## Strong Acids and Bases

## end of week switching to harris text

7.1 The Nature of Acids and Bases
7.2 Acid Strength

FRIDAY QUIZ ON
CHEMICAL
EQUILIBRIUM - some
M ACID/BASE
7.3 The pH Scale
7.4 Calculating the pH of Strong Acid Solutions
7.6 Bases (just the strong ones)

## Le Châtelier's Principle - Change $P$ ( $T$ Constant)

## Law of Mass Action

For $a A+b B<=>c C+d D$ the equilibrium constant $K$ is

$$
K=\frac{P^{c}{ }_{C} P^{d}{ }_{D}}{P^{a}{ }_{A} P_{B}^{b}}
$$

2) add inert gas (one that does not participate in the chemical equilibrium Since $P_{i}=n_{i} R T / V$, the partial pressures of all gases participating in the equilibrium reaction are unaffected by the presence of the inert gas. Hence so is the equilibrium constant.

## Le Châtelier's Principle - Change $P$ ( $T$ Constant)

## Law of Mass Action

For $a A+b B<=>c C+d D$ the equilibrium constant $K$ is

$$
K=\frac{P^{c}{ }_{C} P^{d}{ }_{D}}{P^{a}{ }_{A} P^{b}{ }_{B}}
$$

3) add gaseous reactant or product

Since $P_{i}=n_{i} R T / V$, partial pressures of all other gases participating in the equilibrium reaction are unaffected. But $K$ would change and it is a constant! Therefore if added gas were a reactant, $K$ would decrease unless equilibrium shifts to products => equilibrium must shift to products. Similarly, were the added gas a product, the equilibrium would shift toward reactants.

## Le Châtelier's Principle - Change $P$ ( $T$ Constant)

## Law of Mass Action

For $\quad \mathrm{a} A+\mathrm{bB}<=>\mathrm{cC}+\mathrm{dD}$ the equilibrium constant $K$ is

$$
K=\frac{P^{c}{ }_{C} P^{d}{ }_{D}}{P_{A}^{a} P_{B}^{b}}
$$

4) decrease volume by compression (consider 4-fold decrease)

Since $P_{i}=x_{i} P_{\text {тот }}$, each $P_{i}$ in $K$ (actually $Q$ until new equilibrium established) increases 4-fold. If total \# of moles of reactant gases in balanced chemical equation same as total \# of moles of product gases then no effect - powers that $P_{i}$ are raised to in numerator of $K$ same as in denominator. Otherwise, a $P$ increase shifts equilibrium to side with fewer moles in balanced equation.

## Le Châtelier's Principle - Change $T$ ( $P$ Constant)

Exothermic reactions gives off heat, endothermic reactions require heat
a) the following reaction is exothermic

$$
\mathrm{N}_{2}(g)+3 \mathrm{H}_{2}(g) \rightleftharpoons 2 \mathrm{NH}_{3}(g) \quad+\text { heat }
$$

b) the following reaction is endothermic

$$
+ \text { heat } \quad \mathrm{N}_{2}(g)+\mathrm{O}_{2}(g) \rightleftharpoons 2 \mathrm{NO}(g)
$$

analogy with the stress imposed by adding or removing a gaseous reactant if one were to consider heat as a "reactant" in the case of an endothermic reaction and as a "product" for an exothermic reaction.

## Nature of Acids and Bases

acid: accepts electron pair base: donates electron pair
donates $\mathrm{H}^{+}$ accepts $\mathrm{H}^{+}$
produces $\mathrm{H}^{+}$ produces $\mathrm{OH}^{-}$

problem: most general
must have H
need aqueous solution

## Brønsted-Lowry: Conjugate Acid-Base Pairs



Conjugate acid-base pair


Conjugate acid-base pair

EX 1. For each of the following write the formula of its conjugate.

| ACIDS | BASES |  |  |
| :--- | :--- | :--- | :--- |
| HCl | $\mathrm{Cl}^{-}$ | $\mathrm{NH}_{3}$ | $\mathrm{NH}_{4}^{+}$ |
| $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{OH}^{-}$ | $\mathrm{H}_{2} \mathrm{~S}$ | $\mathrm{H}_{3} \mathrm{~S}^{+}$ |
| $\mathrm{NH}_{3}$ | $\mathrm{NH}_{2}^{-}$ | NaOH | $\mathrm{H}_{2} \mathrm{O}$ |
| $\mathrm{CH}_{3} \mathrm{COOH}$ | $\mathrm{CH}_{3} \mathrm{COO}^{-}$ | $\mathrm{O}^{2-}$ | $\mathrm{OH}^{-}$ |
| $\mathrm{SH}^{-}$ | $\mathrm{S}^{2-}$ | $\mathrm{CN}^{-}$ | HCN |

## Brønsted-Lowry: Acid-Base Pair Chemistry

acids - proton donors $=>$ form a species [ acid $-\mathrm{H}^{+}$] called conjugate base

bases - proton acceptors => form a species [ base $+\mathrm{H}^{+}$] called conjugate acid
weak acid or base uses equilibrium arrow



## Brønsted-Lowry: Acid-Base Pair Chemistry

two acids competing to give up $\mathrm{H}^{+}$- the stronger acid "wins"

two bases competing for the acidic proton - the stronger base "wins"

EX 3. From the Brønsted-Lowry point of view, which is the stronger acid in the following reaction:

$$
\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})+\mathrm{HNO}_{3}(\mathrm{aq})<=>\mathrm{HSO}_{4}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{NO}_{3}^{+}(\mathrm{aq})
$$

## Amphoteric Nature of Water



The pH scale in water depends upon this

## Autoionization

A self-ionization process which depends upon the amphoteric nature of the solvent.. It is exactly this process which defines what acidity and basicity in a particular solvent is (via the autoionization reaction of the solvent).

> of water:

Water acting as both an acid and a base

of ammonia:
$\mathrm{NH}_{3}()+\mathrm{NH}_{3}(I)<=>\mathrm{NH}_{4}{ }^{+}(\mathrm{aq})+\mathrm{NH}_{2}^{-}(\mathrm{aq})$


conjugate acid conjugate base

## Strong Acids and Bases to Know

| seven strong acids to know |  |
| :--- | :--- |
| hydrochloric acid | HCl |
| hydrobromic acid | HBr |
| hydroiodic acid | HI |
| perchloric acid | $\mathrm{HClO}_{4}$ |
| chloric acid | $\mathrm{HClO}_{3}$ |
| sulfuric acid | $\mathrm{H}_{2} \mathrm{SO}_{4}$ |
| nitric acid | $\mathrm{HNO}_{3}$ |


| soluble strong bases to know |  |
| :--- | :--- |
| lithium hydroxide | LiOH |
| sodium hydroxide | NaOH |
| potassium hydroxide | KOH |
| rubidium hydroxide | RbOH |
| cesium hydroxide | CsOH |
| barium hydroxide | $\mathrm{Ba}(\mathrm{OH})_{2}$ |

strong bases - all Group I and Group II hydroxides except Be

## Acid Strength

acid strength - determined by extent of reaction of acid with water to form $\mathrm{H}_{3} \mathrm{O}^{+}(a q)$, or the extent of its ionization or dissociation, as shown by the magnitude of its equilibrium constant, $K_{a}$ - then for any hydrogen-containing compound, HA


EQUATION FOR ACIDITY FOR ANY HA

## EQUILIBRIUM CONSTANT

$K_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}$

Various Ways to Describe Acid Strength

| Property | Strong Acid | Weak Acid |
| :--- | :--- | :--- |
| $K_{\mathrm{a}}$ value | $K_{\mathrm{a}}$ is large | $\mathrm{K}_{\mathrm{a}}$ is small |
| Position of the dissociation equilibrium | Far to the right | Far to the left |
| Equilibrium concentration of $\mathrm{H}^{+}$com- <br> pared with original concentration of HA | $\left[\mathrm{H}^{+}\right] \approx[\mathrm{HA}]_{0}$ | $\left[\mathrm{H}^{+}\right] \lessdot[\mathrm{HA}]_{0}$ |
| Strength of conjugate base compared with <br> that of water | $\mathrm{A}^{-}$much weaker | $\mathrm{A}^{-}$much stronger |
| base than $\mathrm{H}_{2} \mathrm{O}$ | base than $\mathrm{H}_{2} \mathrm{O}$ |  |

## Base Strength

base strength - (aside from Group I and II hydroxides) determined by extent of reaction of base with water to form $\mathrm{OH}^{-}(a q)$, or extent of its ionization, as shown by the magnitude of its equilibrium constant, $K_{\mathrm{b}}$ - then for any base B :


EQUATION FOR BASICITY FOR ANY B:

EQUILIBRIUM CONSTANT

## $K_{\mathrm{b}}=\underline{\left[\mathrm{OH}^{-}\right]\left[\mathrm{BH}^{+}\right]}$ <br> [B:]

Various Ways to Describe Base Strength

| Property | Strong Base | Weak Base |
| :--- | :--- | :--- |
| $K_{\mathrm{b}}$ value | either <br> 1) dissociates to give | $K_{\mathrm{b}}$ is small |
| Position of the dissociation equilibrium <br> Equilibrium concentration of $\mathrm{OH}^{-}$com- <br> pared with original concentration of B: | $\mathrm{OH}^{-}$ions to the solution <br> or 2) reacts with water <br> in either case: | Far to the left <br> $\left[\mathrm{OH}^{-}\right]$« $[\mathrm{B}:]_{0}$ |
| Strength of conjugate acid compared <br> with that of water | $\left[\mathrm{OH}^{-}\right]=[\mathrm{B}:]_{0}$ | $\mathrm{BH}^{+}$much stronger |
| acid than water |  |  |

## Conjugate Acid/Base Pairs

The conjugate base of a weak acid is a weak base. The weaker the acid, the stronger the base. However, if one member of a conjugate pair is weak, so is its conjugate.
The relation between $K_{\mathrm{a}}$ for an acid and $K_{\mathrm{b}}$ for its conjugate base in aqueous solution is $K_{\mathrm{w}}=K_{\mathrm{a}} \times K_{\mathrm{b}}$.

When a strong acid (or base) is added to a weak base (or acid), they react nearly completely.


## Water and the pH Scale

water autoionization: $2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})<=>\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$

$$
K_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.01 \times 10^{-14}\left(\text { at } 25^{\circ} \mathrm{C}\right)
$$

$K_{\mathrm{w}}$ is an equilibrium constant which depends upon temperature.

## pH is temperature dependent

| condition | concentrations | $\mathrm{pH}\left(\right.$ only at $\left.25^{\circ} \mathrm{C}\right)$ |
| :---: | :--- | :---: |
| acidic | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]>\left[\mathrm{OH}^{-}\right]$ | $\mathrm{pH}<7$ |
| neutral | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{OH}^{-}\right]$ | $\mathrm{pH}=7$ |
| basic | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]<\left[\mathrm{OH}^{-}\right]$ | $\mathrm{pH}>7$ |


| Temperature Dependence of $\boldsymbol{K}_{\mathbf{w}}$ |  |
| :---: | :---: |
| Temperature [ $\mathbf{} \mathbf{C}$ 〕 | $\boldsymbol{K}_{\mathbf{w}}$ |
| $\mathbf{0}$ | $0.114 \times 10^{-14}$ |
| $\mathbf{1 0}$ | $0.292 \times 10^{-14}$ |
| $\mathbf{2 0}$ | $0.681 \times 10^{-14}$ |
| $\mathbf{2 5}$ | $1.01 \times 10^{-14}$ |
| $\mathbf{3 0}$ | $1.47 \times 10^{-14}$ |
| $\mathbf{4 0}$ | $2.92 \times 10^{-14}$ |
| $\mathbf{5 0}$ | $5.47 \times 10^{-14}$ |
| $\mathbf{6 0}$ | $9.61 \times 10^{-14}$ |

EX 6. $K_{\mathrm{w}}=2.4 \times 10^{-14}$ at body temperature $\left(98.6^{\circ} \mathrm{C}=37.0^{\circ} \mathrm{C}\right)$.
a) What is the hydrogen ion concentration?

$$
K_{\mathrm{w}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=x^{2} \Rightarrow>\quad \mathrm{x}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{ } K_{\mathrm{w}}=\sqrt{ }\left(2.4 \times 10^{-14}\right)=\mathbf{1 . 5} \times \mathbf{1 0}^{-\mathbf{- 7}} \mathbf{~ M}
$$

b) What is the pH ?

$$
\mathrm{pH}=-\log _{10}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log _{10}\left(1.549 \times 10^{-7}\right)=6.80989=>6.81
$$

## Water and the pH Scale

other " p " functions:

$$
\begin{array}{ll}
\mathrm{pH}=-\log _{10}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] & \mathrm{p} K_{\mathrm{a}}=-\log _{10} K_{\mathrm{a}} \\
\mathrm{pOH}=-\log _{10}\left[\mathrm{OH}^{-}\right] & \mathrm{p} K_{\mathrm{b}}=-\log _{10} K_{\mathrm{b}} \\
\mathrm{p} K_{\mathrm{w}}=-\log _{10} K_{\mathrm{w}} & \mathrm{p} K_{\mathrm{sp}}=-\log _{10} K_{\mathrm{sp}}
\end{array}
$$

EX 7. Answer each of the following
a) $\mathrm{pH}=9.3,\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=$?
$\mathrm{pH}=-\log _{10}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \Rightarrow\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}}=10^{-9.3}=5.01 \times 10^{-10}=>5 \times \mathbf{1 0}^{-10}$
b) 0.40 moles of $\mathrm{Ba}(\mathrm{OH})_{2}$ is dissolved in a liter of water, pOH ?
$\mathrm{Ba}(\mathrm{OH})(\mathrm{s}) \rightarrow \mathrm{Ba}^{2+}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq})=>0.80 \mathrm{M}\left[\mathrm{OH}^{-}\right]$

