

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

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

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

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

[HOAc] = 0.701 and [OAc⁻] = 0.599

New [H₃O⁺] = 2.17 × 10⁻⁵

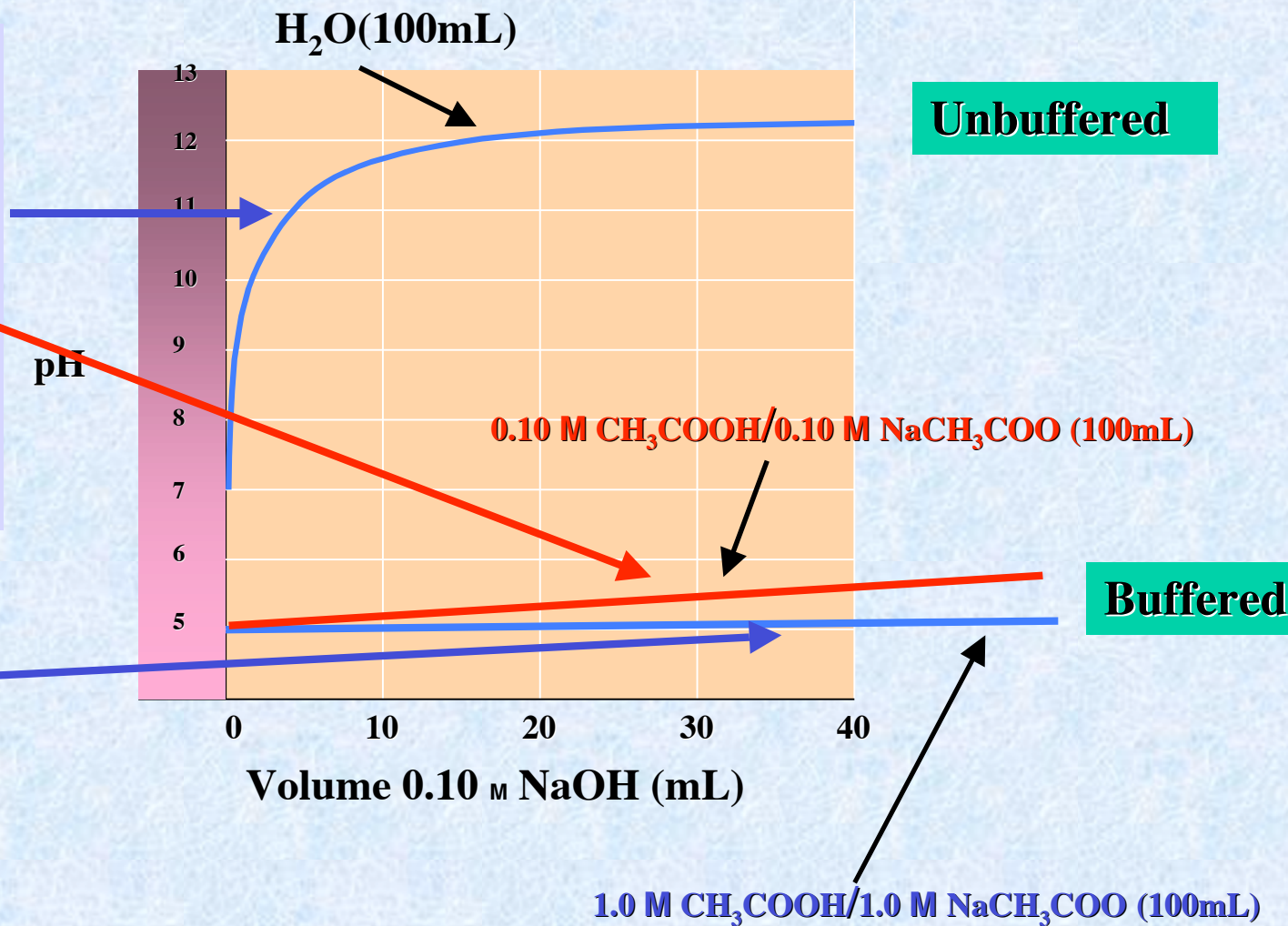
“No” change in [H₃O⁺] when buffered!

If not buffered, get 10⁴ change in H₃O⁺ concentration!!

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

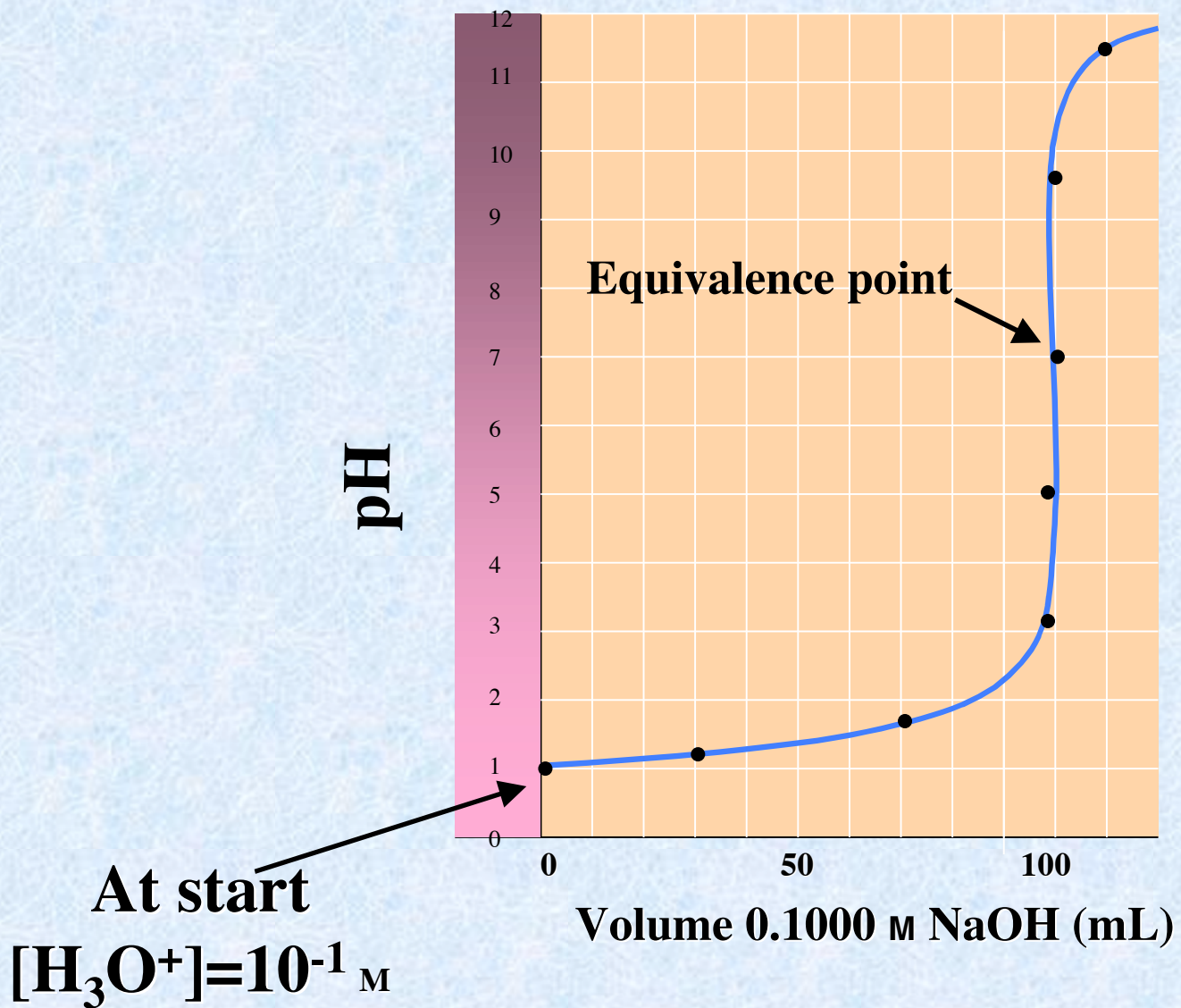
If add OH⁻ also find pH does not change because the OH⁻ reacts with HOAc to give H₂O and OAc⁻!

- 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.**

Titration of a strong acid by a strong base.

Titration Curve for a Weak Acid HA (red curve/points)



**Mostly
HA
at start**



**Mix of HA
and A⁻ in
buffer
region**



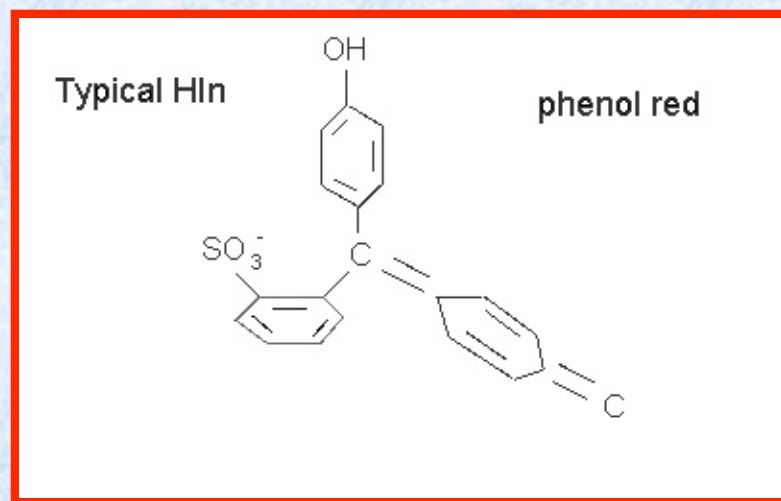
Indicators

Dye molecules whose color changes with pH or $[H^+]$.

Useful way to follow pH changes.

$HIn + H_2O \rightleftharpoons H_3O^+ + In^-$ (Indicators are themselves weak acids or bases.)

In^- yellow, HIn red
 $In =$ Indicator



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

Bonus * Bonus * Bonus * Bonus * Bonus * Bonus

Sensitivity range brackets: $[\text{In}^-]/[\text{HIn}] = 1$

Center of pH range where indicator works best is $\text{pH} = \text{pK}_I$

**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.

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:

(can only pay Paul by robbing Peter)

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

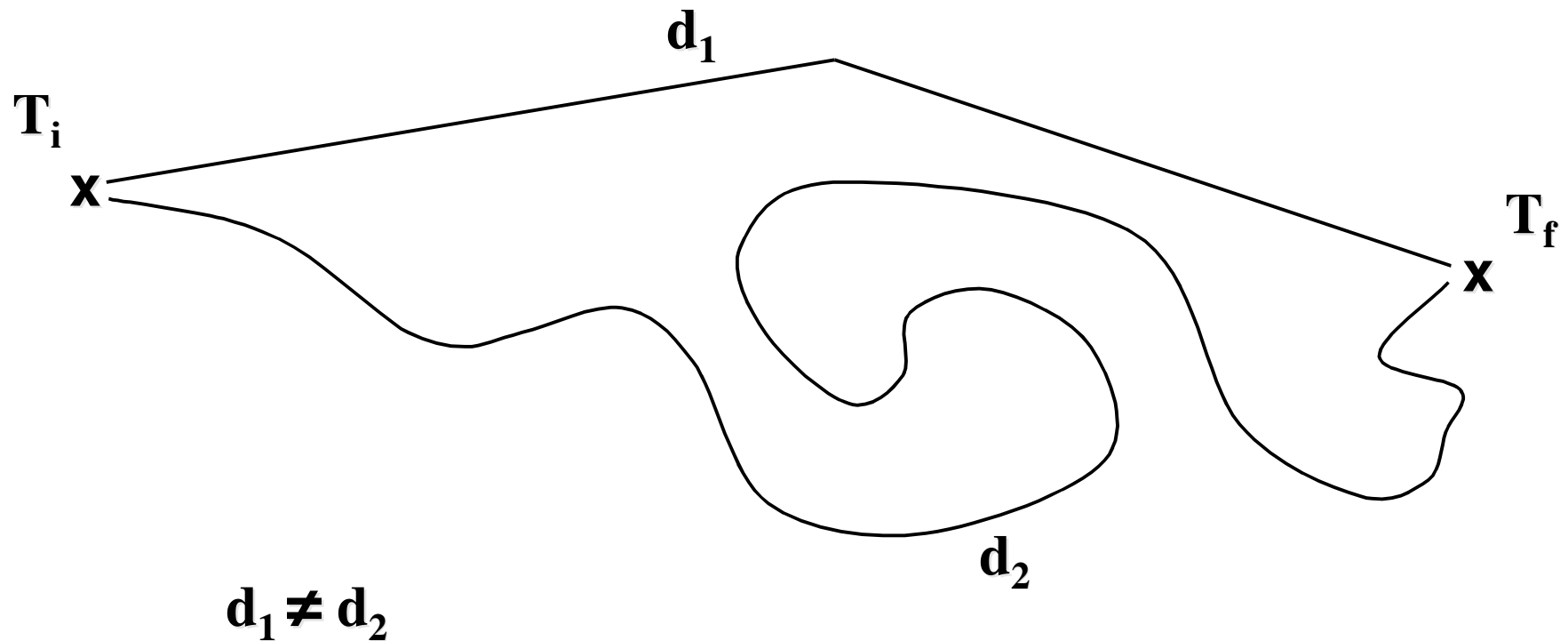
4) State Functions: These are the most important quantities in Thermodynamics and also the most difficult to define.

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

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.



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

Ideal Gas State functions: Consider 1 mole of an ideal gas

$$PV = RT$$

Suppose begin with:

$$P_1 = 5 \text{ atm} \quad V_1 = 4.92 \text{ liters}$$

$$T_1 = 300^\circ \text{ K}$$

And end with:

$$P_2 = 4 \text{ atm} \quad V_2 = 12.3 \text{ liters}$$

$$T_2 = 600^\circ \text{ K}$$

**If we got to the condition 4 atm, 12.3 liters,
and 600°K by going as follows:**

**5 atm, 4.92 liters, 300° \square 4 atm, 6.15 liters, 300° \square 4 atm,
12.3 liters, 600° or by the path:**

**5 atm, 4.92 liters, 300° \square 5 atm, 9.84 liters, 600° \square 4 atm,
12.3 liters, 600°**

Changes in state functions are independent of path.

Important State Functions:

Important Non State Functions: *Work, Heat.*