

CHEM 191
**Energetics & Equilibria in Biological
Systems**

Module 1 Lecture 6

Weak acids and bases

Brown (15th) Chapter 16

1

Module 1 Lecture 6

Learning objectives

- Write K_a and K_b expressions for weak acids and weak bases
- Understand the relationship between K_a and K_b , pK_a and pK_b
- Calculate the pH of solutions of weak acids and bases
- Understand how transition metal complex ions can behave as weak acids

2

Weak acids

- The majority of acids are **weak acids**. This means they undergo incomplete dissociation in water - in other words, they reach an equilibrium



and the equilibrium position lies almost completely to the left.

- Compare 0.10 mol L⁻¹ aqueous solutions of HCl (strong) and HNO₂ (weak)

HCl

$$[\text{H}_3\text{O}^+] = 0.10 \text{ mol L}^{-1}$$

$$[\text{Cl}^-] = 0.10 \text{ mol L}^{-1}$$

$$[\text{HCl}] = 0.00 \text{ mol L}^{-1}$$

HNO₂

$$[\text{H}_3\text{O}^+] = 0.0084 \text{ mol L}^{-1}$$

$$[\text{NO}_2^-] = 0.0084 \text{ mol L}^{-1}$$

$$[\text{HNO}_2] = 0.0916 \text{ mol L}^{-1}$$

3

Acid dissociation constant, K_a

- Can write an equilibrium constant expression for the dissociation of any weak acid HA



$$K_a = \frac{[\text{H}_3\text{O}^+]_e [\text{A}^-]_e}{[\text{HA}]_e}$$

- This is called the **acid dissociation constant (K_a)**. Notice that there is no term for [H₂O] as it is a pure liquid.
- K_a is a measure of acid strength; the larger the value of K_a , the more extensive the dissociation at equilibrium and the stronger the acid.

$$\text{p}K_a = -\log(K_a)$$

4

Base dissociation constant, K_b

- Can write an equilibrium constant expression for the reaction of any weak base B with water



$$K_b = \frac{[\text{BH}^+]_e [\text{OH}^-]_e}{[\text{B}]_e}$$

- K_b is the base dissociation constant. Again, no term for $[\text{H}_2\text{O}]$.
- K_b is a measure of base strength; the larger the value of K_b , the more extensive the formation of OH^- at equilibrium and the stronger the base.

$$\text{p}K_b = -\log(K_b)$$

5

Examples

Acid	K_a	$\text{p}K_a$	Base	K_b	$\text{p}K_b$
CH_3COOH	1.8×10^{-5}	4.74	NH_3	1.8×10^{-5}	4.74
HCN	6.2×10^{-10}	9.21	CH_3NH_2	4.4×10^{-4}	3.36
HCOOH	1.8×10^{-4}	3.74	pyridine	1.7×10^{-9}	8.77
HF	6.8×10^{-4}	3.17	NH_2OH	6.6×10^{-9}	8.18
HOBr	2.3×10^{-9}	8.64	caffeine	4.1×10^{-4}	3.39
HOCl	3.0×10^{-8}	7.52	morphine	7.5×10^{-7}	6.12
HNO_2	7.1×10^{-4}	3.15	nicotine	6.3×10^{-7}	6.20

The *smaller* the K_a or K_b , the *weaker* the acid or base.

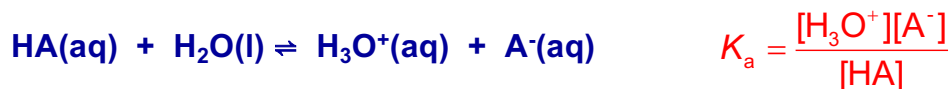
The *larger* the $\text{p}K_a$ or $\text{p}K_b$, the *weaker* the acid or base.

- In all cases, K_a and K_b are $\ll 1$. Therefore extent of dissociation of the weak acid or base is small in water (position of equilibrium lies to the left).

6

Relationship between K_a and K_b

Consider a weak acid and **its** conjugate base



$$K_a \times K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

Thus $K_a K_b = K_w$ or $\text{p}K_a + \text{p}K_b = \text{p}K_w = 14.00$ at 25.0 °C

7

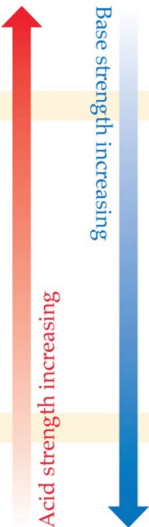
Conjugate strengths

- The relationship $\text{p}K_a + \text{p}K_b = \text{p}K_w$ means that, ***the stronger the acid, the weaker its conjugate base.***
- The conjugate base of a strong acid is **very** weak
- The conjugate acid of a strong base is **very** weak
- What about the conjugate base of a weak acid?

e.g. CH_3COOH	$\text{p}K_a = 4.74$	weak acid
CH_3COO^-	$\text{p}K_b = 9.26$	weak base
- Difficult to generalise in the case of weak acids and bases. However, you **cannot** say that the conjugate base of a weak acid is strong.

8

Conjugate strengths

	ACID		BASE	
Strong acids	HCl		Cl ⁻	Negligible basicity
	H ₂ SO ₄		HSO ₄ ⁻	
	HNO ₃		NO ₃ ⁻	
	H ₃ O ⁺ (aq)		H ₂ O	
	HSO ₄ ⁻		SO ₄ ²⁻	
Weak acids	H ₃ PO ₄		H ₂ PO ₄ ⁻	Weak bases
	HF		F ⁻	
	CH ₃ COOH		CH ₃ COO ⁻	
	H ₂ CO ₃		HCO ₃ ⁻	
	H ₂ S		HS ⁻	
	H ₂ PO ₄ ⁻	HPO ₄ ²⁻		
	NH ₄ ⁺	NH ₃		
	HCO ₃ ⁻	CO ₃ ²⁻		
	HPO ₄ ²⁻	PO ₄ ³⁻		
	Negligible acidity	H ₂ O	OH ⁻	
OH ⁻		O ²⁻		
H ₂		H ⁻		
CH ₄		CH ₃ ⁻		

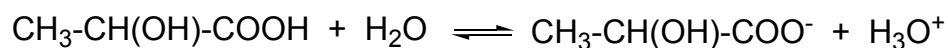
▲ **FIGURE 17.2** Relative strengths of select conjugate acid-base pairs. The two members of each pair are listed opposite each other in the two columns.

9

Calculation

Lactic acid, CH₃-CH(OH)-COOH, is produced in excessive amounts during strenuous, anaerobic exercise, leading to sore muscles. A normal lactic acid concentration is about 1 × 10⁻³ mol L⁻¹.

Calculate the pH of lactic acid at this concentration.
pK_a(lactic acid) = 3.86



$$K_a = \frac{[\text{CH}_3\text{-CH(OH)-COO}^-]_e [\text{H}_3\text{O}^+]_e}{[\text{CH}_3\text{-CH(OH)-COOH}]_e}$$



10

Calculation

$$K_a = \frac{[\text{CH}_3\text{-CH(OH)-COO}^-]_e [\text{H}_3\text{O}^+]_e}{[\text{CH}_3\text{-CH(OH)-COOH}]_e}$$

We can solve this exactly (using quadratic formula) but can also get a good approximation of the answer by making two (normally legitimate) **assumptions**.

1. Assume that $[\text{CH}_3\text{-CH(OH)-COO}^-]_e = [\text{H}_3\text{O}^+]_e$
due to the 1:1 stoichiometry
2. Assume that $[\text{CH}_3\text{-CH(OH)-COOH}]_e \cong [\text{CH}_3\text{-CH(OH)-COOH}]_{\text{initial}}$
because K_a is small

11

Calculation

$$K_a = \frac{[\text{CH}_3\text{-CH(OH)-COO}^-]_e [\text{H}_3\text{O}^+]_e}{[\text{CH}_3\text{-CH(OH)-COOH}]_e}$$

By Assumption 1

$$K_a = \frac{[\text{H}_3\text{O}^+]_e^2}{[\text{CH}_3\text{-CH(OH)-COOH}]_e}$$

By Assumption 2

$$K_a = \frac{[\text{H}_3\text{O}^+]_e^2}{[\text{CH}_3\text{-CH(OH)-COOH}]_{\text{initial}}}$$

Rearranging

$$[\text{H}_3\text{O}^+]_e^2 = K_a \times [\text{CH}_3\text{-CH(OH)-COOH}]_{\text{initial}}$$

$$[\text{H}_3\text{O}^+]_e = \sqrt{K_a \times [\text{CH}_3\text{-CH(OH)-COOH}]_{\text{initial}}}$$

12

Calculation

$$[\text{H}_3\text{O}^+]_e = \sqrt{K_a \times [\text{CH}_3\text{-CH(OH)-COOH}]_{\text{initial}}}$$

$$K_a = 10^{-\text{p}K_a} = 10^{-3.86} = 1.38 \times 10^{-4}$$

$$[\text{H}_3\text{O}^+]_e = \sqrt{1.38 \times 10^{-4} \times 1 \times 10^{-3}} = 3.71 \times 10^{-4} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(3.71 \times 10^{-4}) = \mathbf{3.43}$$

13

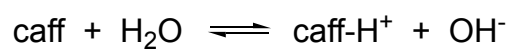
Weak bases

- All the previous calculations concerning weak acids are equally applicable to weak bases.
- Use K_b rather than K_a in these calculations, and solve for OH^- rather than H_3O^+
- Must also be aware of the contribution to $[\text{OH}^-]$ from water to the total $[\text{OH}^-]$. Again, maximum possible contribution is $1 \times 10^{-7} \text{ mol L}^{-1}$

14

Calculation

Caffeine is the most widely consumed psychoactive drug in the world. It is also a weak base, with a $K_b = 4.1 \times 10^{-4}$. Calculate the pH of 0.025 mol L^{-1} solution of caffeine.



$$K_b = \frac{[\text{caff-H}^+]_e [\text{OH}^-]_e}{[\text{caff}]_e}$$

15

Calculation

$$K_b = \frac{[\text{caff-H}^+]_e [\text{OH}^-]_e}{[\text{caff}]_e}$$

We make the same assumptions as previously

$$K_b = \frac{[\text{OH}^-]_e^2}{[\text{caff}]_{\text{initial}}}$$

$$[\text{OH}^-]_e = \sqrt{K_b \times [\text{caff}]_{\text{initial}}}$$

$$[\text{OH}^-]_e = \sqrt{4.1 \times 10^{-4} \times 0.025} = 3.2 \times 10^{-3} \text{ mol L}^{-1}$$

16

Calculation

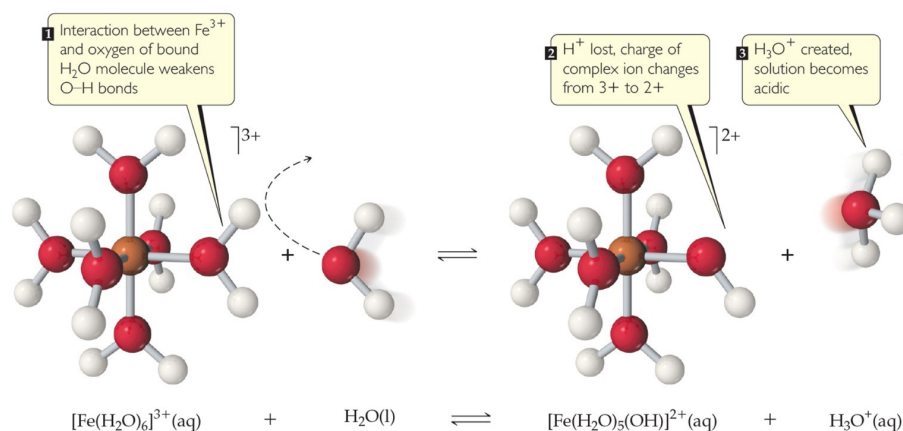
$$\text{pOH} = -\log[\text{OH}^-] = -\log(3.2 \times 10^{-3}) = 2.49$$

$$\text{pH} = 14 - \text{pOH} = \mathbf{11.51}$$

17

Transition metal compounds as weak acids

Transition metal complexes are a class of molecules where molecules called **ligands** (which are Lewis bases) form bonds to a transition metal cation (a Lewis acid). When the ligands are water molecules, the resulting complex can act as a weak acid.



18

Transition metal compounds as weak acids

Because the complex is behaving as a weak acid, we can calculate the pH of its solution in the same way as we have now seen.



$$K_a = \frac{[\text{Ni}(\text{H}_2\text{O})_5(\text{OH})]^+ [\text{H}_3\text{O}^+]}{[\text{Ni}(\text{H}_2\text{O})_6]^{2+}} = 1.38 \times 10^{-10} \rightarrow \text{p}K_a = 9.86$$

Complex ion	p <i>K</i> _a
[Ni(H ₂ O) ₆] ²⁺	9.86
[Fe(H ₂ O) ₆] ³⁺	2.17
[U(H ₂ O) ₆] ⁴⁺	0.68

p*K*_a decreases (complex becomes more acidic) as positive charge on the metal ion increases.

19

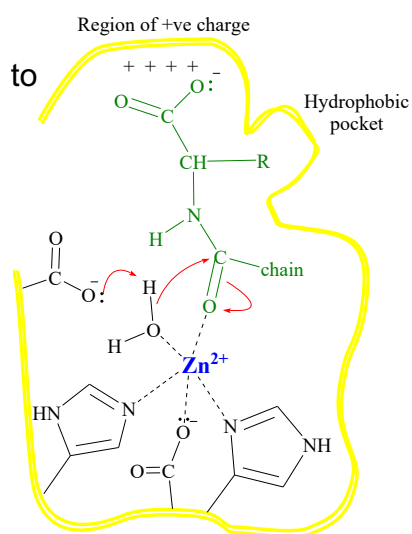
Transition metal compounds as weak acids

This activation of coordinated water molecules is central to the action of many enzymes

eg carboxypeptidase, an enzyme which breaks up protein chains.

The reaction is fast with OH⁻ as the reactant but slow if water is the reactant.

Bonding the water to the zinc ion in the enzyme turns it into OH⁻ and so speeds up the reaction.



20

*** Homework ***

Brown (15th)

Problems 16.81, 16.86, 16.91, 16.92

Answers on Blackboard