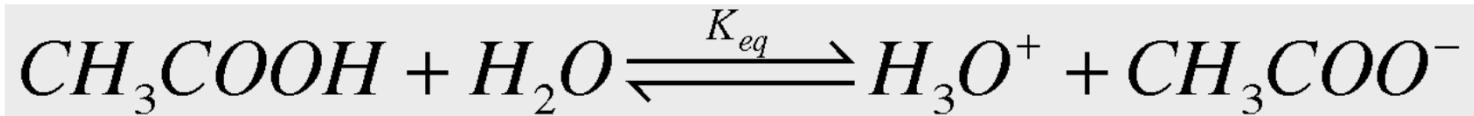
$$\ln K_{eq} = -\frac{\Delta H_{total}}{RT} + \frac{\Delta S_{total}}{R} \quad (\text{van't Hoff equation})$$

...so a plot of $\ln K_{eq}$ vs T^{-1} gives a straight line, $y = mx + b$

$$\text{slope} = m = -\frac{\Delta H_{total}}{R} \quad \text{intercept} = b = \frac{\Delta S_{total}}{R}$$

Direct Thermodynamic Measurements

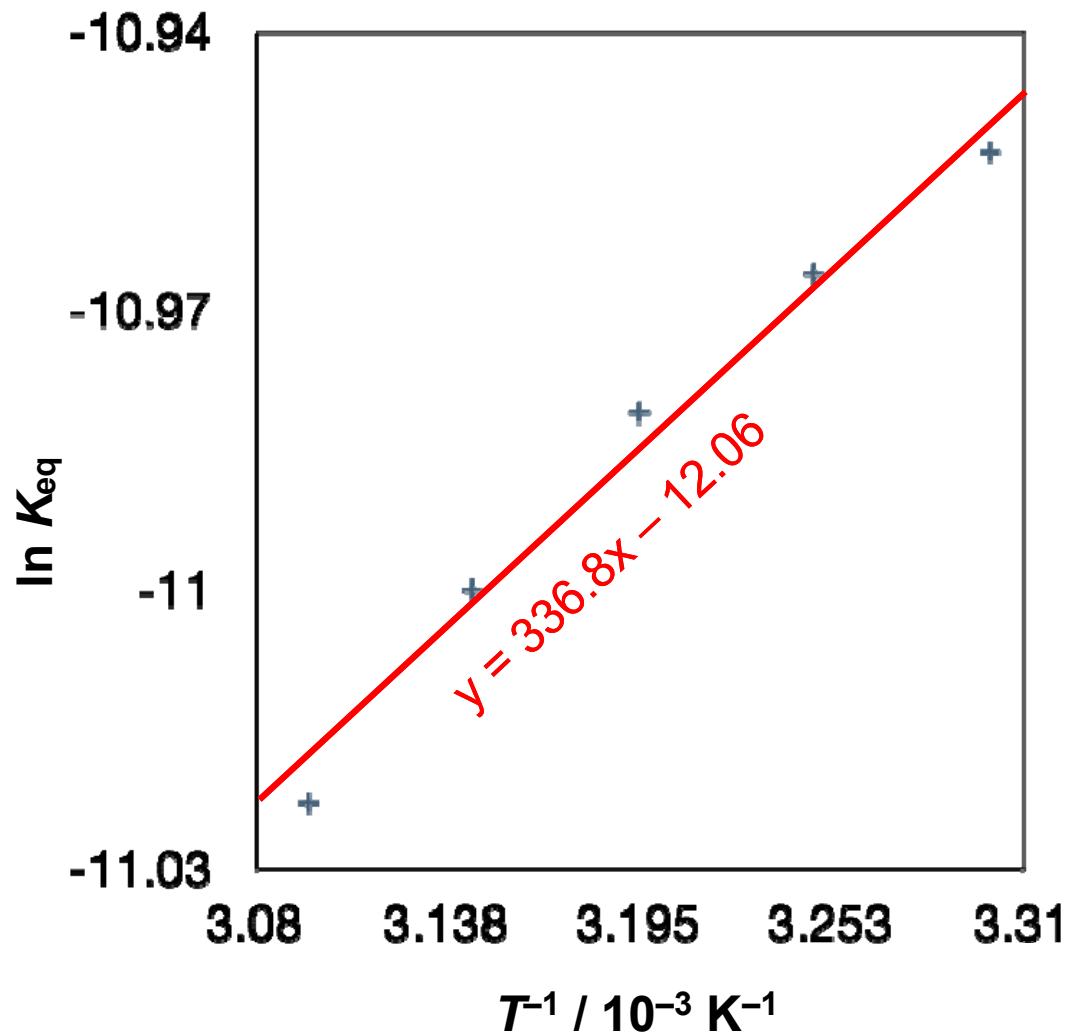
If a reaction doesn't go to completion, the procedure is a little more complicated:



T / K	$K_{eq} / 10^{-5}$
303	1.750
308	1.728
313	1.703
318	1.670
323	1.633

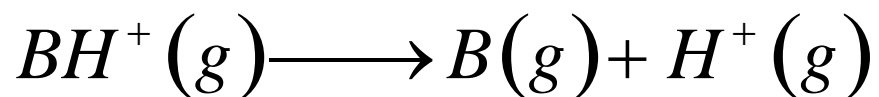
$$\Delta H_{total} = -mR = -2.8 \frac{kJ}{mol}$$

$$\Delta S_{total} = bR = -100 \frac{J}{mol \cdot K}$$

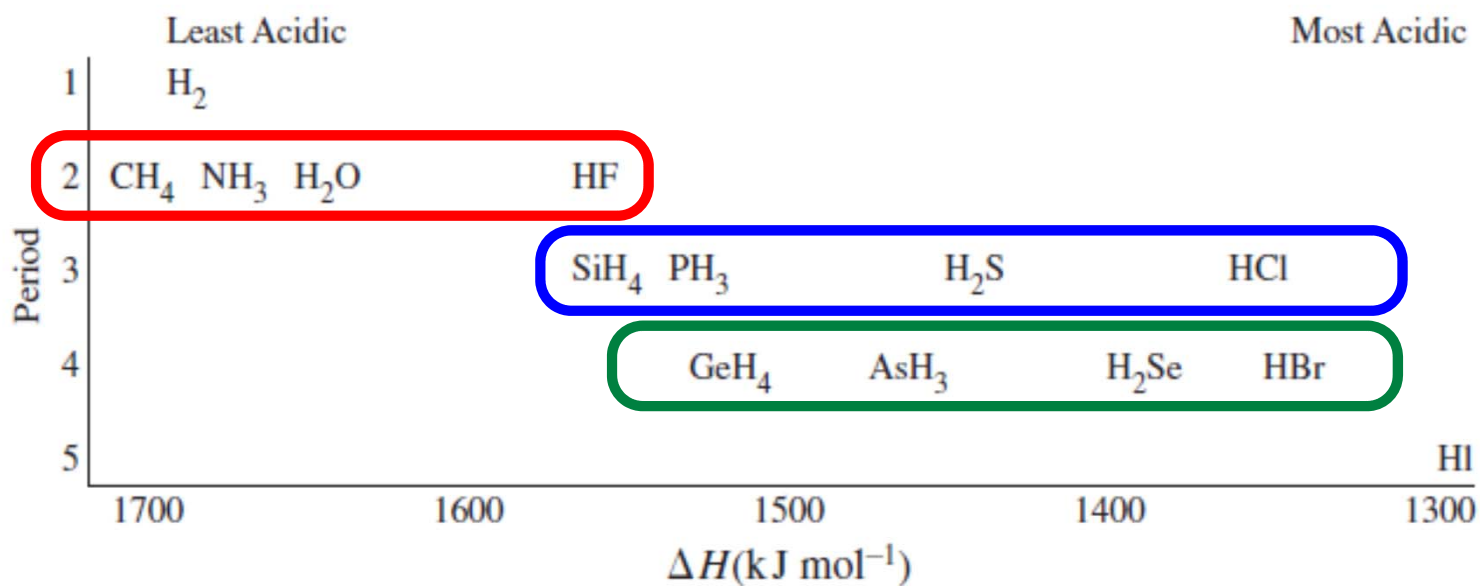


Gas Phase Proton Affinity

Proton affinity is a thermodynamic measurement conducted in the gas phase:

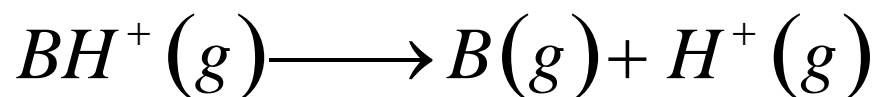


These measurements give us a “pure” view of base/acid strength, without complications from solvent effects (solvation).

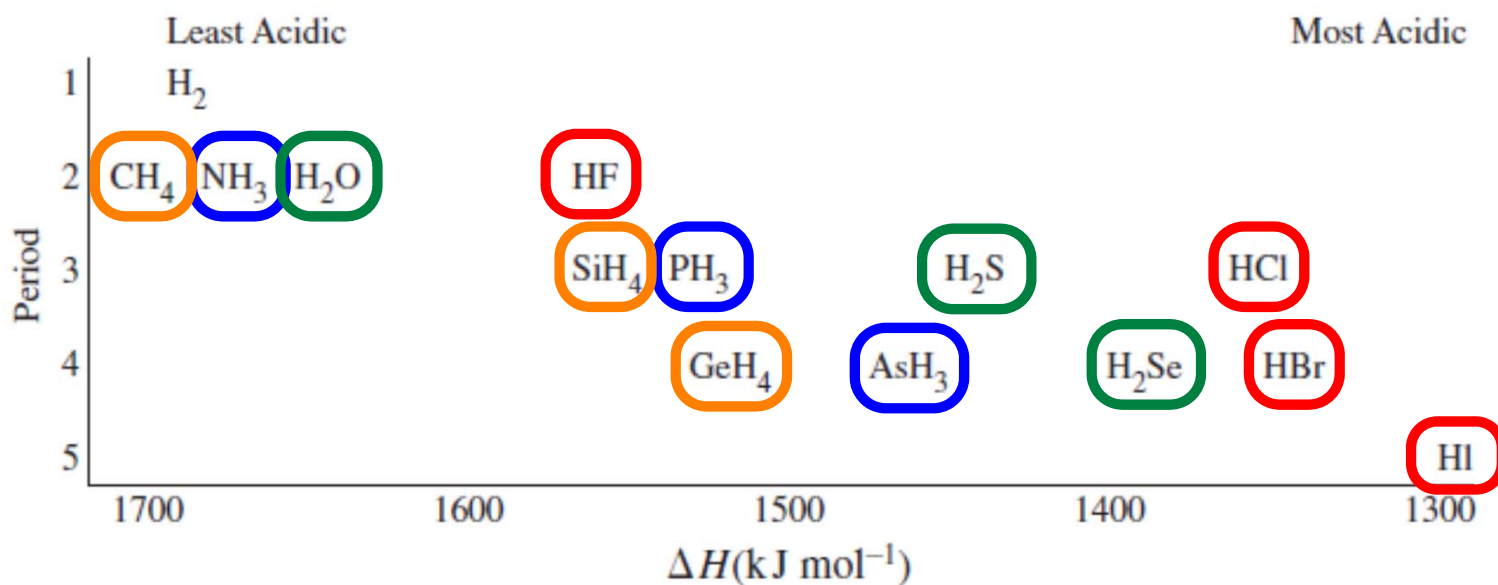


Gas Phase Proton Affinity

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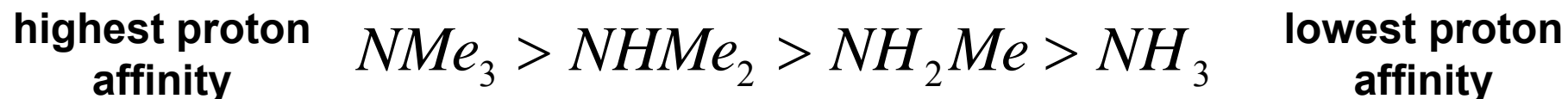


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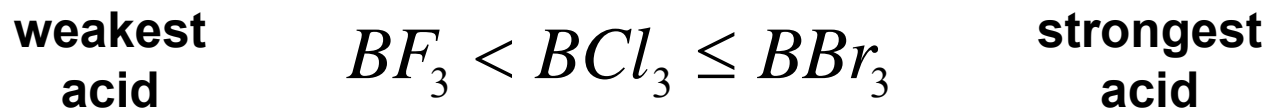
Substituent Effects – Electronic

Gas phase proton affinity measurements make it easy to examine how substituent changes can impact acidity/basicity.



This trend is an example of an inductive electronic effect. CH_3 is more electron releasing than H, making the nitrogen lone pair more basic.

Inductive effects tend to be fairly weak and can be overridden by π effects, for example in the boron halide acids,

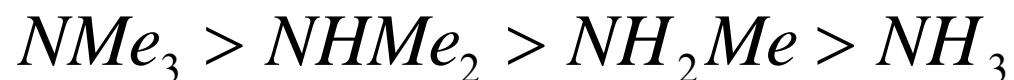


The best π bonding occurs between B and F, which overrides any inductive effect from the electronegative fluorine and quenches the Lewis acidity of BF_3

Substituent Effects – Steric

Gas phase proton affinity measurements make it easy to examine how substituent changes can impact acidity/basicity.

highest proton
affinity



lowest proton
affinity

Sterics can influence or override electronic trends in basicity (or acidity). When the gas phase measurement is made for bulky Lewis acids, different trends are observed:

highest BF_3
affinity



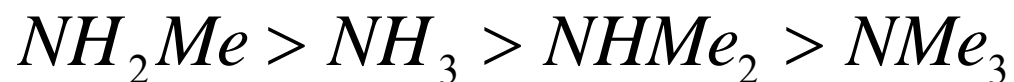
lowest BF_3
affinity

highest BMe_3
affinity



lowest BMe_3
affinity

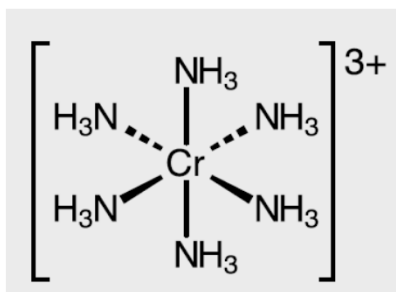
highest B^tBu_3
affinity



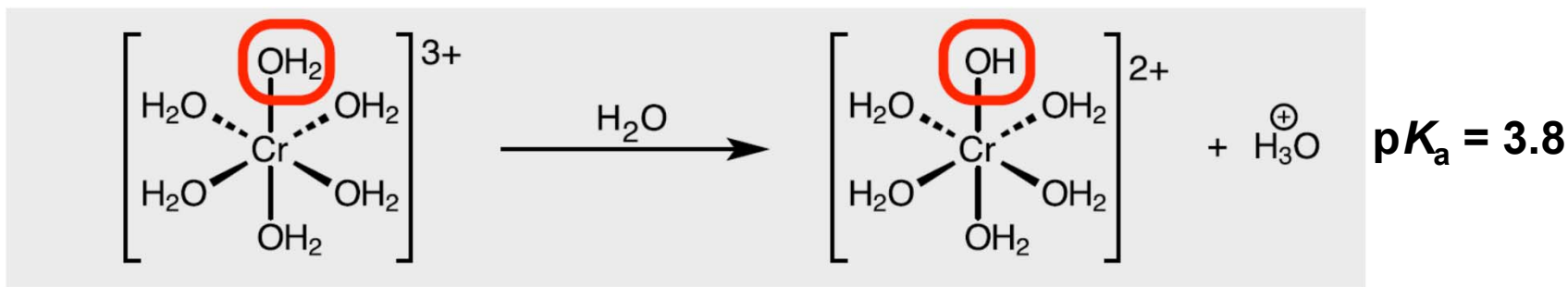
lowest B^tBu_3
affinity

Metals as Acids

Metals can act as Lewis acids, readily forming adducts with Lewis bases. These adducts are called coordination compounds.

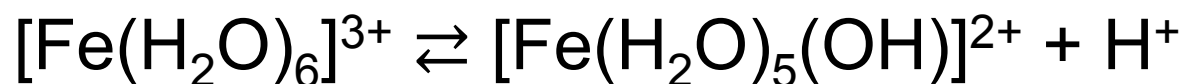
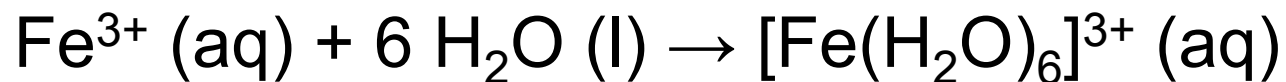


When the ligand (Lewis base) is water, the following secondary acid-base reactions can occur:



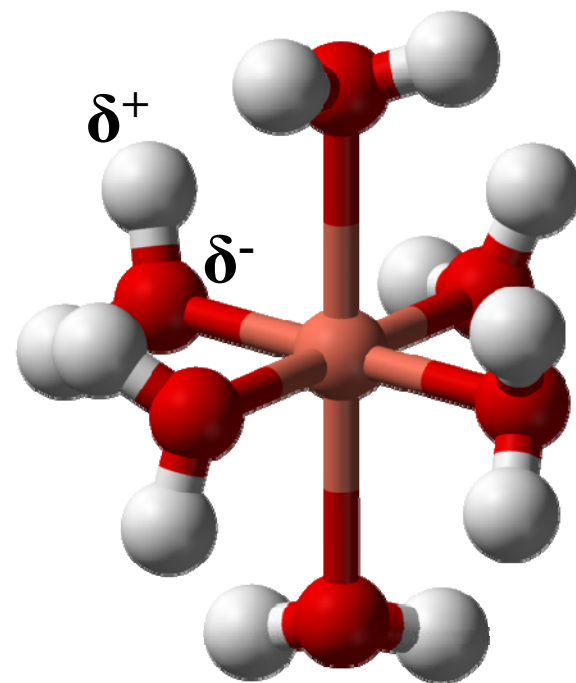
Metals as Acids

Salts of small, highly charged metal cations are acidic.

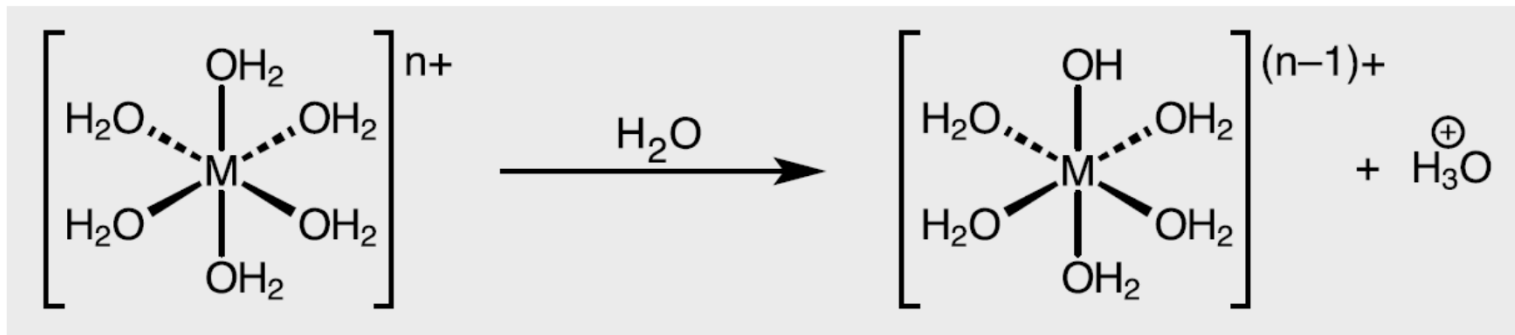


pH < 7

Other acidic metal cations: Cr³⁺, Al³⁺, Cu²⁺



Metals as Acids



M^{n+}	$\text{p}K_a$	M^{n+}	$\text{p}K_a$
Fe^{3+}	2.2	Fe^{2+}	8.3
Cr^{3+}	3.8	Cu^{2+}	8.3
Al^{3+}	5.0	Ni^{2+}	9.3
Sc^{3+}	5.0	Zn^{2+}	9.6

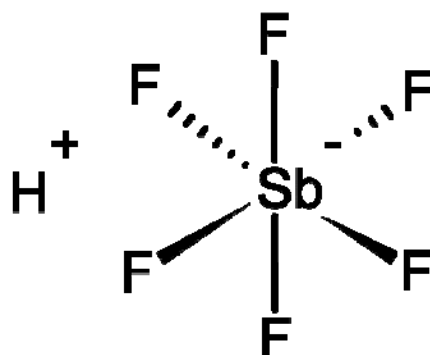
Superacids

Superacids are acids more acidic than pure sulfuric acid. Some are capable of protonating nearly anything, including hydrocarbons (they can dissolve candles!).

TABLE 6.3 Common Superacids and Their Acidities

Acid		H_0
Hydrofluoric acid ^a	HF	-11.0
Sulfuric acid	H ₂ SO ₄	-11.9
Perchloric acid	HClO ₄	-13.0
Trifluoromethanesulfonic acid (triflic acid)	HSO ₃ CF ₃	-14.6
Fluorosulfonic acid	HSO ₃ F	-15.6
<i>Magic Acid</i> ^b	HSO ₃ F—SbF ₅	-21 to -25 ^c
Fluoroantimonic acid	HF—SbF ₅	-21 to -28 ^c

Strongest superacids are formed by mixing strong Brønsted and Lewis acids



Fluoroantimonic acid
(HF-SbF₅)

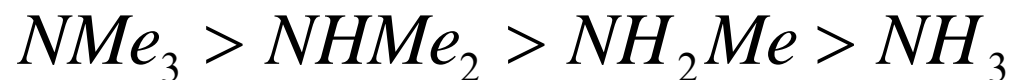
- strongest known superacid (10^{16} times stronger than sulfuric acid)
- very loosely held (“naked”) proton is highly reactive
- very stable conjugate base (SbF₆⁻) promotes proton transfer

Solvation Effects

Solvents have a huge impact on the observed strength of acids and bases. Compare these trends in gas phase proton affinities and aqueous pK_b values:

Gas Phase Proton Affinity

highest proton
affinity



lowest proton
affinity

Aqueous pK_b

strongest base



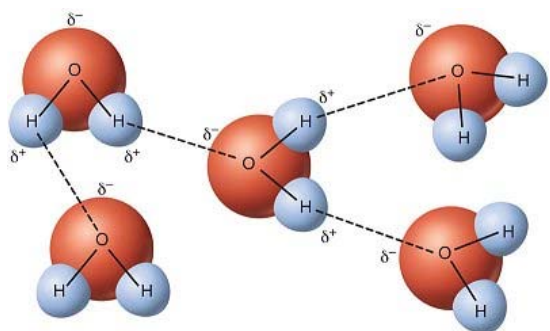
weakest base

These differences arise because of water's ability to solvate and hydrogen bond to the resulting ammonium cation, NHR_3^+

Solvation Effects

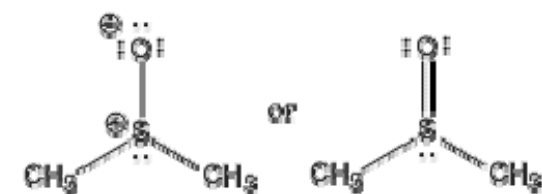
Because water is a strong hydrogen bond donor and acceptor, it has a strong influence on acid-base properties. Consider how the following acid pK_a values differ between water and DMSO:

Water



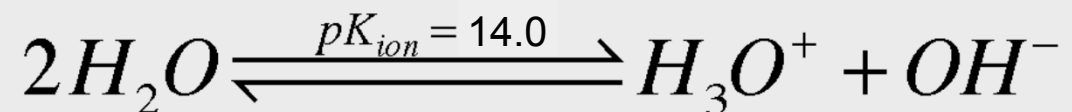
HA	$pK_a(\text{H}_2\text{O})$	$pK_a(\text{DMSO})$
HCl	-8.00	1.8
H_2SO_4	-3.0	1.99
CH_3COOH	4.76	12.3
H_2O	15.7	31.2
MeOH	15.5	27.9
PhOH	9.95	18.0
PhNH ₂	--	30.6
Et ₃ NH ⁺	10.75	9.00
PhNH ₃ ⁺	4.6	3.6

DMSO



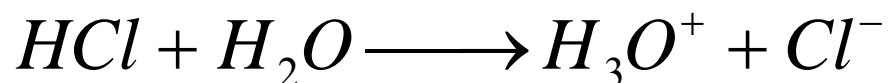
Leveling Effects

Another role that solvents play is to level the strength of an acid or base. This effect is a function of the solvent auto-dissociation:



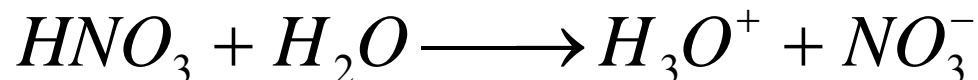
In water, the strongest acid you can have is H_3O^+ . A stronger acid, like HCl, protonates a water molecule to make H_3O^+ , thus leveling the strength of HCl.

$$pK_a = -8$$



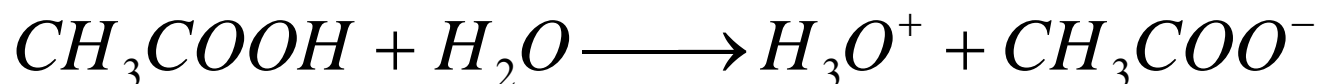
100% in 0.1 M solution

$$pK_a = -1.3$$



100% in 0.1 M solution

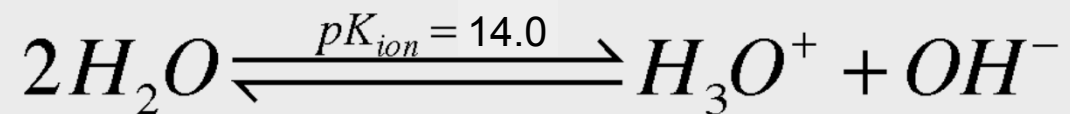
$$pK_a = 4.8$$



1.3% in 0.1 M solution

Leveling Effects

Another role that solvents play is to level the strength of an acid or base. This effect is a function of the solvent auto-dissociation:



This leveling effect means that each solvent has an acid-base window. The acidity of the solution can only be changed within that window. Outside of the window, solvent leveling will take over.

