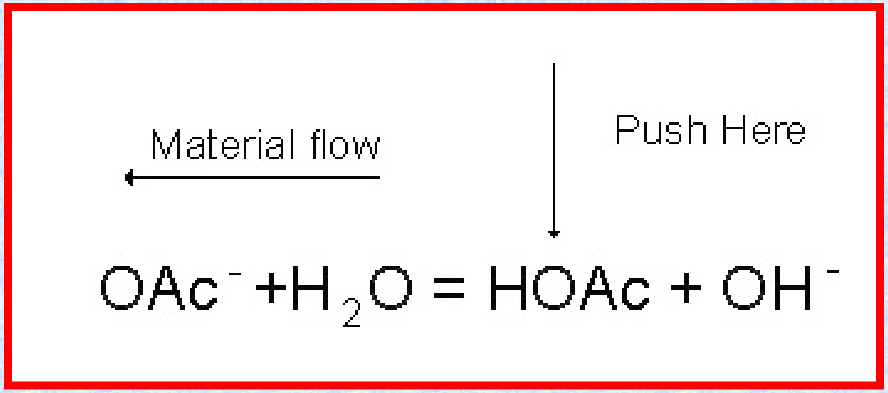


$OAc^- + H_2O = HOAc + OH^-$

Addition of large amounts of a weak acid and its conjugate base to the same solution nullifies both the ionization of the acid and the hydrolysis of the base!!

$HOAc + H_2O \rightarrow OAc^- + H_3O^+$

0.7 M 0.6 M

$OAc^- + H_2O \rightarrow HOAc + OH^-$

0.6 M 0.7 M

$K_a = [OAc^-]\,[H_3O^+] / [HOAc] = 1.85 \times 10^{-5}$

$K_h = [HOAc][OH^-] / [OAc^-] = 5.4 \times 10^{-10}$

Both equilibria must be satisfied simultaneously.

$[OAc^-] \cong 0.6$ M and $[HOAc] \cong 0.7$ M

Thus have $[H_3O^+]$ =

$\{[HOAc]/[OAc^-]\} \times K_a \cong (0.70/0.60) \times (1.85 \times 10^{-5})$

$[H_3O^+]=2.185\mathrm{x}10^{-5}$ M} This result is accurate to 4 significant figures (gives same result as solving quadratic to this accuracy)!

A solution containing substantial amounts of a weak acid and its conjugate base is known as a buffer solution.

Thus, have $[H_3O^+]$ = {[acid]/[salt]} K_a

Depends only on K_a and the ratio of [acid] to [salt]

If we dilute such a solution, $[H_3O^+]$ will not change since [acid] and [salt] change identically when such a solution is diluted!

Example: 1 liter of 0.25 M HCl, add 0.600 moles of NaOAc(s)
Assume no volume change occurs upon addition of salt.

Find $[OAc^-]$, $[HOAc]$, $[H_3O^+]$, $[OH^-]$

$NaOAc \rightarrow Na^+ + OAc^-$ $\qquad$ $H_2O + HCl \rightarrow H_3O^+ + Cl^-$

(1) $OAc^- + H_3O^+ \rightarrow HOAc + H_2O$
$0.600 \quad 0.250 \qquad \sim 0$ initially

$$K_a = \frac{[OAc^-][H_3O^+]}{[HOAc]} = 1.85 \times 10^{-5}$$

Equation far to the right

(2) $OAc^- + H_3O^+ \rightarrow HOAc + H_2O$
$\sim .350 \quad \sim 0 \qquad \sim .250$

Recognizing a buffer when you see it. Not always an easy task.

Buffer conditions!

$[OAc^-] = .350$ $\qquad$ $[HOAc] = .250$

$$[H_3O^+] = K_a\frac{[HOAc]}{[OAc^-]} \approx 1.855\times10^{-5}\left(\frac{.25}{.35}\right)$$

$= 1.325\text{x}10^{-5}$ M

Clamping of $[H_3O^+]$ by a buffer solution

1) Add 1 ml of 1 M HCl to 1 liter of pure H_2O:

$[H_3O^+] \cong 0.001$ Or, the H_3O^+ concentration changes From 10^{-7} to 10^{-3} (4 orders of magnitude)!

2) Now add 1 ml of 1M HCl to one liter of solution containing 0.7 moles of HOAc and 0.6 moles of NaOAc.

Remember, this is a buffer, so $[HOAc] \cong$ 0.7M and $[OAc^-] \cong$ 0.6M

Initially:

$$\begin{array}{llll} OAc^- & + H_3O^+ & \rightarrow HOAc & + H_2O \\ 0.600 & 0.001 & 0.700 & \end{array}$$

Max change in HOAc occurs if all H^+ added reacts with OAc^- →HOAc: Reaction stoichiometry is as follows:

$$\begin{array}{llll} OAc^- & + H_3O^+ & \rightarrow HOAc & + H_2O \\ 0.599 & \cong 0 & 0.701 & \end{array}$$

$[HOAc] = 0.701$ and $[OAc^-] = 0.599$

$$\text{and } [H_3O^+] = \frac{[\text{acid}]}{[\text{anion}]} K_a = \frac{0.701}{0.599} 1.85 \times 10^{-5}$$

New $[H_3O^+] = 2.17 \times 10^{-5}$

Before addition of HCl, $[H_3O^+] = \frac{.700}{.600} 1.85 \times 10^{-5} = 2.16 \times 10^{-5}$

“No” change in $[H_3O^+]$ when buffered!

If not buffered, get 10^4 change in H_3O^+ concentration!!

“Physically” the H^+ is being “stored” as undissociated HOAc:

$$OAc^- + H_3O^+ \rightarrow HOAc + H_2O$$

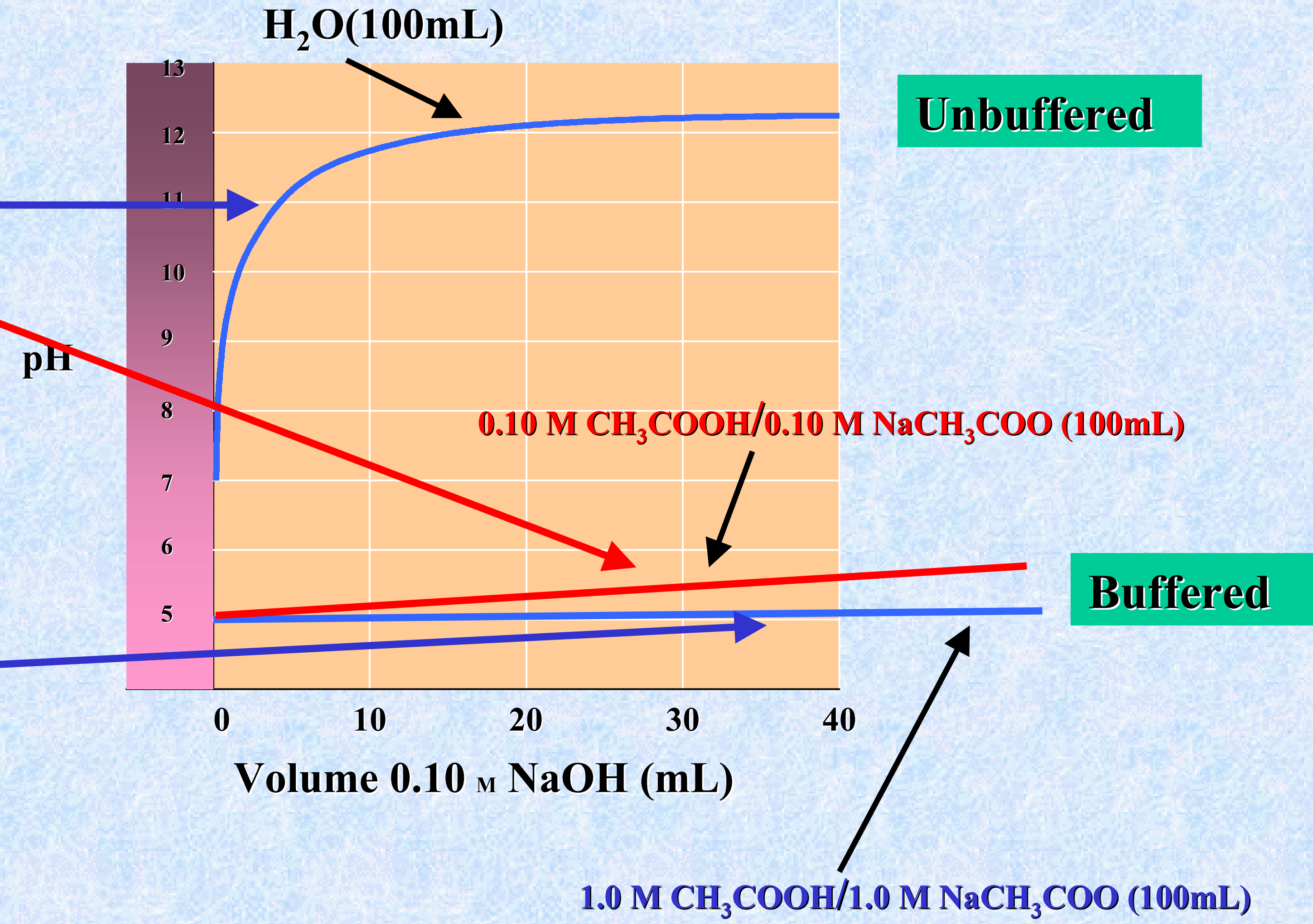
If add OH^- also find pH does not change because the OH^- reacts with HOAc to give H_2O and OAc^-!

Add strong base to:

1) Pure water

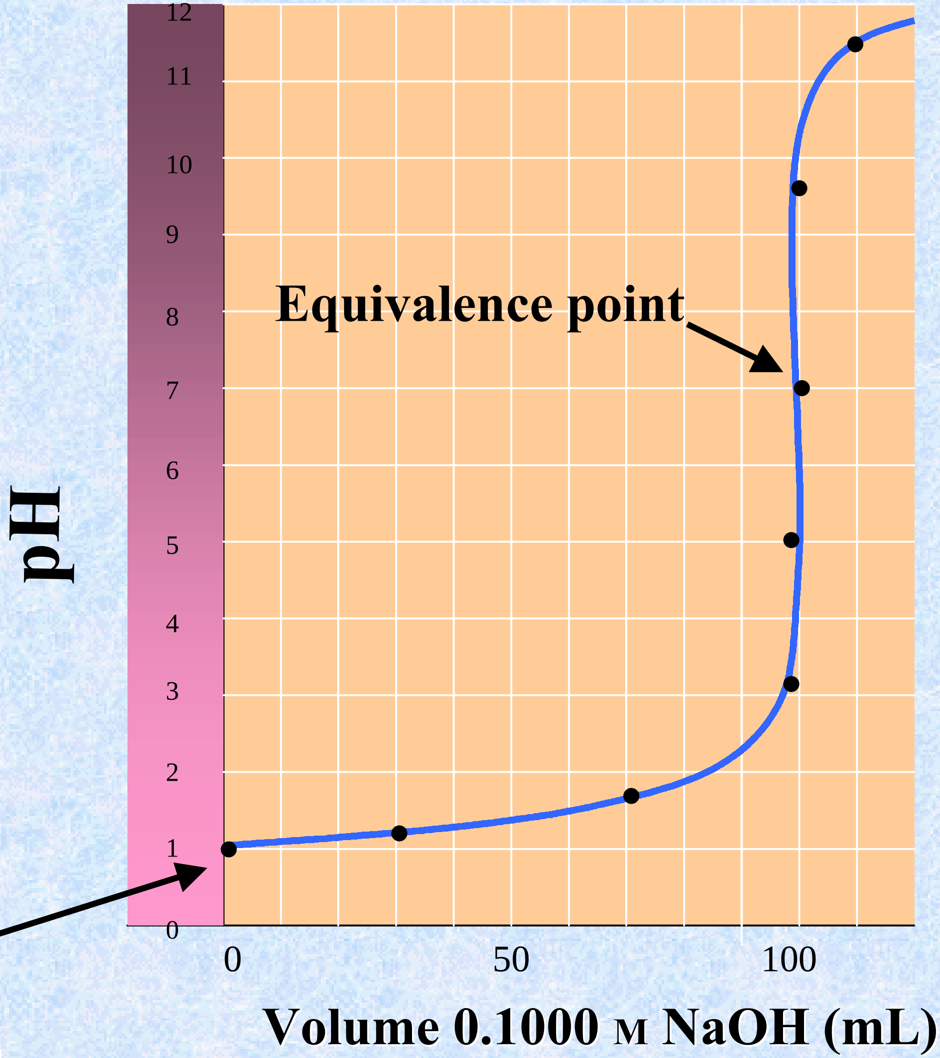
2) 0.1 M/0.1 M Acetate buffer

3) 1.0 M/1.0M Acetate buffer



Buffered: small change in pH compared to unbuffered.

Higher buffer concentration resists pH changes more effectively.



100.0 mL of
0.1000 M HCl
titrated with
0.1000 M NaOH.

At start
$[H_3O^+]=10^{-1}$ M

Titration of a strong acid by a strong base.

Titration Curve for aWeak Acid HA (red curve/points)

$$HA + OH^- \rightarrow H_2O + A^-$$

Mix of HA and A^- in buffer region

Mostly HA at start

Indicators

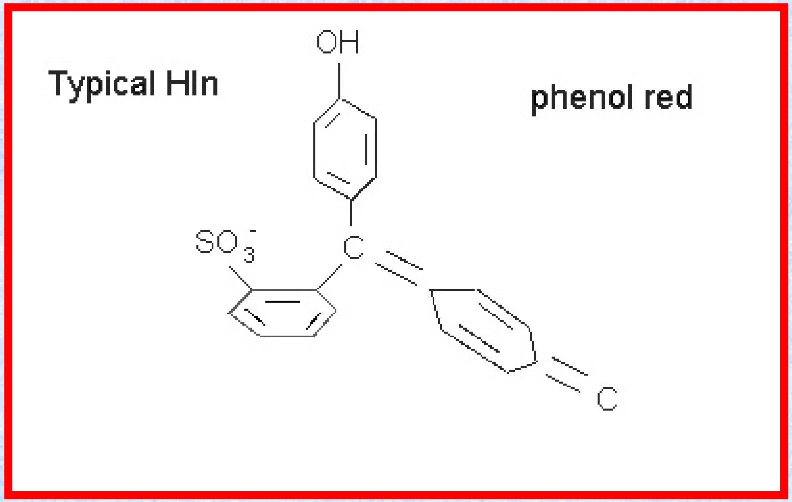
Dye molecules whose color changes with pH or $[H^+]$.
Useful way to follow pH changes.

$HIn + H_2O \rightarrow H_3O^+ + In^-$

(Indicators are themselves weak acids or bases.)

In^- yellow, HIn red
In = Indicator

$$K_I = \frac{[H_3O^+][In^-]}{[HIn]}$$



Ratio of yellow, In^- form, to red, HIn form, controlled only by $[H_3O^+]$ for a given K_I

$$[In^-] / [HIn] = K_I / [H_3O^+]$$

Bonus * Bonus * Bonus * Bonus * Bonus * Bonus

Sensitivity range brackets: $[In^-]/[HIn] = 1$

$\rightarrow K_I / [H_3O^+] = 1 \rightarrow [H_3O^+] = K_I$

$\rightarrow pH = pK_I$ where
$pK_I = -\log_{10} K_I$

Center of pH range where indicator works best is $pH = pK_I$

Some Important Acid-Base Indicators
(Skoog and West p 189, table 9-1)

Indicator	Sensitive pH Range	Acid Color	Base Color
Thymolphthalein	9.3 - 10.5	colorless	blue
Phenolphthalein	8.0 - 9.8	colorless	red-violet
Methyl Yellow	2.9 - 4.4	red	orange-yellow

Thermodynamics (1st part)

Introduction

Thermodynamics is the study of energy flow for bulk matter. It is not a subject which concerns itself with the behavior of individual molecules.

Rather it describes the behavior only of large numbers of molecules taken together.

Thermodynamics is only valid under certain relatively restricted conditions. Most simply Thermodynamics describes equilibrium situations and change between equilibrium situations.

All of Thermodynamic principles are based completely on experimental findings in the laboratory.

As such it is a totally empirical science. Example: Sun rises every morning. Statement based on experience or measurement.

Thermodynamics is a discipline with only 3 laws:

1st Law : Energy of the Universe is constant

(can only pay Paul by robbing Peter)

2nd Law : Entropy of the universe can only increase, (more sophisticated).

3rd Law: Entropy vanishes at T=0 Kelvin.

Some Definitions :

1) System : Object or box or part of the physical universe which we want to study.

2) Surroundings: Every thing that isn't the system (i.e. the remainder of the universe)

3) Equilibrium states or more simply and sloppily just states: A situation in which a system does not change with time i.e. The bulk properties don't change.

To describe the state of a system we usually need to know several things such as

Temperature
Pressure
Density
Composition (chemical)

4) State Functions: These are the most important quantities in Thermodynamics and also the most difficult to define.

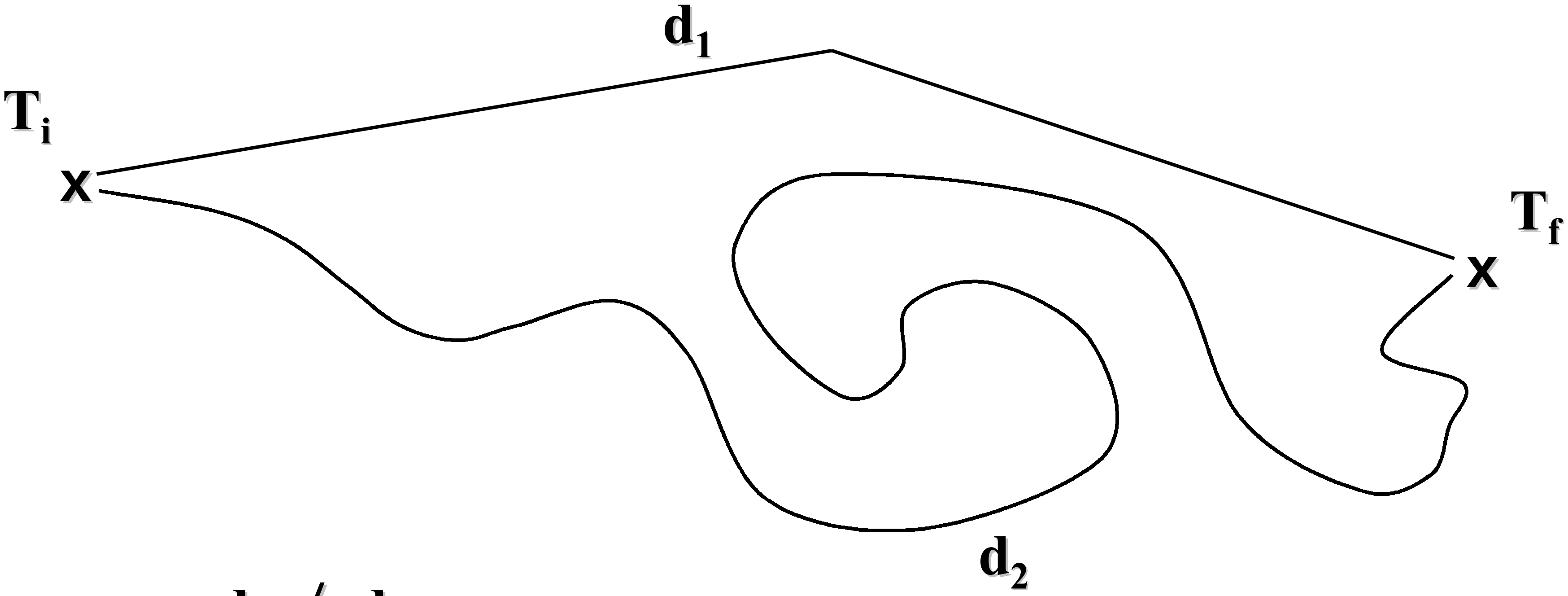
A state function is a property of a system which may have different values for different equilibrium states of the system ;

but a state function always has exactly the same value in a given equilibrium state regardless of the past history of the system.

Changes in values of state functions are easy to determine because the change depends only on the initial and final equilibrium states of the system.

Example :Temperature is a state function

Distance traveled between 2 points is not a state function.



$d_1 \neq d_2$

$\Delta T = T_f - T_i$ (Either path)