CHE680
Advanced Analytical Chemistry
Lecture 2

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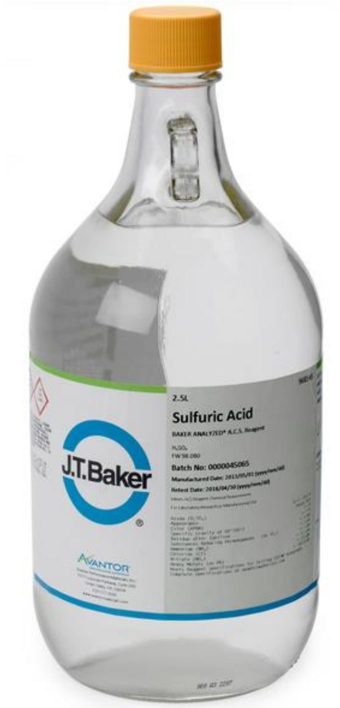
Question 1



98 % H_2SO_4

Can you make it?
How?
Which tool(s) do you need?

1.0 M H_2SO_4

SI –Derived Units

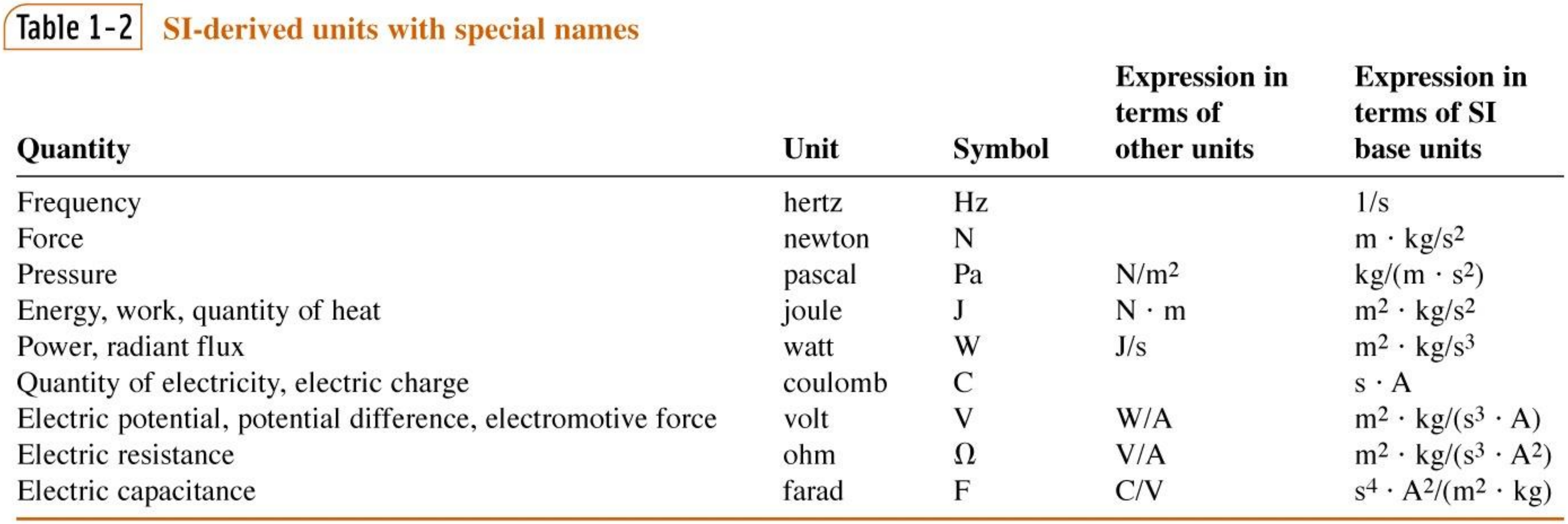


Table 1-2 SI-derived units with special names

Quantity	Unit	Symbol	Expression in terms of other units	Expression in terms of SI base units
Frequency	hertz	Hz		1/s
Force	newton	N		$\text{m} \cdot \text{kg}/\text{s}^2$
Pressure	pascal	Pa	N/m^2	$\text{kg}/(\text{m} \cdot \text{s}^2)$
Energy, work, quantity of heat	joule	J	$\text{N} \cdot \text{m}$	$\text{m}^2 \cdot \text{kg}/\text{s}^2$
Power, radiant flux	watt	W	J/s	$\text{m}^2 \cdot \text{kg}/\text{s}^3$
Quantity of electricity, electric charge	coulomb	C		$\text{s} \cdot \text{A}$
Electric potential, potential difference, electromotive force	volt	V	W/A	$\text{m}^2 \cdot \text{kg}/(\text{s}^3 \cdot \text{A})$
Electric resistance	ohm	Ω	V/A	$\text{m}^2 \cdot \text{kg}/(\text{s}^3 \cdot \text{A}^2)$
Electric capacitance	farad	F	C/V	$\text{s}^4 \cdot \text{A}^2/(\text{m}^2 \cdot \text{kg})$

speed (v) = distance/time = m/s
acceleration (a): [speed change]/time = [m/s]/s = m/s^2
force (F) = (mass)•(acceleration) = kg•m/s^2
pressure (P) = (force)/(area) = $(\text{kg•m/s}^2)/\text{m}^2 = \text{kg}/(\text{m•s}^2)$
work (W) = (force)•(distance) = $(\text{kg•m/s}^2)\text{•m} = \text{kg•m}^2/\text{s}^2$

Prefixes

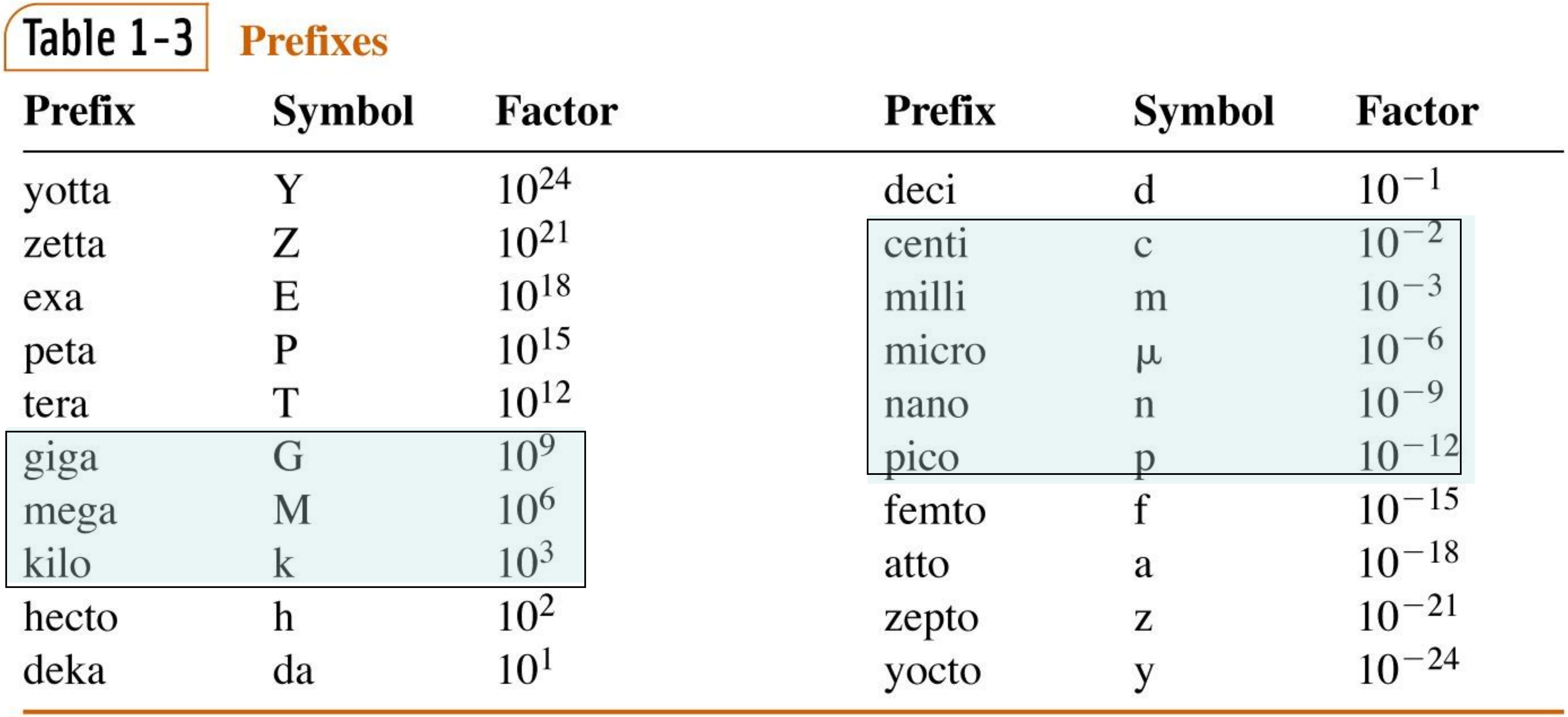


Table 1-3 **Prefixes**

Prefix	Symbol	Factor	Prefix	Symbol	Factor
yotta	Y	10^{24}	deci	d	10^{-1}
zetta	Z	10^{21}	centi	c	10^{-2}
exa	E	10^{18}	milli	m	10^{-3}
peta	P	10^{15}	micro	μ	10^{-6}
tera	T	10^{12}	nano	n	10^{-9}
giga	G	10^{9}	pico	p	10^{-12}
mega	M	10^{6}	femto	f	10^{-15}
kilo	k	10^{3}	atto	a	10^{-18}
hecto	h	10^{2}	zepto	z	10^{-21}
deka	da	10^{1}	yocto	y	10^{-24}

1 Å = 10^{-8} cm = 10^{-10} m = 10^{-1} nm

Hydrogen atom r = 0.52 Å = 5.2×10^{-11} m

Unit Conversion

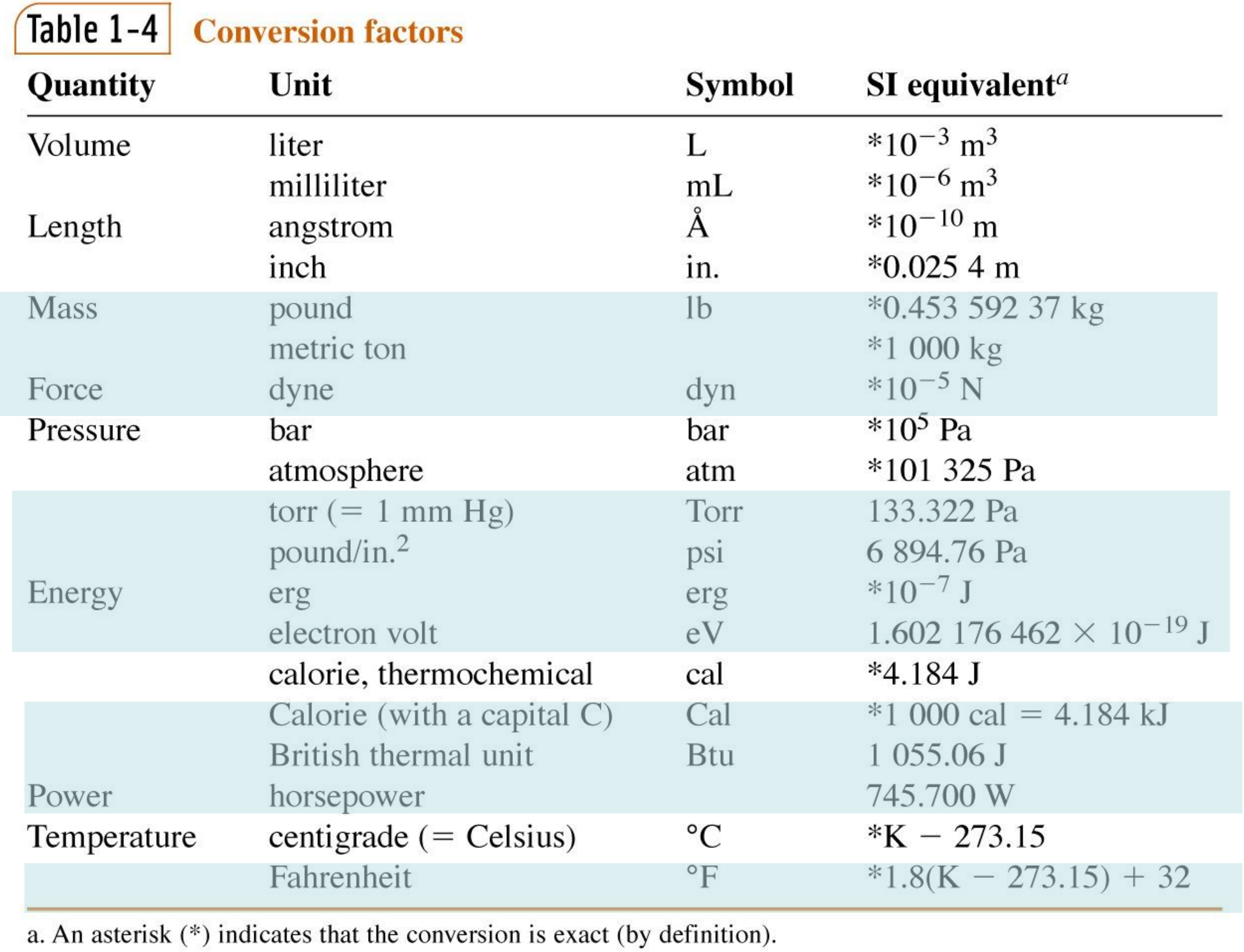


Table 1-4 Conversion factors

Quantity	Unit	Symbol	SI equivalent[a]
Volume	liter	L	*10^{-3} m^3
	milliliter	mL	*10^{-6} m^3
Length	angstrom	Å	*10^{-10} m
	inch	in.	*0.025 4 m
Mass	pound	lb	*0.453 592 37 kg
	metric ton		*1 000 kg
Force	dyne	dyn	*10^{-5} N
Pressure	bar	bar	*10^5 Pa
	atmosphere	atm	*101 325 Pa
	torr (= 1 mm Hg)	Torr	133.322 Pa
	pound/in.^{2}	psi	6 894.76 Pa
Energy	erg	erg	*10^{-7} J
	electron volt	eV	$1.602\ 176\ 462 \times 10^{-19}$ J
	calorie, thermochemical	cal	*4.184 J
	Calorie (with a capital C)	Cal	*1 000 cal = 4.184 kJ
	British thermal unit	Btu	1 055.06 J
Power	horsepower		745.700 W
Temperature	centigrade (= Celsius)	°C	*K − 273.15
	Fahrenheit	°F	*1.8(K − 273.15) + 32

a. An asterisk (*) indicates that the conversion is exact (by definition).

Density vs. Specific Gravity

Density = mass/volume (unit: **kg/L or g/mL = g/cm^3 = kg/dm^3 = kg/L)**

Density of water @ 4 °C = 1.0 g/mL

Specific gravity = (density)/(density of water @ 4 °C), dimensionless

Targets of Quantitative Chemical Analysis

- Concentration of target compound?
- Total target amount in the sample?

Concentration:

Weight-to-weight (w/w, %, ppm, ppb)

Weight-to-volume (w/v, %)

Volume to volume (v/v, %)

Number-to-volume (molarity, M)

percent (%), parts per million (ppm), and parts per billion (ppb)

- All methods involve quantifying amount of solute per amount of solvent (or solution).
- Generally amounts or measures are masses, moles or liters.
- Definitions:

$$\text{mass \% of component} = \frac{\text{mass of component in solution}}{\text{total mass of solution}} \times 100$$

$$\text{ppm of component} = \frac{\text{mass of component in solution}}{\text{total mass of solution}} \times 10^6$$

$$\text{ppb of component} = \frac{\text{mass of component in solution}}{\text{total mass of solution}} \times 10^9$$

Example 1

(a) A solution made by dissolving 13.5 g of glucose in 0.1kg of water. What's the %, ppm, and ppb of glucose?

(b) A 2.5 g sample of ground water containing 5.4 µg of Zn^{2+}

Molarity (*M*) and Molality (m)

$$Molarity\,(M) = \frac{moles\ \ solute}{liters\,of\ \ solution}$$

$$Molality\,(m) = \frac{moles\,solute}{kg\,of\ \ solvent}$$

- Converting between molarity (*M*) and molality (*m*) requires density.
- kg of solvent = kg of solution – kg of solute

  = [(liters of solution × density)] – [(moles solute) × (molecular weight) × (0.001)]

Example 2

(a)Typical seawater contains 2.7 g of salt (sodium chloride, NaCl) per 100 mL (= 100 × 10^{-3} L). What is the molarity (M) of NaCl in the ocean?

Keys:
What’s the # of moles of NaCl?

What’s the volume (L) and molarity (M)?

(b) $MgCl_2$ has a concentration of 0.054 M in the ocean. How many grams of $MgCl_2$ are present in 25 mL of seawater?

Example 3

A solution made by dissolving 4.35 g of glucose in 25 mL of water. What's the molality (m) (assume the density of water is 1g/cm^3)?

Example 4

Find the molarity (M) and molality (m) of 37.0 wt % HCl. The **density** of a substance is the mass per unit volume. The table inside the back cover of this book tells us that the density of the reagent is <u>1.19 g/mL</u>.

Conversion of *m* into *M*

What's the Molarity (*M*) of 1.0 Molality (m) of NaCl (molecular weight: 58.44 g/mol) water solution (density of solution is 1.05 g/cm^3)?

Conversion of *M* into *m*

What's the Molality (m) of 1.0 Molarity (M) of NaCl (molecular weight: 58.44 g/mol) water solution (density of solution is 1.05 g/cm^3)?

How to Prepare 1000 mL of 1 M and 1 m NaCl solution, respectively

What you need?

How to prepare?

of Moles (Amount)

$$Molarity\,(M) = \frac{\#\ of\ \ moles\ \ of\ \ solute}{liters\ of\ \ solution}$$

$$\#\ of\ \ moles\ \ of\ \ solute = \left(Molarity\,(M)\right)\left(liters\ of\ \ solution\left(L\right)\right)$$

$$\#\ of\ \ moles\ \ of\ \ solute = \frac{mass\ of\ \ solute\,(g)}{MW\ of\ \ solute\,(g/mole)}$$

e.g.,

(a) # of moles and grams of HCl in 100 mL of 0.1 M solution?

(b) # of moles for 1 g HCl?

Dilution 1

of moles (amount) in solution does not change before and after dilution.

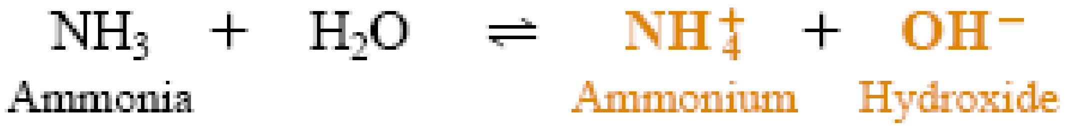
Simple dilution,

$M_{initial} \cdot V_{initial} = M_{final} \cdot V_{final}$ = (# of moles/L)(L) = # of moles

e.g., the molarity of “concentrated” HCl purchased for laboratory use is approximately 12.1 M. How many milliliters of this reagent should be diluted to 1.000 L to make 0.100 M HCl?

Dilution 2

A solution of ammonia in water is called “ammonium hydroxide” because of the equilibrium



$$\underset{\text{Ammonia}}{NH_3} + H_2O \rightleftharpoons \underset{\text{Ammonium}}{NH_4^+} + \underset{\text{Hydroxide}}{OH^-}$$

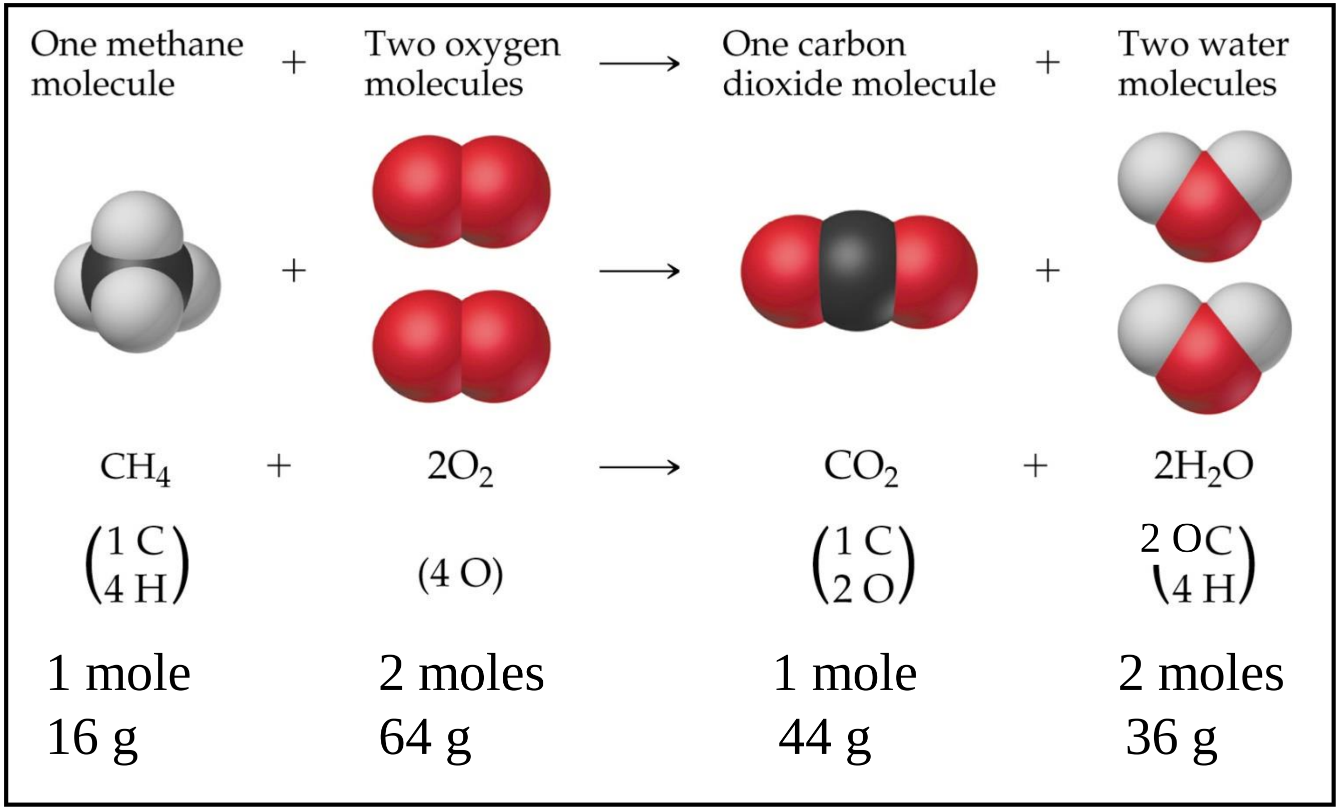
The density of concentrated ammonium hydroxide, which contains 28.0 wt % NH_3, is 0.899 g/mL. What volume of this reagent should be diluted to 500.0 mL to make 0.250 M NH_3?

1. Molarity of 28.0 wt % of NH_3?
2. $M_{\text{initial}} \bullet V_{\text{initial}} = M_{\text{final}} \bullet V_{\text{final}}$

Chemical Equations & Stoichiometry

The information from stoichiometry is useful as long as it is balanced

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$



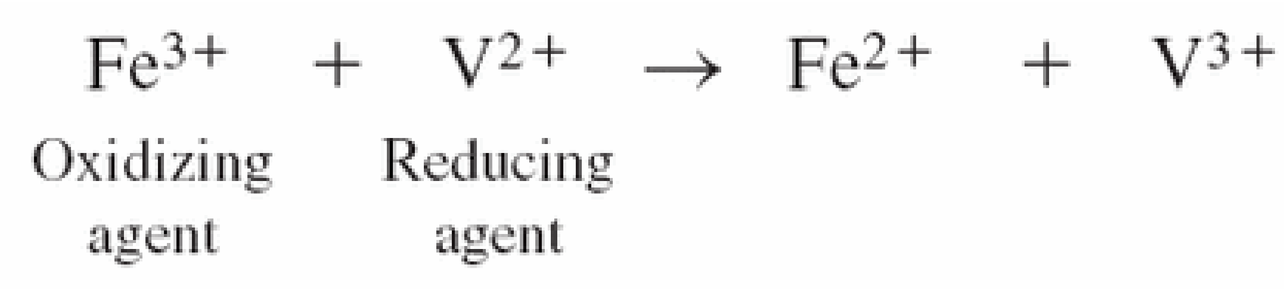
One methane molecule	+	Two oxygen molecules	$\longrightarrow$	One carbon dioxide molecule	+	Two water molecules
CH_4	+	$2O_2$	$\longrightarrow$	CO_2	+	$2H_2O$
(1 C 4 H)		(4 O)		(1 C 2 O)		(2 OC 4 H)
1 mole 16 g		2 moles 64 g		1 mole 44 g		2 moles 36 g

Balancing

$C_3H_8(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$

Not balanced and how to balance?

Oxidation and Reduction



$$Fe^{3+} + V^{2+} \rightarrow Fe^{2+} + V^{3+}$$

Oxidizing agent

Reducing agent

reduced

oxidized

Balancing Oxidation-Reduction Reactions (Acidic Condition)

$MnO_4^-(aq) + C_2O_4^{2-}(aq) \rightarrow Mn^{2+}(aq) + CO_2(g)$

Two half-reactions are:

1. $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$

2. $C_2O_4^{2-}(aq) \rightarrow CO_2(g)$

How to Balance Oxidation Reaction

In acidic solution

$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$

$MnO_4^{-} + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+}$

In basic solution?

Revisit pH

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

$$pH = -\log_{10}[H_3O^+] = -\log_{10}[H^+]$$

$$pOH = -\log_{10}[OH^-]$$

$$pH + pOH = 14$$

$$[H^+] = 10^{-pH}$$

$$[OH^-] = 10^{-pOH}$$

Strong Acids

(a) pH of 0.05 M of $HClO_4$?

(b) pH of 0.0005 M of HCl?

(c) pH of 0.00000001 (10^{-8}) M HCl?

Strong Bases

(a)What’s the pH of 0.05 M of NaOH?

(b) What’s the pH of 0.005 M of $Ca(OH)_2$?

(solubility of $Ca(OH)_2$ =1.73 g/L at 20 °C)

(c) 0.2 M $Ca(OH)_2$?

Weak Acids and Bases

- Weak acids (or bases) are only partially ionized in solution.
- There is a mixture of ions and unionized acid (or base) in solution.
- Therefore, weak acids are in equilibrium:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$pK_a = -\log_{10} K_a$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

pH of H_2SO_4

e.g., 0.02 M H_2SO_4 pH = ?,

$H_2SO_4 \longrightarrow HSO_4^- + H^+$ (strong acid)

0.02 0.02 0.02

$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$ (weak acid, pKa = 1.987)

0.02 0.02

0.02 –x x 0.02 + x

$$k_a = \frac{x \cdot (0.02 + x)}{0.02 - x} = 0.012, \; x = 0.00562M$$

$[H^+]$ = 0.02 + 0.0562 = 0.02562

pH = -log(0.02562) = 1.59

Conjugate Acids and Bases

- For acetic acid, CH_3COOH, $K_a = 1.75 \times 10^{-5}$

weak acid conjugate base

- $\mathbf{CH_3COOH} \rightleftharpoons \mathbf{CH_3COO^-} + H^+$,

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

- $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$, $K_b = ?$

$$pX = -log_{10}[\,X\,]$$

$$pK_a = -log_{10} K_a$$

$$K_w = K_a \times K_b$$

$$pK_w = pK_a + pK_b = 14$$

Typical Weak-Acid Problem

- What's the pH of 0.01 M acetic acid (CH_3COOH, $K_a = 1.75 \times 10^{-5}$)?

	• $CH_3COOH \rightleftharpoons$	CH_3COO^- +	H^+
before	0.01	0.0	0.0
after	0.01- x	x	x

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x^2}{0.01 - x} = 1.75 \times 10^{-5},\ x = 4.1 \times 10^{-4}$$

Do not take negative *x* because concentration can't be negative

Typical Weak-Acid Problem

- What’s the pH of 0.1 M ammonia (NH_3)
- pK_a of NH_4^+ is 9.244, NH_3 is conjugate base of NH_4^+ (why?)
- So, pK_b of NH_3 =14 – 9.244 = 4.756, $K_b = 10^{-4.756} = 1.75 \times 10^{-5}$.

- $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

- $[NH_4^+] \approx [OH^-] = x$, $[NH_3] = 0.01 - x$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.1 - x} = 1.75 \times 10^{-5},\ x = 1.31 \times 10^{-3}$$

X= $[OH^-]$, $[H^+] = 10^{-14}/[OH^-] = 7.61 \times 10^{-12}$, pH =11.12

pH of Salts

- Identify acid, basic, or neutral first
- Calculate pH of following solutions
- 0.1 M NaCl
- 0.1 M CH_3COONa
- 0.1 M NH_4Cl

Dissociation of Weak Diprotic Acids and Bases

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + 2H^+$$

Diprotic acid

Amphoteric

Diprotic base

Diprotic acid: $H_2CO_3 \rightleftharpoons HCO_3^- + H^+, \quad K_{a1} \equiv K_1$

$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+, \quad K_{a2} \equiv K_2$

Diprotic base: $CO_2^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-, \quad K_{b1}$

$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-, \quad K_{b2}$

Relations between K_a and K_b:

$$K_{a1} \cdot K_{b2} = K_w$$

$$K_{a2} \cdot K_{b1} = K_w$$

Mass Balance

- When electrolytes (including acids and bases) are dissolved in water, their total amount should preserved after dissociation.

- If you add H_3PO_4 in water, H_3PO4 will be present one of the following forms, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, and plus H_3PO4 (undissociated form).

- Total Initial $[H_3PO_4] = \underset{\uparrow}{[H_3PO_4]} + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$

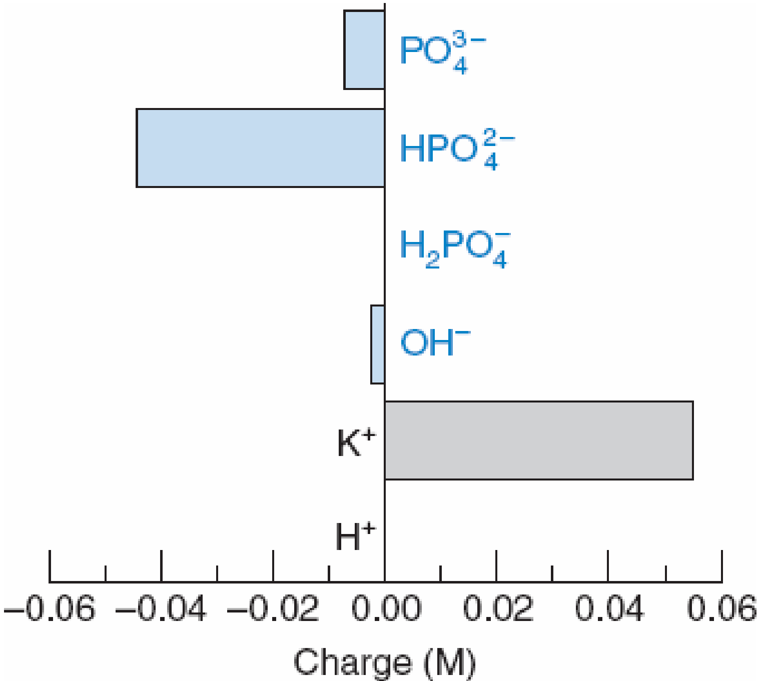
Undissociated because it is weak acid

Charge Balance

- When electrolytes (including acids and bases) are dissolved in water, solution should be electrically neutral. This means that total charge of cations is identical to that of anions.

- If you add KOH and H_3PO_4 in water, there are K^+, OH^-, H^+, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} in solution.

- Total positive charge = $[K^+] + [H^+]$
- Total negative charge = $[OH^-] + [H_2PO_4^-] + \mathbf{2}[HPO_4^{2-}] + \mathbf{3}[PO_4^{3-}]$



Charge contributed by each ion in solution containing 0.0250 M KH_2PO4 plus 0.0300 M KOH.

pH of Diprotic Acids, Salts, & Bases

1. H_2A is treated as a monoprotic weak acid, with $K_a = K_1$.

$$K_a = \frac{x^2}{0.01 - x}, \; x = [H^+]$$

e.g., pH of 0.1 M H_2CO_3?, $K_1 = 4.46 \times 10^{-7}$, $K_2 = 4.69 \times 10^{-11}$

2. A^{2-} is treated as monobasic, with $K_b = K_{b1} = K_w/K_2$.

$$K_b = \frac{x^2}{0.01 - x}, \; x = [OH^-]$$

e.g., pH of 0.1 M Na_2CO_3? $K_1 = 4.46 \times 10^{-7}$, $K_2 = 4.69 \times 10^{-11}$

pH of Diprotic Acids and Bases (continued)

3. HA⁻ is treated as the intermediate form of a diprotic acid (F; formal concentration of HA⁻)

$$\left[H^+\right] \approx \sqrt{\frac{K_1K_2F + K_1K_w}{K_1 + F}}$$

How? Prove it by charge and mass balance

e.g., pH of 0.1 M $NaHCO_3$? $K_1 = 4.46 \times 10^{-7}$, $K_2 = 4.69 \times 10^{-11}$

pK_a vs. pH

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$$

$$K_a = \frac{[H^+][X^-]}{[HX]}, then\, [H^+] = K_a \frac{[HX]}{[X^-]}$$

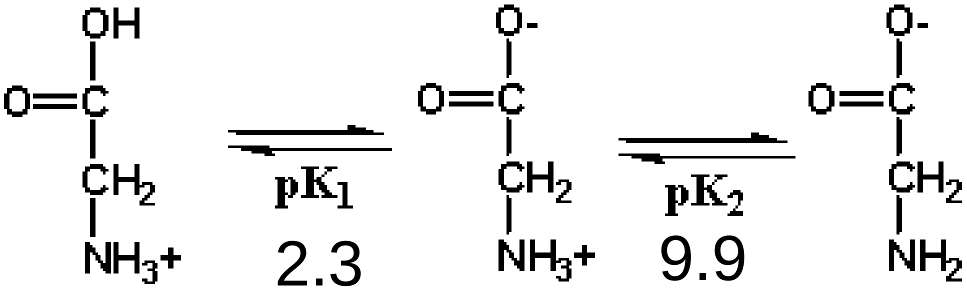
$$-\log[H^+] = -\log K_a - \log\frac{[HX]}{[X^-]}$$

$$\therefore pH = pK_a + \log\frac{[X^-]}{[HX]}$$

$$\therefore pH = pK_a, if\ [HX] = [X^-]$$

- pK_a is the pH where 50% of acids is deprotonated.
- If pH > pK_a, more than 50% of acids are deprotonated
- If pH < pK_a, less than 50% of acids are deprotonated

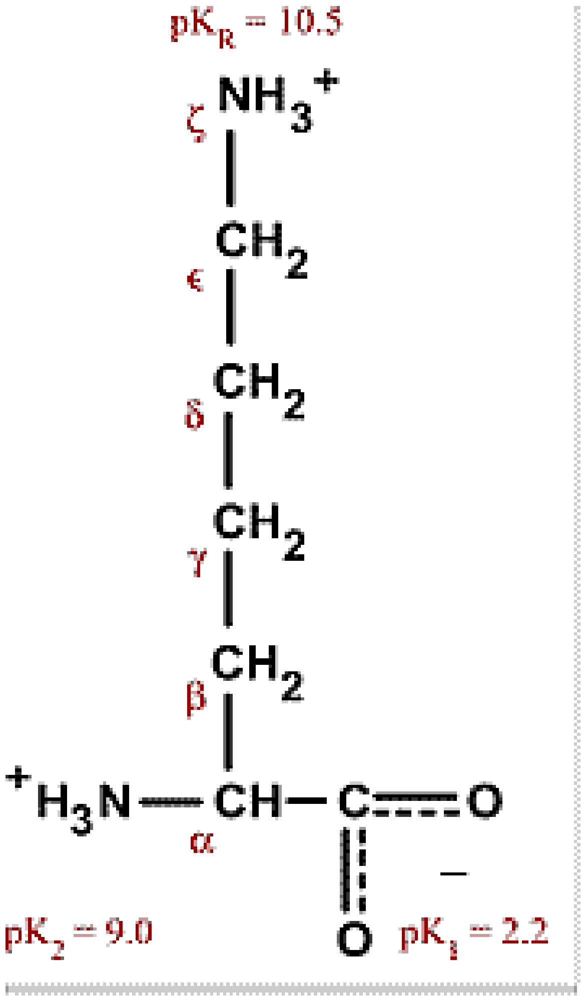
pH Effect on Net Charge



+ 0 -

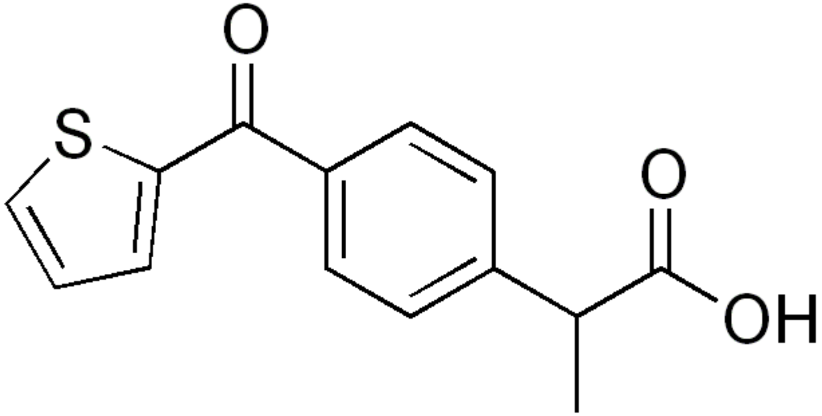
Glycine

+2,	pH < 2.2
+1,	2.2 < pH < 9.0
0,	9.0 < pH < 10.5
-1,	10.5 < pH



Lysine

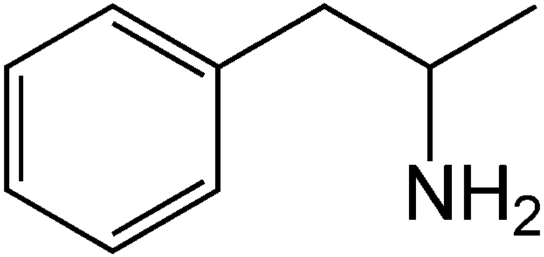
Suprofen



$pK_a = 3.9$

composition at pH = 7.2?

amphetamine



$pK_a = 9.8$

Buffered Solutions

- A buffer consists of a mixture of a **weak acid (HA)** and its **conjugate base (A^-) (or weak base and conjugate acid):**
- The K_a expression is

$$\mathrm{HA}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{A}^-(aq)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\therefore [H^+] = K_a \frac{[HA]}{[A^-]}$$

- A buffer resists a change in pH when a small amount of OH^- or H^+ is added.

Henderson-Hasselbalch Equation

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\therefore [H^+] = K_a \frac{[HA]}{[A^-]}$$

$$-\log[H^+] = -\log K_a - \log \frac{[HA]}{[A^-]}$$

$$\therefore pH = pK_a + \log \frac{[A^-]}{[HA]}$$

If we know $[A^-]$ and $[HA]$, and K_a, then we can calculate pH of buffer

Example 5

What’s the pH of a buffer that is 0.12 M in lactic acid ($HC_3H_5O_3$) and 0.1 M in sodium lactate? For lactic acid, $K_a = 1.4 \times 10^{-4}$.

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

Example 6

A buffer is made by adding 0.3 mol CH_3COOH and 0.3 mol CH_3COONa to enough water to make 1.0 L of solution. For CH_3COOH, $K_a = 1.8 \times 10^{-5}$.

(a) what’s the pH of this buffer?

(b) what’s the pH after 0.02 mole of NaOH is added?

(c) what’s the pH after 0.02 mole of HCl is added?

Strong Acid- Strong Base Titration

HCl (analyte) + NaOH (titrant) $\longrightarrow$ NaCl (salt) + H_2O
0.02 M, 50 mL 0.1 M

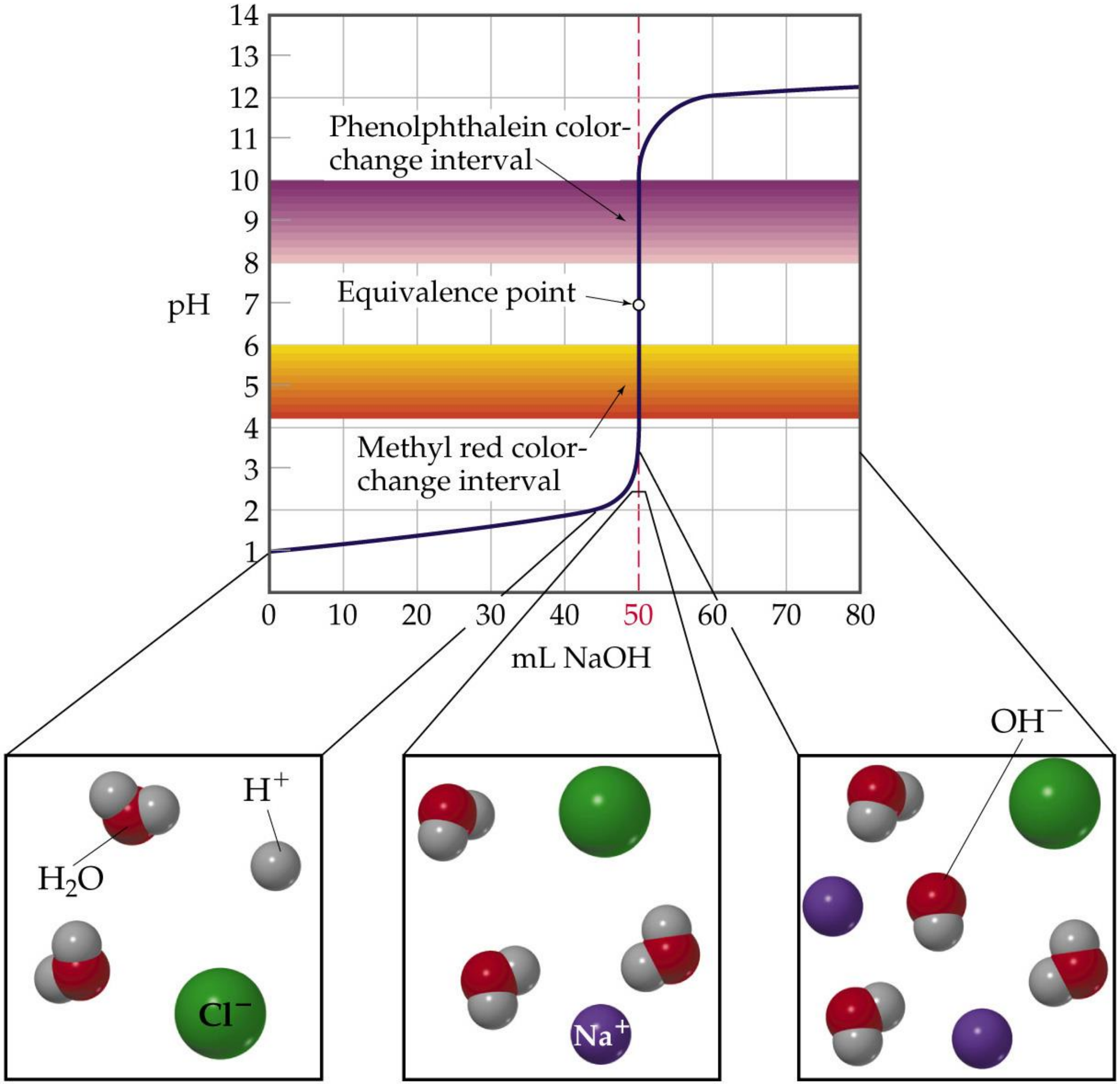
1: Before equivalence point: 9.50 mL of 0.1 M NaOH was added

Step 1: # of mole of HCl and # of mole of NaOH before reaction
Step 2: # of mole of HCl after reaction
Step 3: [HCl]
Step 4: $[H^+]$
Step 5: pH

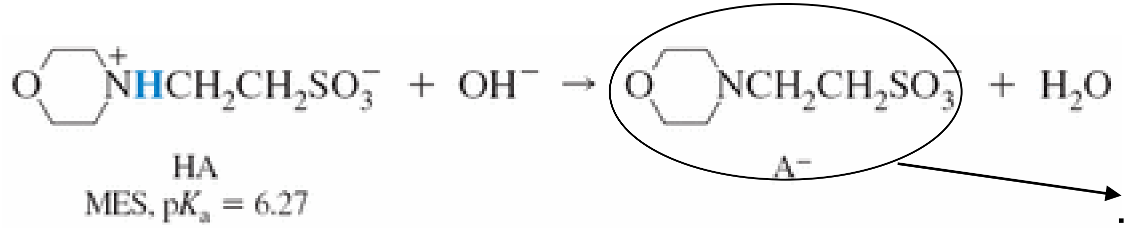
2. At the equivalence point: 10.00 mL of 0.1 M NaOH was added

3. After equivalence point: 10.50 mL of 0.1 M NaOH was added

Strong Acid-Base Titration



Weak Acid- Strong Base Titration



conjugate base

0.02 M, 50 mL

0.1 M, *x* mL

1. Before base is added, it is a solution of weak acid (pH can be found from K_a)

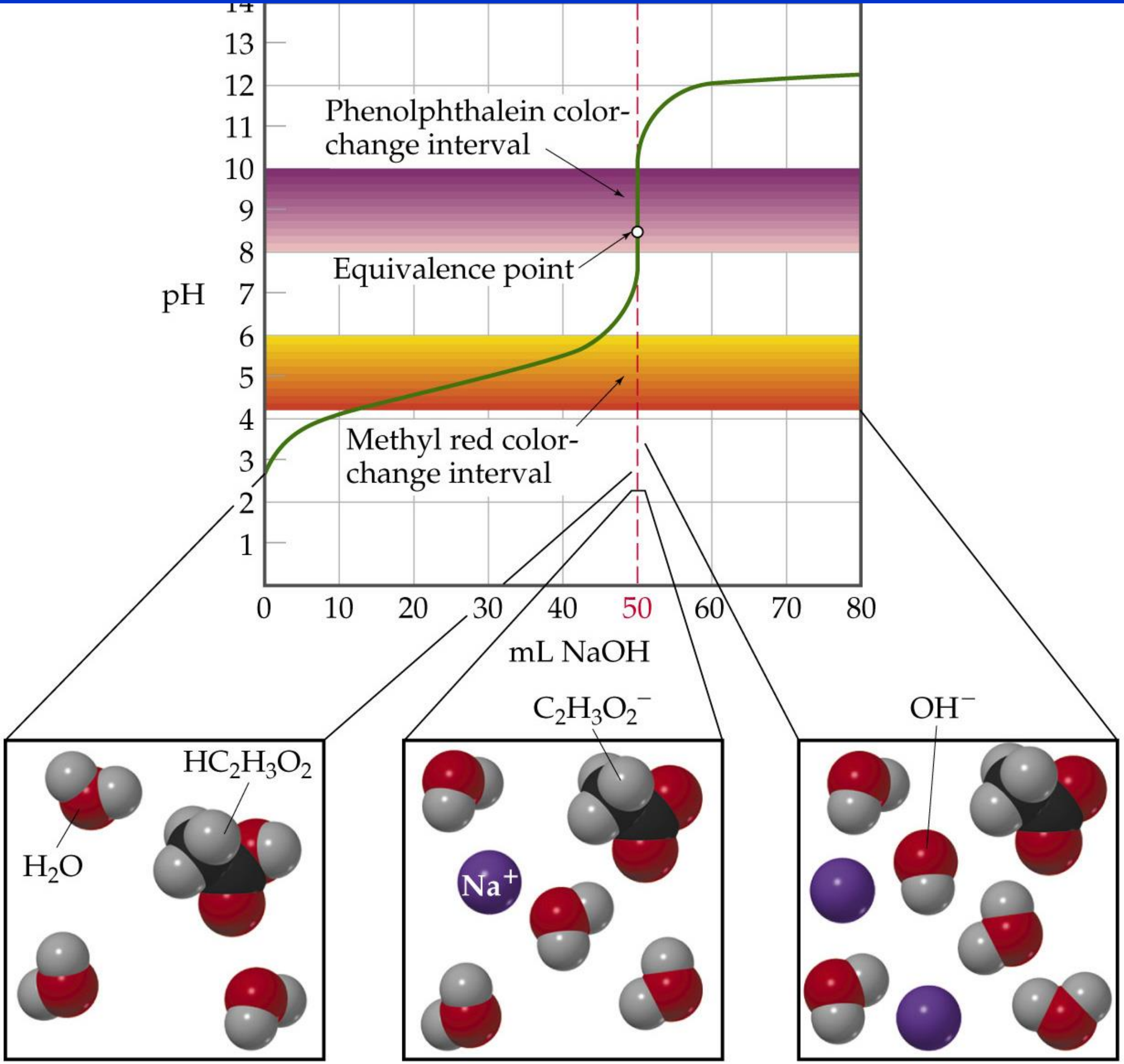
2. Before equivalence point: 3.0 mL of 0.1 M NaOH was added
It is a buffer solution containing weak acid (HA) and its conjugate base (A^-)

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

3. At the equivalence point: 10 mL of 0.1 M NaOH was added
Only conjugate base exists (pH > 7, can be calculated from K_b or K_a)

4. After equivalence point: 10.10 mL of 0.1 M NaOH was added
Two bases are exist, NaOH and A^-, we can calculate pH

Weak Acid- Strong Base Titration



Diprotic Acid- Strong Base Titration

H_2A (analyte) + 2NaOH (titrant) $\longrightarrow$ Na_2A (salt) + $2H_2O$
0.1 M, 20 mL 0.1 M
$K_1 = 1.4 \times 10^{-2}$, $K_2 = 6.5 \times 10^{-8}$

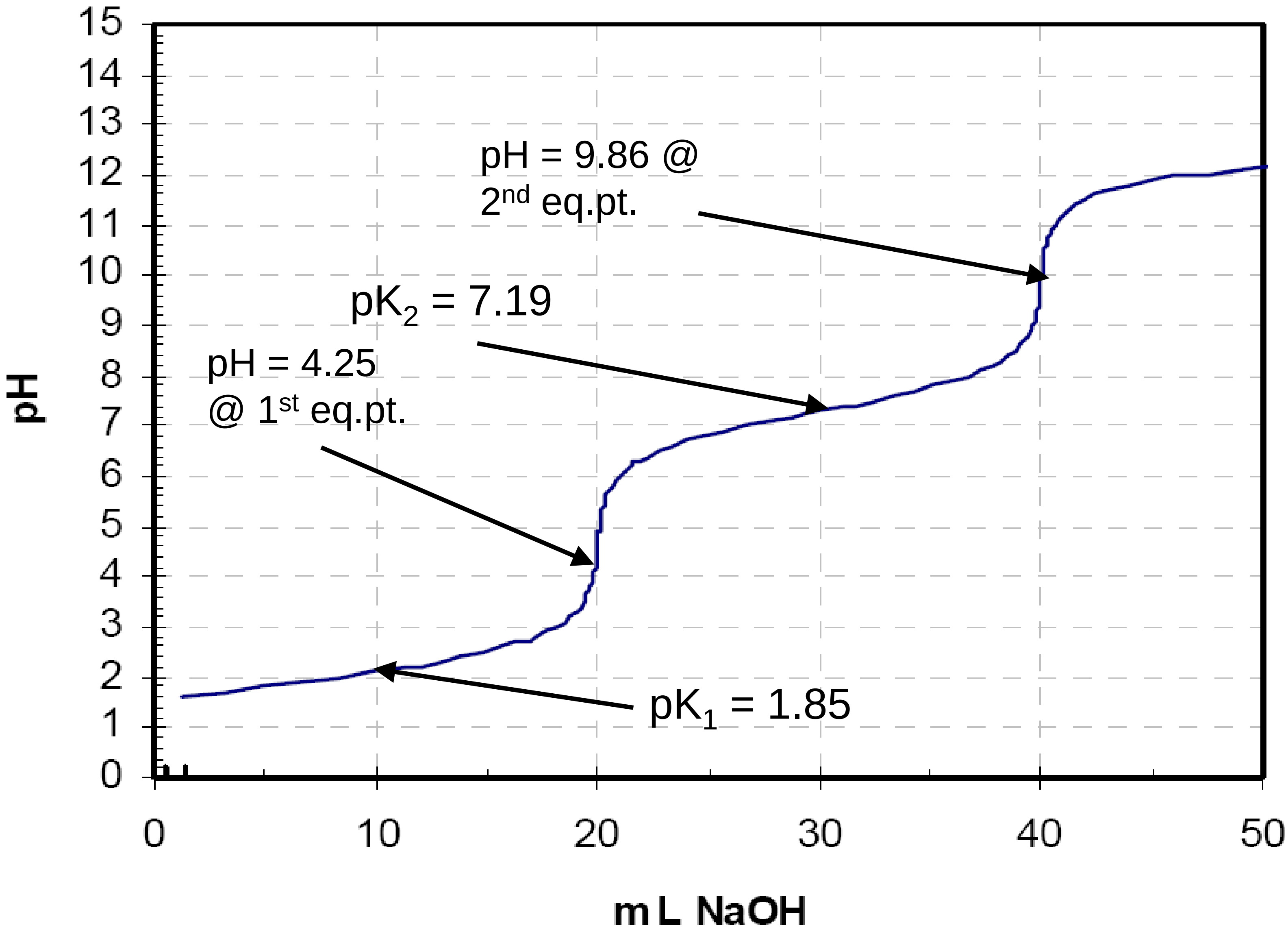
1: Before equivalence point: 19 mL of 0.1 M NaOH was added
H_2A (analyte) + NaOH (titrant) $\longrightarrow$ NaHA (salt) + H_2O

Step 1: # of mole of H_2A and # of mole of NaOH before reaction
Step 2: # of mole of H_2A after reaction
Step 3: $[H_2A]$
Step 4: $[H^+]$
Step 5: pH

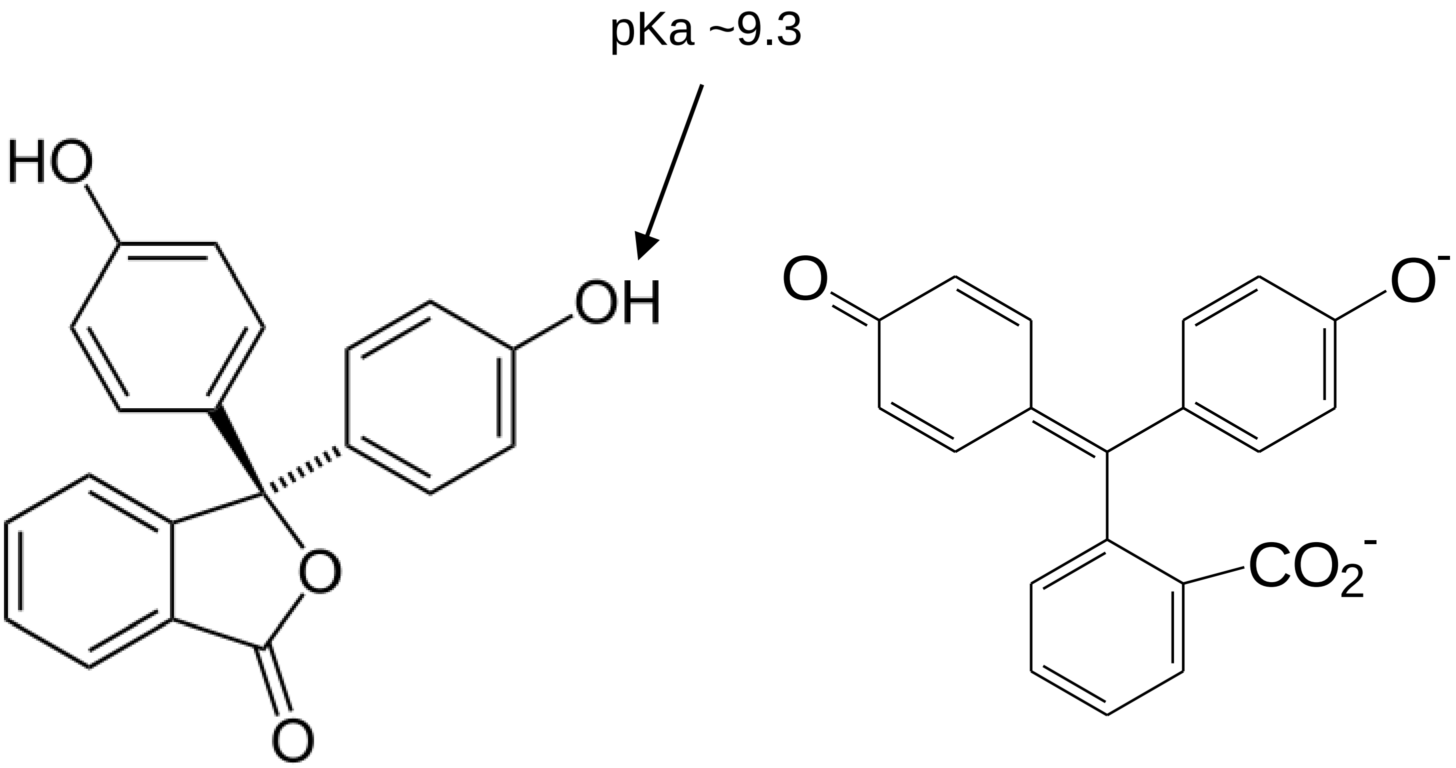
2. At the 1st equivalence point: 20.00 mL of 0.1 M NaOH was added
3. After 1st equivalence point: 30 mL of 0.1 M NaOH was added
NaHA (analyte) + NaOH (titrant) $\longrightarrow$ Na_2A (salt) + H_2O

4. At the 2nd equivalence point: 40.00 mL of 0.1 M NaOH was added
5. After the 2nd equivalence point: 50.00 mL of 0.1 M NaOH was added

Titration Curve



Chemistry of Indicators



Phenolphthalein pH < 8.0 ⬜ 🟥 pH > 9.6

Color change why?

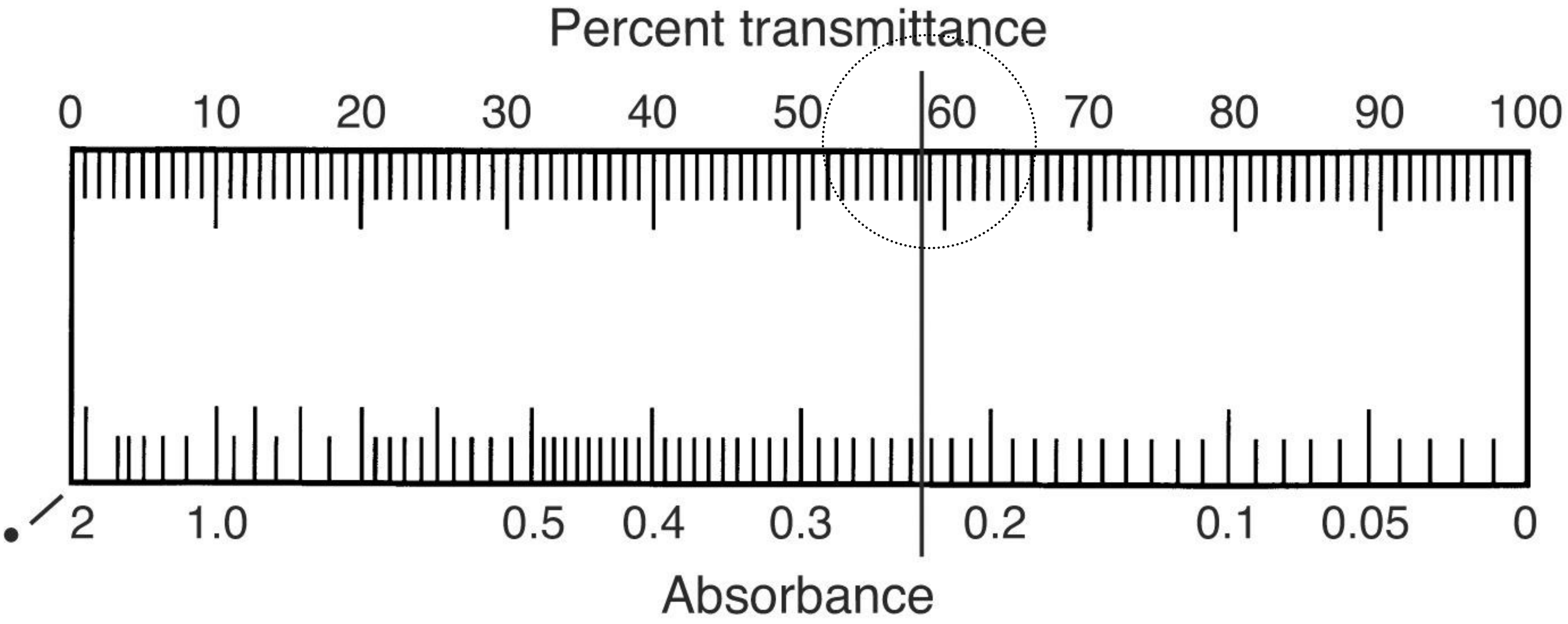
Significant Figures

9.25×10^4	3 significant figures
9.250×10^4	4 significant figures
$9.250\ 0 \times 10^4$	5 significant figures

0.0050	two significant figures
0.00500	three significant figures

The last significant figure has always uncertainty

What's your reading?



58.2 or 58.3 or 58.4 … …

The last significant figure has always uncertainty

Addition and subtraction

1000000000000000000 + 0.000001 = 1000000000000000000.000001

Is this meaningful? answer is no

$$\begin{array}{r} 5.345 \\ +\ 6.728 \\ \hline 12.073 \end{array}$$

$$\begin{array}{r} 7.26 \times 10^{14} \\ -6.69 \times 10^{14} \\ \hline 0.57 \times 10^{14} \end{array}$$

$$\begin{array}{rl} 18.998\,403\,2 & \text{(F)} \\ +\ 18.998\,403\,2 & \text{(F)} \\ +\ 83.80 & \text{(Kr)} \\ \hline 121.79\underbrace{\boxed{6}\,806\,4}_{\text{Not significant}} & \end{array}$$

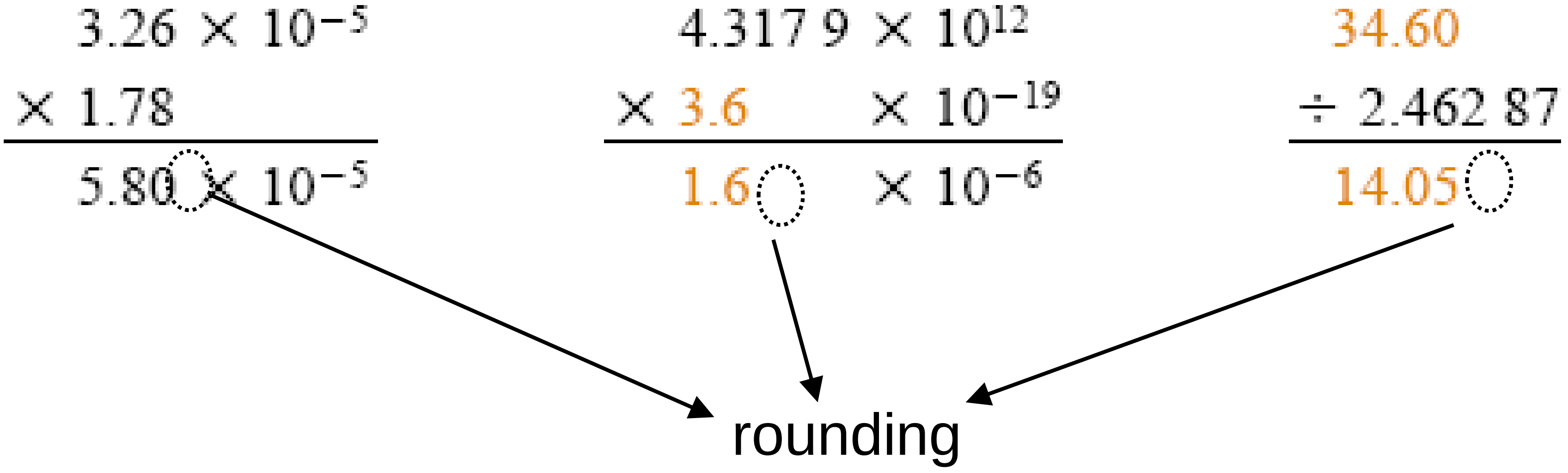
rounding

$$\begin{array}{r} 1.632 \times 10^{5} \\ +\ 4.107 \times 10^{3} \\ +\ 0.984 \times 10^{6} \\ \hline \end{array} \quad \Rightarrow \quad \begin{array}{rl} 1.632 & \times 10^{5} \\ +\ 0.041\,07 & \times 10^{5} \\ +\ 9.84 & \times 10^{5} \\ \hline 11.51 & \times 10^{5} \end{array}$$

Now, 1000000000000000000 + 0.000001 = ?

Multiplication and division

In multiplication and division, we are normally limited to the number of digits contained in the number with the fewest significant figures



$$\begin{array}{r} 3.26 \times 10^{-5} \\ \times\ 1.78 \qquad\quad \\ \hline 5.80 \times 10^{-5} \end{array} \qquad \begin{array}{lr} \quad 4.317\,9 & \times\ 10^{12} \\ \times\ 3.6 & \times\ 10^{-19} \\ \hline \quad 1.6 & \times\ 10^{-6} \end{array} \qquad \begin{array}{r} 34.60 \\ \div\ 2.462\,87 \\ \hline 14.05 \end{array}$$

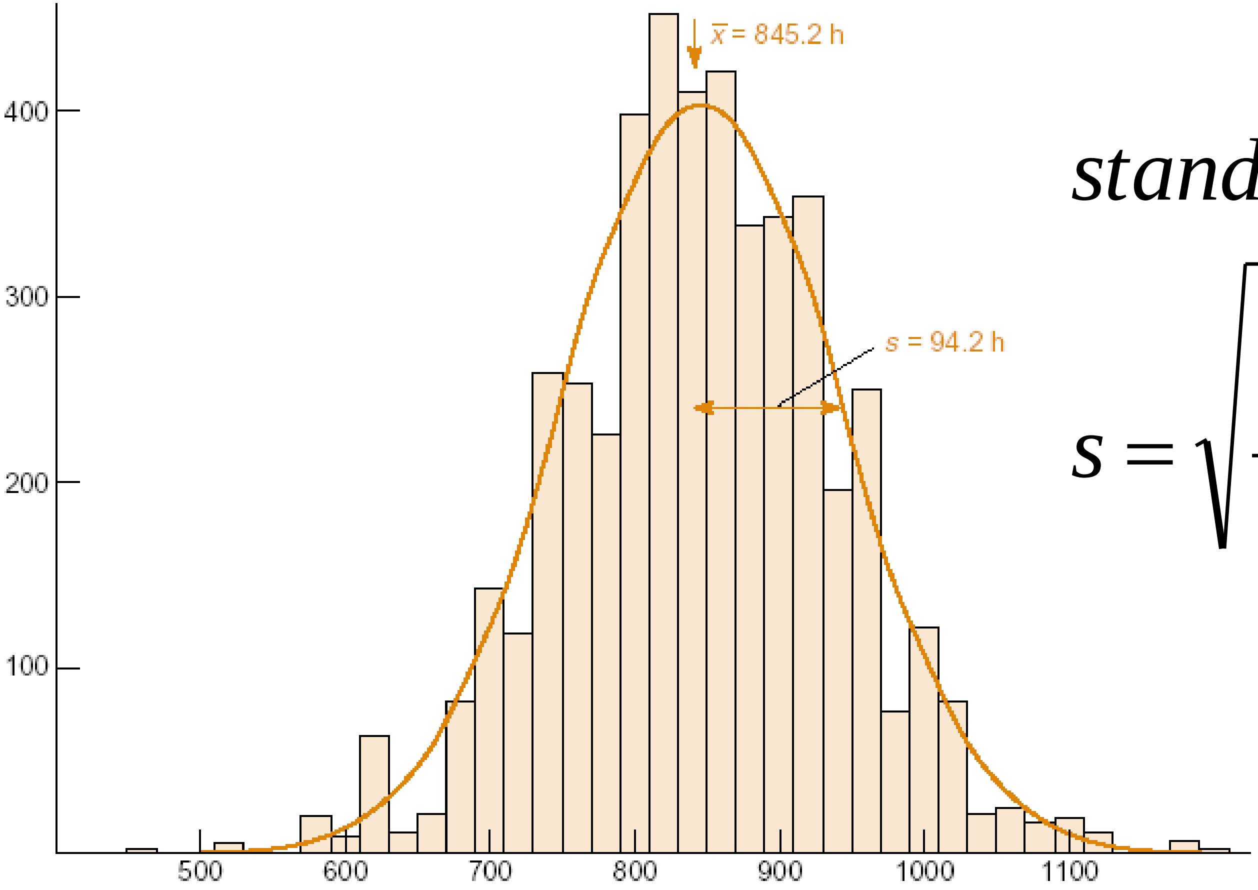
rounding

Gaussian distribution

$$mean: \bar{x} = \frac{\sum_i x_i}{n}$$

$$standard\ deviation:$$

$$s = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n-1}}$$



Example 7

Find the average and the standard deviation for 821, 783, 834, and 855.

$$\bar{x} = \frac{821 + 783 + 834 + 855}{4} = 823._2$$

$$s = \sqrt{\frac{(821 - 823.2)^2 + (783 - 823.2)^2 + (834 - 823.2)^2 + (855 - 823.2)^2}{(4 - 1)}}$$
$$= 30._3$$

823.2 ± 30.3 → **good for continued calculation**

823 ± 30
820 ± 30 → **good for final calculation**

Confidence interval

The **confidence interval** is an expression stating that the true mean, μ, is likely to lie within a certain distance from the measured mean, $\bar{x}$.

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

s: measured standard deviation
n: # of measurements
t: student’s t value (see table in the next page)

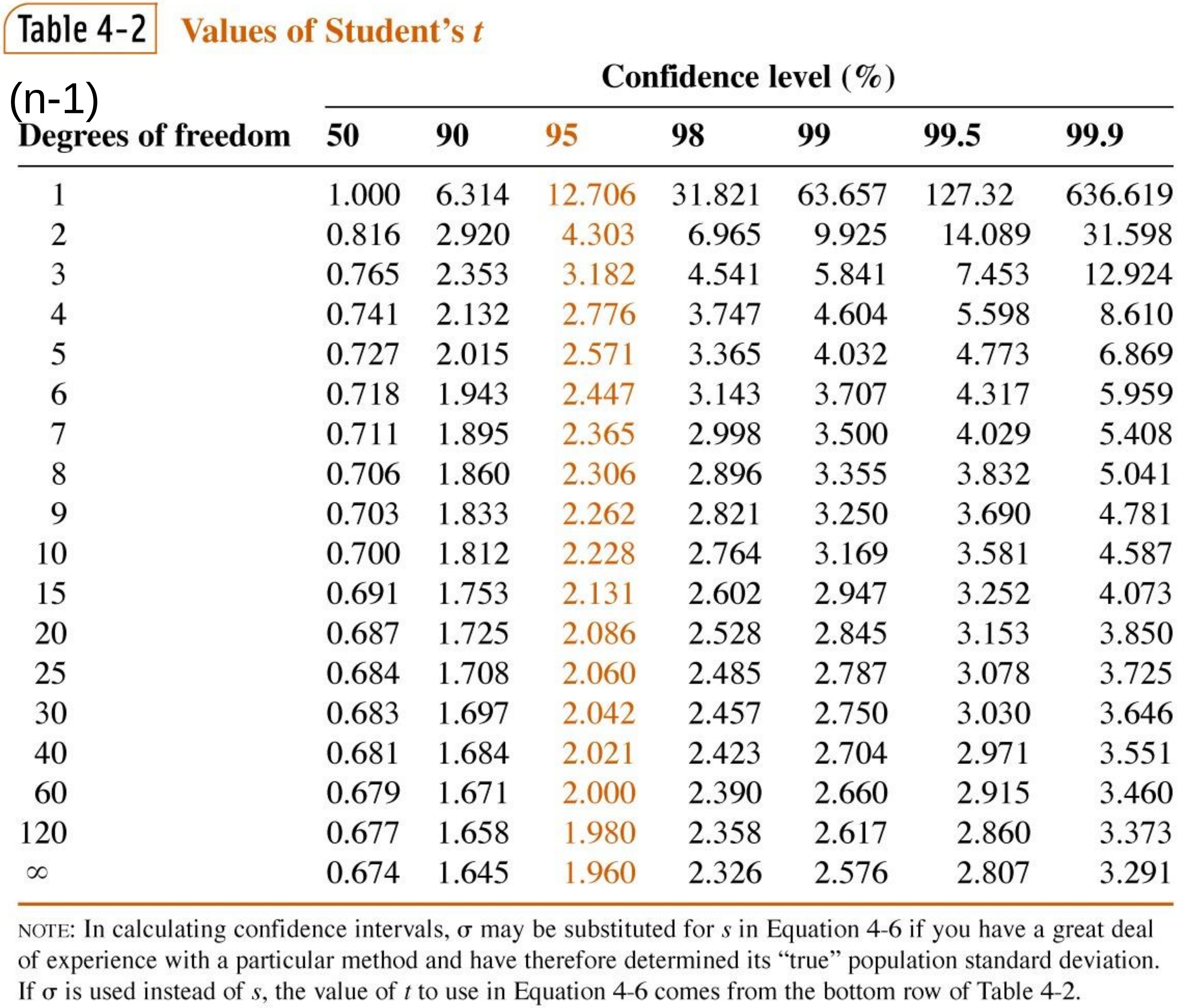


Table 4-2 Values of Student's *t*

(n-1) **Degrees of freedom**	**Confidence level (%)** **50**	**90**	**95**	**98**	**99**	**99.5**	**99.9**
1	1.000	6.314	12.706	31.821	63.657	127.32	636.619
2	0.816	2.920	4.303	6.965	9.925	14.089	31.598
3	0.765	2.353	3.182	4.541	5.841	7.453	12.924
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959
7	0.711	1.895	2.365	2.998	3.500	4.029	5.408
8	0.706	1.860	2.306	2.896	3.355	3.832	5.041
9	0.703	1.833	2.262	2.821	3.250	3.690	4.781
10	0.700	1.812	2.228	2.764	3.169	3.581	4.587
15	0.691	1.753	2.131	2.602	2.947	3.252	4.073
20	0.687	1.725	2.086	2.528	2.845	3.153	3.850
25	0.684	1.708	2.060	2.485	2.787	3.078	3.725
30	0.683	1.697	2.042	2.457	2.750	3.030	3.646
40	0.681	1.684	2.021	2.423	2.704	2.971	3.551
60	0.679	1.671	2.000	2.390	2.660	2.915	3.460
120	0.677	1.658	1.980	2.358	2.617	2.860	3.373
∞	0.674	1.645	1.960	2.326	2.576	2.807	3.291

NOTE: In calculating confidence intervals, σ may be substituted for s in Equation 4-6 if you have a great deal of experience with a particular method and have therefore determined its "true" population standard deviation. If σ is used instead of s, the value of t to use in Equation 4-6 comes from the bottom row of Table 4-2.

Example 8

The carbohydrate content of a glycoprotein (a protein with sugars attached to it) is determined to be 12.6, 11.9, 13.0, 12.7, and 12.5 g of carbohydrate per 100 g of protein in replicate analyses. Find the 50% and 90% confidence intervals for the carbohydrate content.

$$\bar{x} = 12.54, s = 0.40$$

50 % confidence interval,

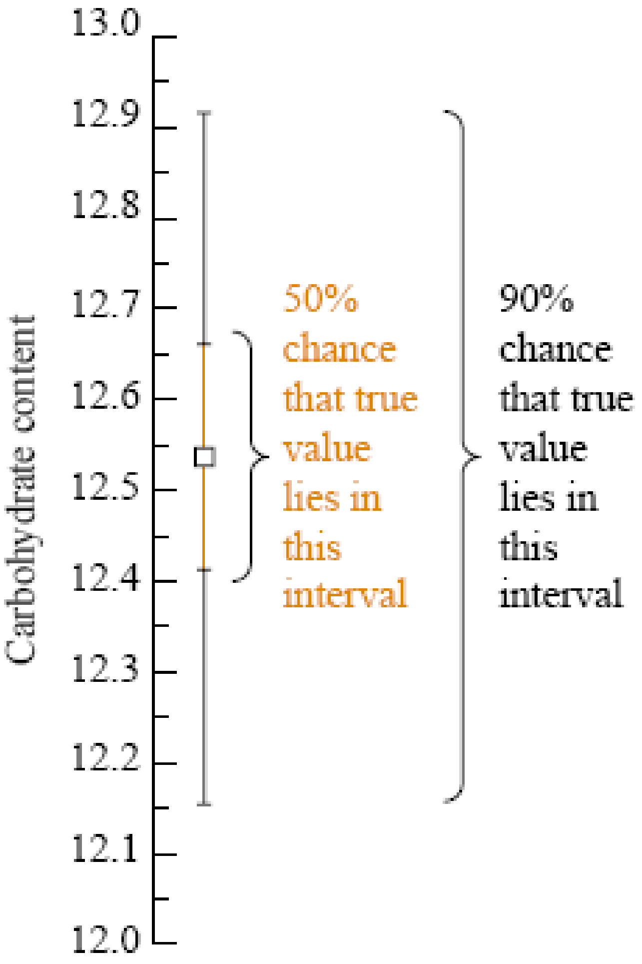
$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}} = 12.5_4 \pm \frac{(0.741)(0.4_0)}{\sqrt{5}} = 12.5_4 \pm 0.1_3$$

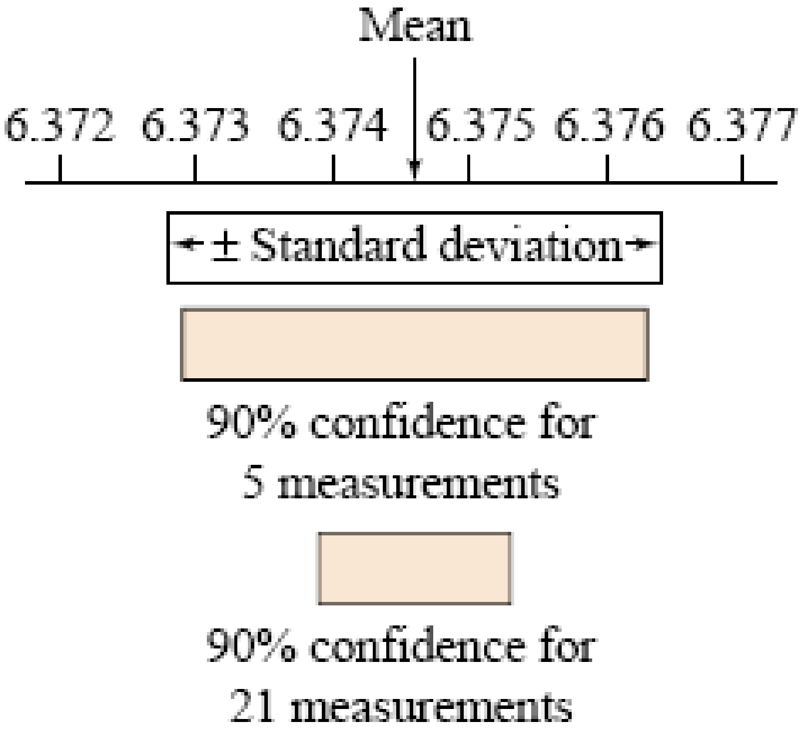
90 % confidence interval,

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}} = 12.5_4 \pm \frac{(2.132)(0.4_0)}{\sqrt{5}} = 12.5_4 \pm 0.3_8$$

Confidence interval vs. *n*

50% confidence interval is narrower than 90% confidence interval

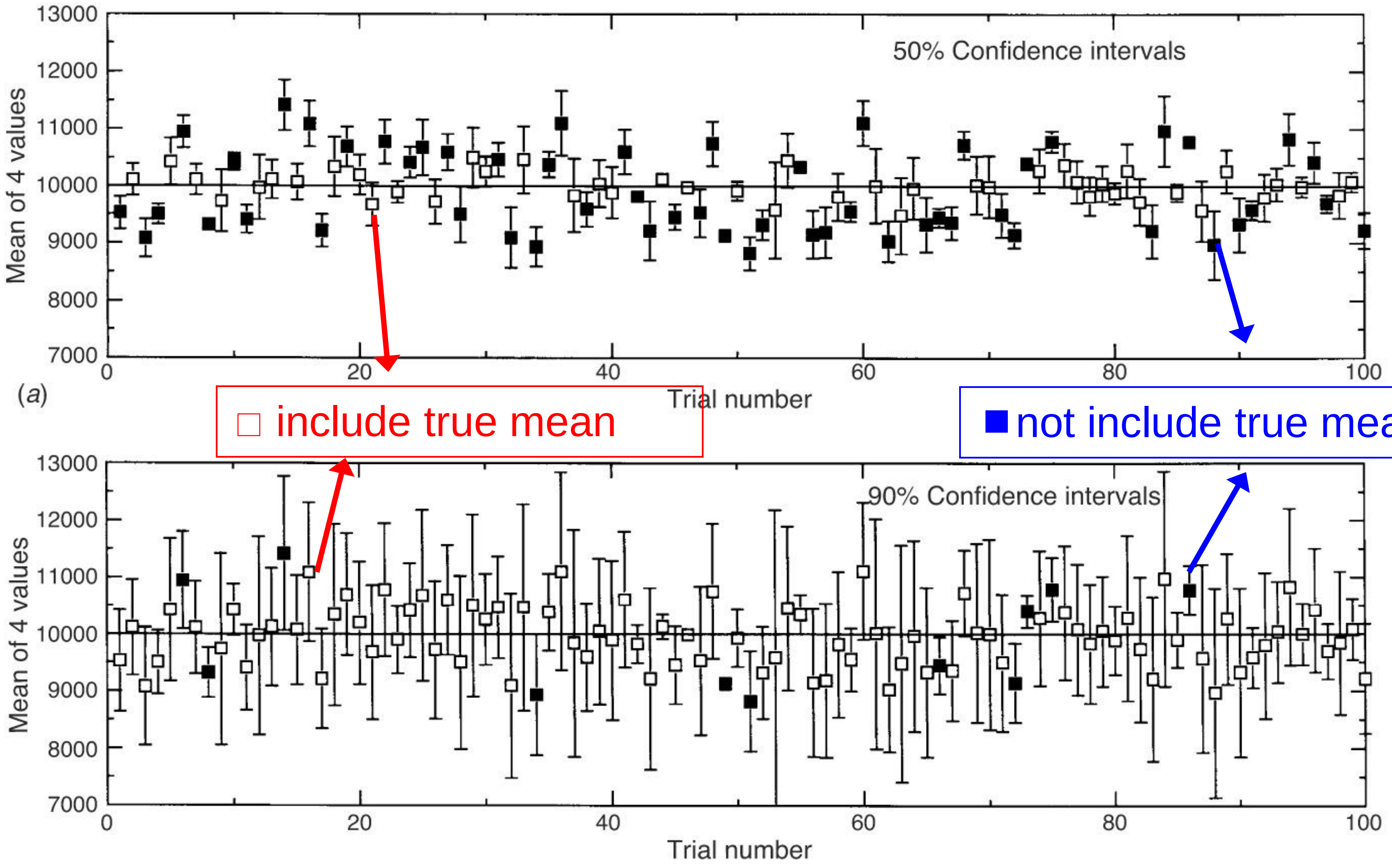




Confidence interval becomes narrower by more measurements

What does it mean by confidence interval?

50% of confidence interval will include true mean



□ include true mean

■ not include true mean

90% of confidence interval will include true mean

t-Test

A *t* test can be used to compare one set of measurements with another to decide whether or not they are the same.

Three different cases,

Case 1: Comparing measure results with a “known” value

Case 2: Comparing replicate measurements

Case 3: Comparing individual difference

Case 1: Comparing measure results with a "known" value

You purchased a Standard Reference Material coal sample certified by NIST to contain 3.19 wt % sulfur. You are testing a new analytical method to see whether it can reproduce the known value. The measured values are 3.29, 3.22, 3.30, and 3.23 wt % sulfur, giving a mean of $\bar{x} = 3.26_0$ and a standard deviation of $s = 0.04_1$. Does your answer agree with the known answer?

To find out, compute $t_{calculated}$ and compare it with t_{table} in Table 4-2. *If $t_{calculated}$ is greater than t_{table} at the 95% confidence level, the two results are considered to be different.*

$$t_{\text{calculated}} = \frac{|\bar{x} - \text{known value}|}{s}\sqrt{n}$$

$$t_{\text{calculated}} = \frac{|3.26_0 - 3.19|}{0.04_1}\sqrt{4} = 3._{41}$$

$$t_{\text{calculated}}\ (= 3.41) > t_{\text{table}}\ (= 3.182)$$

Result is different from the known value. The chance that you made a mistake when concluding that they are different is 5%.

Case 2: Comparing replicate measurements

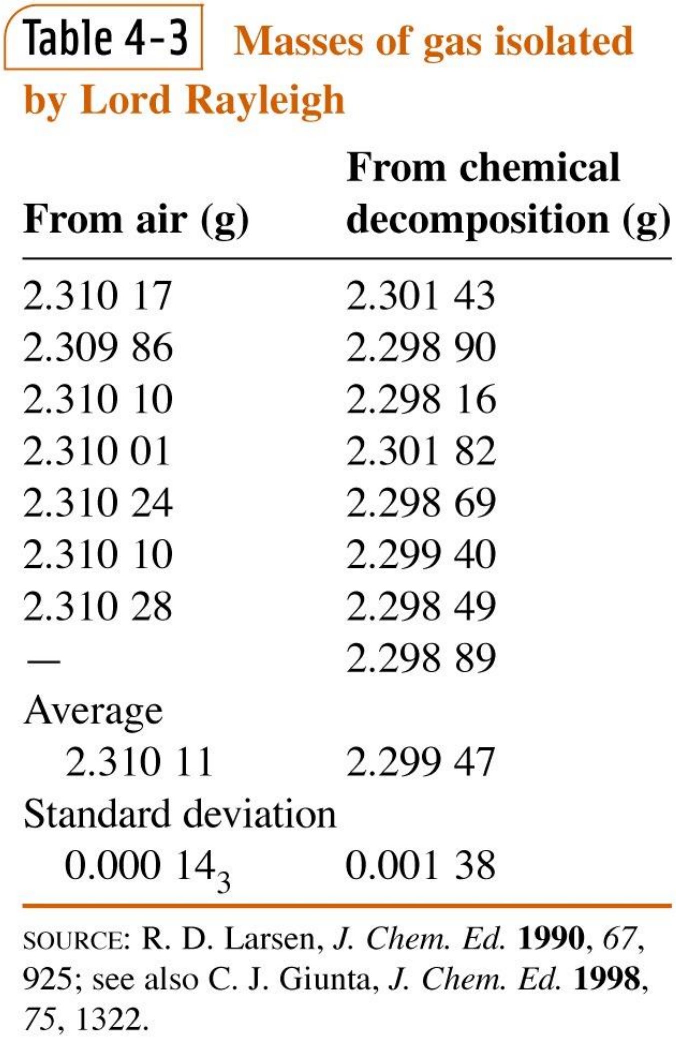


Table 4-3 **Masses of gas isolated by Lord Rayleigh**

From air (g)	From chemical decomposition (g)
2.310 17	2.301 43
2.309 86	2.298 90
2.310 10	2.298 16
2.310 01	2.301 82
2.310 24	2.298 69
2.310 10	2.299 40
2.310 28	2.298 49
—	2.298 89
Average	
2.310 11	2.299 47
Standard deviation	
$0.000\ 14_3$	0.001 38

SOURCE: R. D. Larsen, *J. Chem. Ed.* **1990**, *67*, 925; see also C. J. Giunta, *J. Chem. Ed.* **1998**, *75*, 1322.

Are they same?

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\text{pooled}}}\sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

$$s_{\text{pooled}} = \sqrt{\frac{\sum\limits_{\text{set 1}} (x_i - \bar{x}_1)^2 + \sum\limits_{\text{set 2}} (x_j - \bar{x}_2)^2}{n_1 + n_2 - 2}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$$

s_{pooled} is a *pooled* standard deviation making use of both sets of data.

$$t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\text{pooled}}}\sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

$$s_{\text{pooled}} = \sqrt{\frac{\sum_{\text{set 1}} (x_i - \bar{x}_1)^2 + \sum_{\text{set 2}} (x_j - \bar{x}_2)^2}{n_1 + n_2 - 2}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$$

x_1 = 2.31011 g, s_1 = 0.00014$_3$, n_1 = 7 measurements
x_2 = 2.29947 g, s_2 = 0.00138, n_2 = 8 measurements

$$s_{\text{pooled}} = \sqrt{\frac{0.000\,14_3^2\,(7 - 1) + 0.001\,38^2\,(8 - 1)}{7 + 8 - 2}} = 0.001\,02$$

$$t_{\text{calculated}} = \frac{|2.310\,11 - 2.299\,47|}{0.001\,02}\sqrt{\frac{7 \cdot 8}{7 + 8}} = 20.2$$

For 13 (7 + 8 - 2) degrees of freedom in Table 4-2, t_{table} lies between 2.228 and 2.131 for 95% confidence. Because $t_{\text{calculated}} \gg t_{\text{table}}$, the difference is significant. In fact, t_{table} for 99.9% confidence is ~4.3. The difference is significant beyond the 99.9% confidence level.

Case 3: Comparing Individual Difference

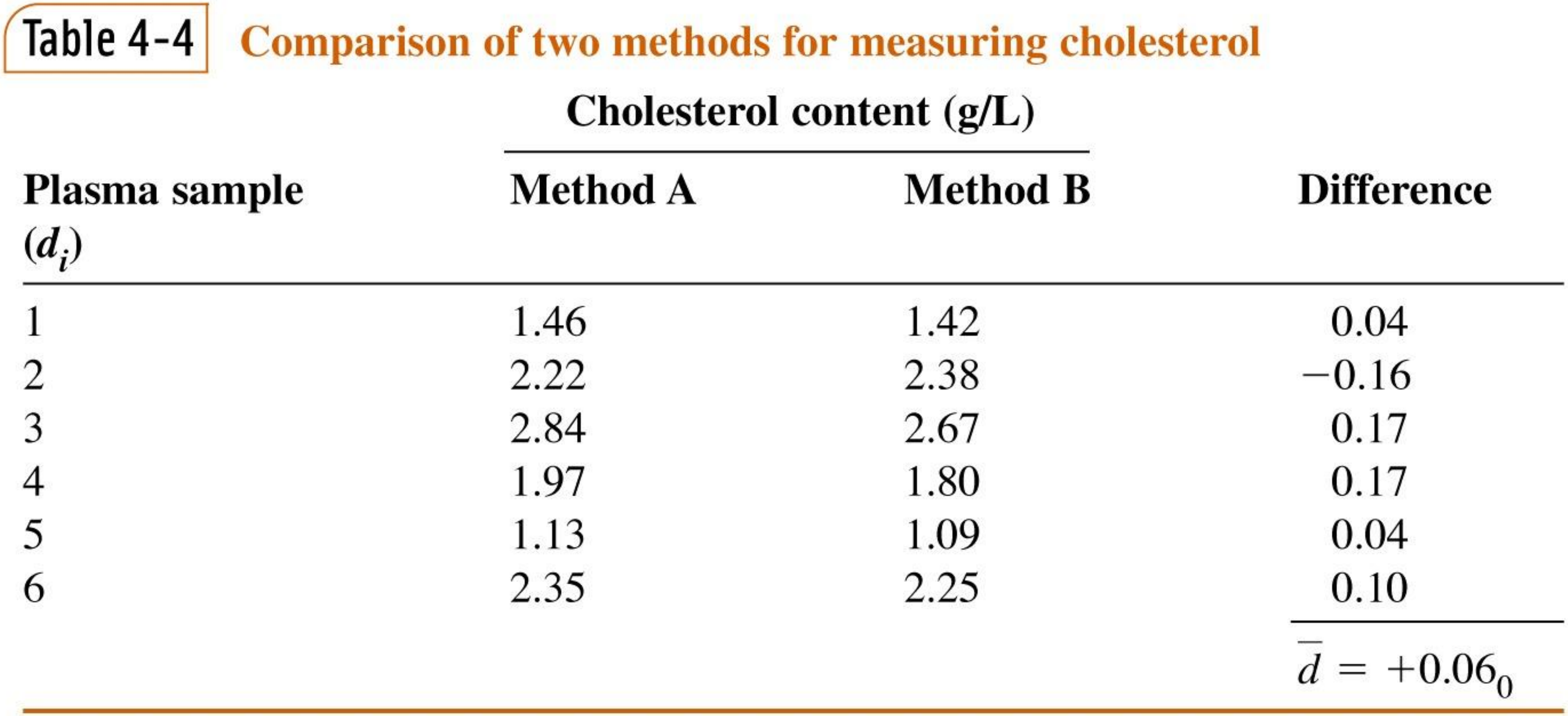


Table 4-4 Comparison of two methods for measuring cholesterol

Plasma sample (d_i)	Cholesterol content (g/L) Method A	Cholesterol content (g/L) Method B	Difference
1	1.46	1.42	0.04
2	2.22	2.38	−0.16
3	2.84	2.67	0.17
4	1.97	1.80	0.17
5	1.13	1.09	0.04
6	2.35	2.25	0.10
			$\bar{d} = +0.06_0$

Is method **B** systematically different from method **A**?

$$t_{calculated} = \frac{\bar{d}}{s_d}\sqrt{n} \qquad s_d = \sqrt{\frac{\sum\left(d_i - \bar{d}\right)^2}{n-1}}$$

The quantity $\bar{d}$ is the average difference between methods A and B, and *n* is the number of pairs of data (six in this case).

$$s_d = \sqrt{\frac{(0.04-\bar{d})^2 + (-0.16-\bar{d})^2 + (0.17-\bar{d})^2 + (0.17-\bar{d})^2 + (0.04-\bar{d})^2 + (0.10-\bar{d})^2}{6-1}}$$

$$= 0.12_2 \text{ (using } \bar{d} = 0.06_0\text{)}$$

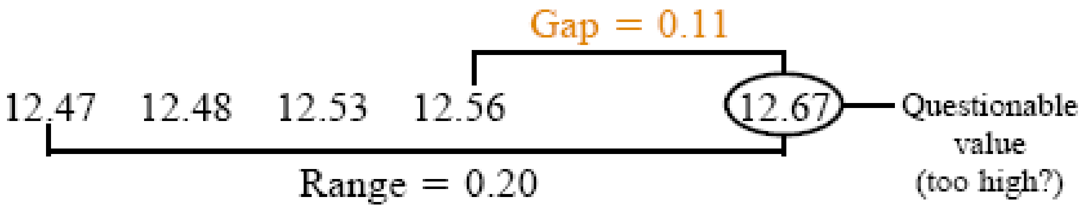
$$t_{\text{calculated}} = \frac{0.06_0}{0.12_2}\sqrt{6} = 1.20$$

We find that $t_{\text{calculated}}$ (1.20) is less than t_{table} (2.571) listed in Table 4-2 for 95% confidence and 5 degrees of freedom. The two techniques are *not* significantly different at the 95% confidence level.

Q test for bad data

The ***Q* test** helps decide whether to retain or disregard a questionable data.

$$Q_{calculated} = \frac{gap}{range}$$



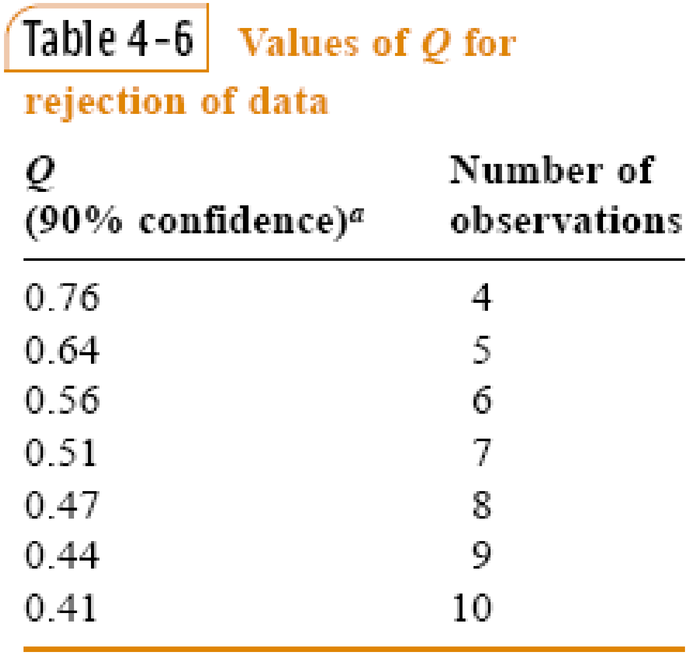


Table 4-6 Values of *Q* for rejection of data

Q (90% confidence)[a]	Number of observations
0.76	4
0.64	5
0.56	6
0.51	7
0.47	8
0.44	9
0.41	10

If $Q_{\text{calculated}} > Q_{\text{table}}$, the questionable point should be discarded. For the numbers above, $Q_{\text{calculated}} = 0.11/0.20 = 0.55$. In Table 4-6, we find $Q_{\text{table}} = 0.64$. *Because* $Q_{calculated} < Q_{table}$, *the questionable point should be retained.* There is more than a 10% chance that the value 12.67 is a member of the same population as the other four numbers.