

Chemistry BC2001x: General Chemistry I

Lecture 12: Tuesday October 20, 2009

Topics: K_{eq} and Le Chatelier's Principle.
 K_a , K_b and K_w



Pick up

1. Graded problem set 5, answers on Courseworks
2. Relative strengths of acids and bases (2 pages)
3. Table of acids with K_a values (2 pages)

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Conventions for writing K_{eq}

Start with the balanced reaction:

- 1) Products in numerator, reactants in denominator.
- 2) Stoichiometric coefficients become exponents.
- 3) For dissolved species, use the molarity [A].
- 4) For gases, use the partial pressure P_A in atmospheres.
- 5) Pure solids and liquids are omitted.
- 6) The solvent is omitted.

The reason for these last two facts is that the *concentrations* of pure condensed phases and solvent do not vary (even though the amounts may do so).

Example: $\text{CaCO}_3(\text{s}) + 2 \text{H}^+(\text{aq}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{H}_2\text{O}(\ell) + \text{CO}_2(\text{g})$

$$K_{eq} = [\text{Ca}^{2+}] P_{\text{CO}_2} / [\text{H}^+]^2 = 2.0 \times 10^{-32}$$

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Le Chatelier's Principle

Le Chatelier



If a system at equilibrium is disturbed, the reaction will shift in the direction that will offset the disturbance.

If you add **reactants**, more **products** will form, decreasing the amount of reactants.

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Start with a saturated solution of $\text{Ca}_3(\text{PO}_4)_2$



Add a pinch of solid $\text{CaCl}_2(\text{s})$ (soluble, so Ca^{2+} and Cl^- are added) what happens to the equilibrium above?

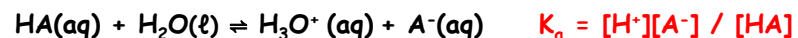
It shifts to the left, forming more solid calcium phosphate.

We could also use Q and K to show this: adding Ca^{2+} makes $Q > K_{sp}$: precipitate forms, lowering $[\text{Ca}^{2+}]$ and $[\text{PO}_4^{3-}]$.
This is, again, the common ion effect.

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Acidity and Basicity Constants (K_a and K_b)

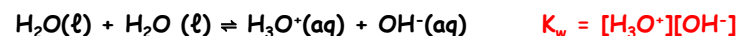
K_a is the equilibrium constant for the hydrolysis (reaction with water) of an acid HA:



K_b is the equilibrium constant for the hydrolysis (reaction with water) of an base B:



K_w is the equilibrium constant for the hydrolysis of water!



By convention, the reaction must be balanced with a coefficient of 1 for the acid or base, and only one proton is transferred. Thus K_a and K_b values are typically tabulated according to the acid or base: the reaction to which they correspond is implied.

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Acidity Constants (K_a)

HYDROLYSIS of WEAK ACIDS Acid + H ₂ O ⇌ Conjugate Base + H ₃ O ⁺	$K_a = \frac{[\text{Base}][\text{H}_3\text{O}^+]}{[\text{Acid}]}$
$\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + \text{H}_3\text{O}^+$	$K_a = 1.2 \times 10^{-2}$
$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$	$K_a = 1.8 \times 10^{-5}$
$\text{H}_2\text{S} + \text{H}_2\text{O} \rightleftharpoons \text{HS}^- + \text{H}_3\text{O}^+$	$K_a = 1.0 \times 10^{-7}$
$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$	$K_a = 5.7 \times 10^{-10}$
$\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{CN}^- + \text{H}_3\text{O}^+$	$K_a = 4.9 \times 10^{-10}$
$\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+$	$K_a = 4.7 \times 10^{-11}$

The larger the K_a value, the stronger the acid.

Weak acids all have K_a values less than one.

The species that has lost the proton is a base:
(it can accept a proton and regenerate the acid)
it is called the conjugate base.

The acid and base are a **conjugate acid-base pair**.

The stronger an acid, the weaker its conjugate base.

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ACID	K_a	CONJUGATE BASE
VERY STRONG ACIDS: more acidic than H ⁺ HNO₃, HCl... never found associated in water	> 1	NOT BASIC at all: do not react as bases with water NO₃⁻, Cl⁻
H₃O⁺	1	H₂O
WEAK ACIDS HNO ₂ CH ₃ COOH HCO ₃ ⁻ HS ⁻	Stronger ↑ ↓ Weaker	WEAK BASES: NO ₂ ⁻ slightly basic CH ₃ COO ⁻ CO ₃ ²⁻ S ²⁻ quite basic (ET-1)
H₂O	10⁻¹⁴	OH⁻
NOT ACIDIC at all do not react as acids with water: CH₃OH, OH⁻ in other solvents, can donate H ⁺	< 10⁻¹⁴	VERY STRONG BASES: more basic than OH ⁻ CH₃O⁻, O²⁻ never found as ions in water

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Handout: Selected acids in order of Acidity beginning of table: stronger acids

ACID FORMULA	NAME OF ACID	K_a	CONJUGATE BASE
HClO ₄	Perchloric acid	← The six acids on the left are all VERY STRONG. In aqueous solution they dissociate 100%, forming H ₃ O ⁺ and the conjugate base on the right. None is ever found as acid in water. These six anions on the right → are totally negligible weak bases.	ClO ₄ ⁻
HI	Hydroiodic acid		I ⁻
HBr	Hydrobromic acid		Br ⁻
H ₂ SO ₄	Sulfuric acid		HSO ₄ ⁻
HCl	Hydrochloric acid		Cl ⁻
HNO ₃	Nitric acid		NO ₃ ⁻
H ₃ O ⁺	HYDRONIUM ION	1.0	H₂O
H ₂ C ₂ O ₄	Oxalic acid	5.9 × 10 ⁻²	HC ₂ O ₄ ⁻
H ₂ SO ₃	Sulfurous acid (= SO ₂ + H ₂ O)	1.2 × 10 ⁻²	HSO ₃ ⁻
HSO ₄ ⁻	Hydrogen sulfate ion (bisulfate ion)	1.2 × 10 ⁻²	SO ₄ ²⁻
HClO ₂	Chlorous acid	1.1 × 10 ⁻²	ClO ₂ ⁻
H ₃ PO ₄	Phosphoric acid (orthophosphoric acid)	7.5 × 10 ⁻³	H ₂ PO ₄ ⁻

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Selected acids in order of acidity, end of table

ACID FORMULA	NAME OF ACID	K_a	Conjugate BASE
NH ₄ ⁺	Ammonium ion	5.7 × 10 ⁻¹⁰	NH ₃
HCN	Hydrocyanic acid (hydrogen cyanide)	4.9 × 10 ⁻¹⁰	CN ⁻
C ₆ H ₅ OH	Phenol	1.3 × 10 ⁻¹⁰	C ₆ H ₅ O ⁻
HCO ₃ ⁻	Hydrogen carbonate (bicarbonate) ion	4.7 × 10 ⁻¹¹	CO ₃ ²⁻
CH ₃ NH ₃ ⁺	Methylammonium ion	2.4 × 10 ⁻¹¹	CH ₃ NH ₂
HOI	Hypoiodous acid	1.0 × 10 ⁻¹¹	OI ⁻
HAso ₄ ²⁻	Hydrogen arsenate ion	4.0 × 10 ⁻¹²	AsO ₄ ³⁻
HPO ₄ ²⁻	Hydrogen (monohydrogen) phosphate ion	4.0 × 10 ⁻¹³	PO ₄ ³⁻
HS ⁻	Hydrosulfide (bisulfide) ion	1.3 × 10 ⁻¹³	S ²⁻
H ₂ O	WATER	1.0 × 10⁻¹⁴	OH⁻
C ₂ H ₅ OH	Ethanol	Each of the anions on the right → is a VERY STRONG base. Each reacts 100% with water, forming OH ⁻ and the conjugate negligibly weak acid on the left. The conjugate acids are thus not considered to be acidic in water.	C ₂ H ₅ O ⁻
NH ₃	Ammonia		NH ₂ ⁻
H ₂	Hydrogen		H ⁻
OH ⁻	Hydroxide ion		O ²⁻

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