UMassAmherst

An interactive demonstration on the use of pH and water activity meters for establishing food safety control

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Agenda

- **Chemistry** — *pH*, Aw
- **Demonstration** — pH
- **Food Safety** — *Controls*

Chemistry

pH

Aw

pH & Aw

pH:

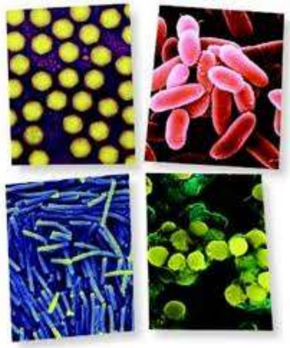
- Concentration of free H+ ions
- Measure of active acidity
- Affects reactions in foods

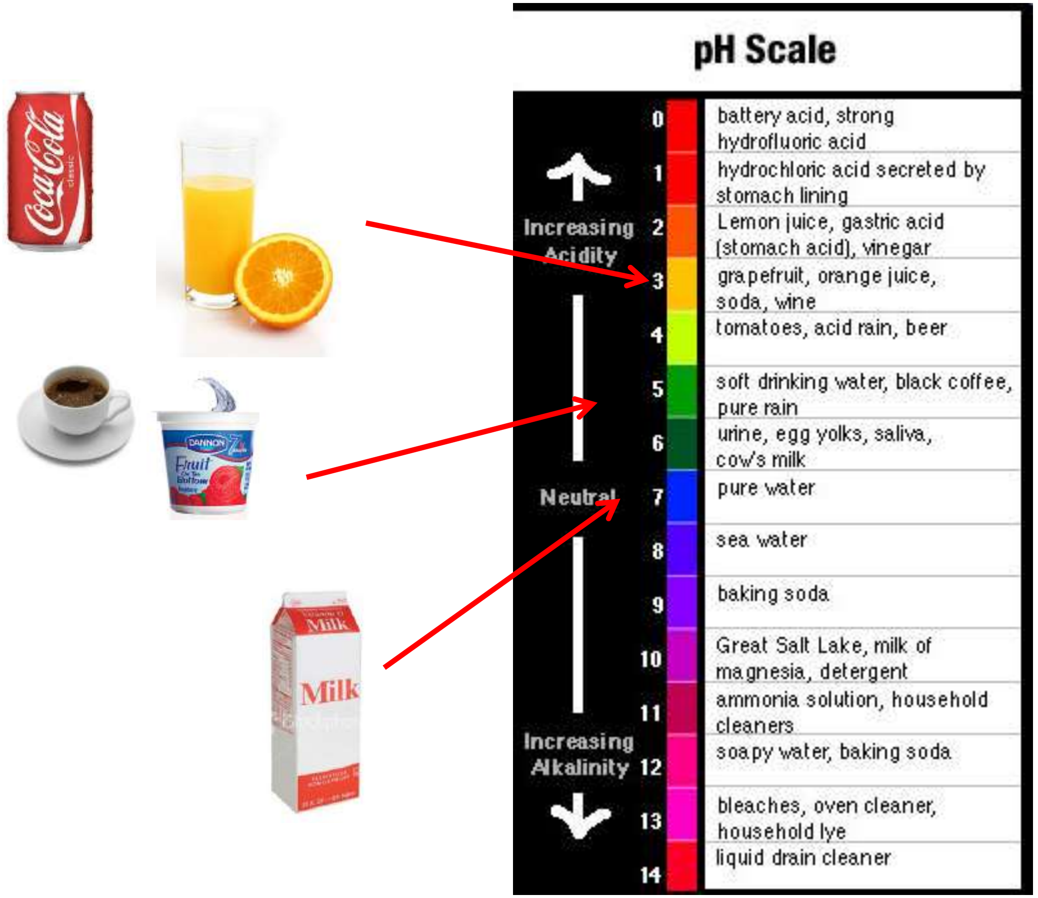
Aw:

- Measures “available water”
- Scale 0-1
- Influence on Chemical, Biochemical and Microbial Reaction Rates

pH

Acids, Bases, & Buffers





Importance of pH in foods

- **Influences flavor**
  - tartness, sourness
- **Influences stability and reactivity**
  - Physical, chemical & microbial
- **Influences texture & appearance**
  - Aggregation, gelation

pH & Titratable Acidity

In wine industry, acid makes wine more tart or sharp tasting. (titratable acidity).

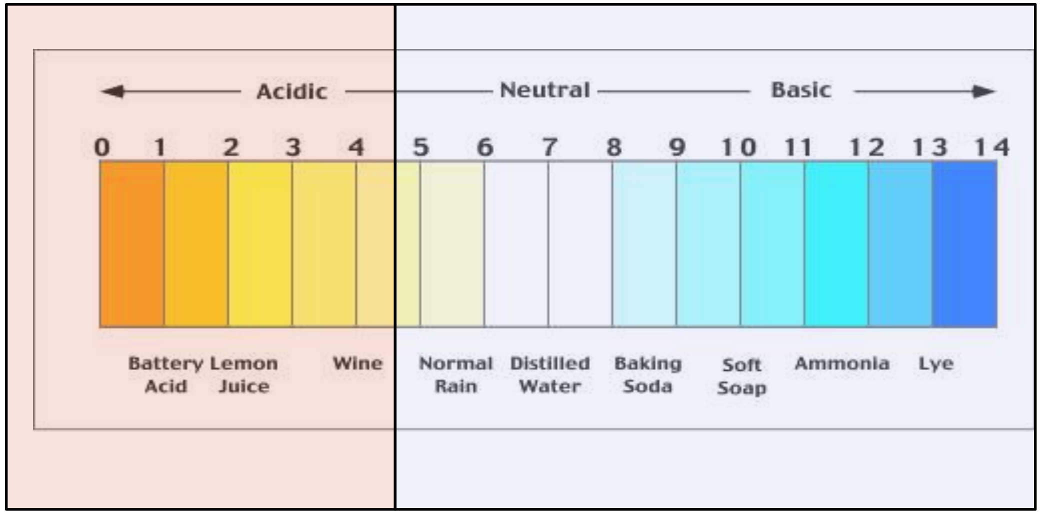
Acid also makes wine more stable: against mold, bacteria, or oxidation (pH).

pH & Titratable Acidity

0.1 N of HCl vs. 0.1 N CH_3COOH

- $HCl \rightleftharpoons H^+ + Cl^-$
  strong acid, fully dissociates, pH 1.02 at 25ºC
- $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
  weak acid, 1% dissociates, pH 2.89 at 25ºC

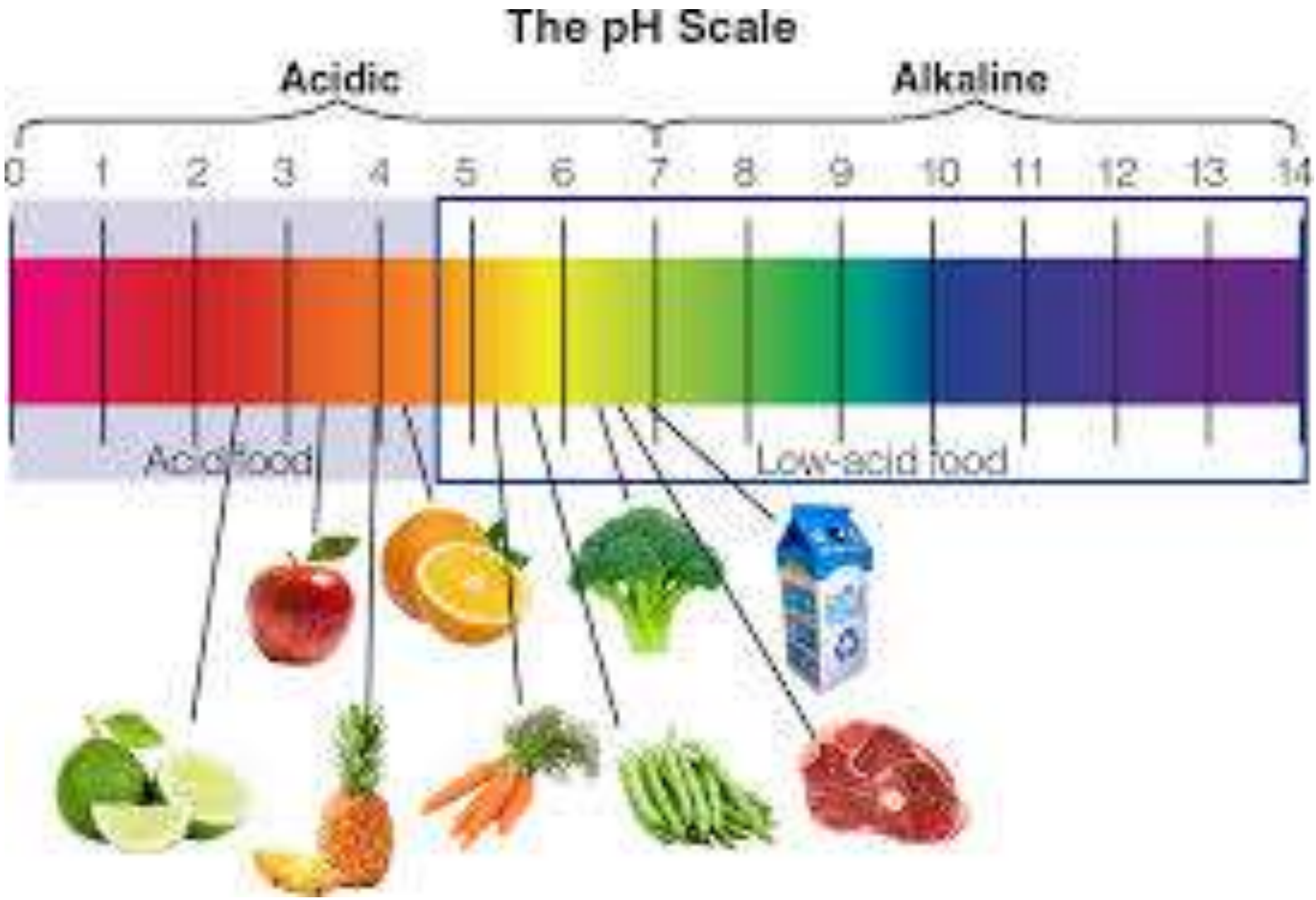
pH



Acid Food Low Acid Food

- An intrinsic factor inherent to food.
- Low pH means that the cell utilizes more energy to maintain a pH near neutral intracellular it has less energy to grow or produce toxins
- pH ranges in between 0 to 14, where 7 is neutral below is acid and above is alkaline
- Foods
  - 'acidic' >4.6
  - 'low acid' < 4.6

pH Measurements of Common Foods



pH

Definition

The logarithm of the reciprocal of the hydrogen ion concentration of a solution

$$pH = -\log[H^+]$$

pH units represent a 10-fold change
in hydrogen ion concentration

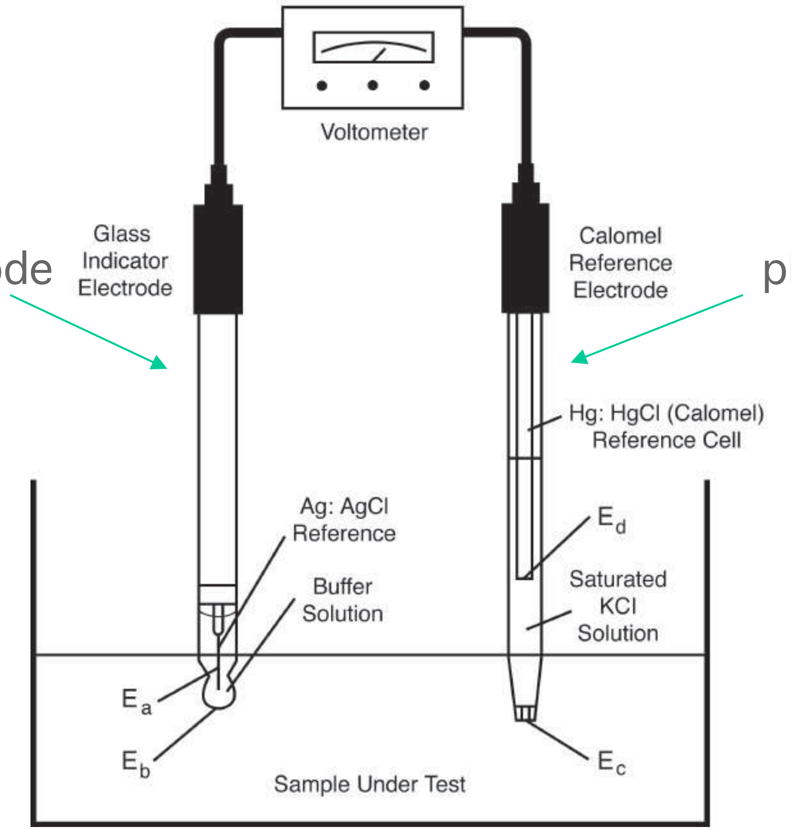
pH: Problem

- **Beer has a pH = 4, $[H^+]$ = ?**
  - $pH = -\log [H^+]$
  - $4 = -\log [H^+]$
  - $[H^+] = 10^{-4}$ mol/L

http://pngimg.com/uploads/beer/beer_PNG2376.png

pH Meter

reference electrode



pH electrode

http://chem1.com/acad/webtext/acid2/acid2-images/tit-pHMeter.jpg

The pH meter measures the difference in electrical potential between a pH electrode and a reference electrode.

Cleaning an Electrode

- Food components can foul an electrode
  Fat, proteins, minerals

- Clean with detergent, ethanol, or acetone
  Clean if: **response time is slow**
  readings drift
  calibration can't be achieved
  slope of calibration is poor

https://upload.wikimedia.org/wikipedia/commons/thumb/c/c9/Zilverchloridereferentie-_en_PH-glaselektrode.jpg/100px-Zilverchloridereferentie-_en_PH-glaselektrode.jpg

pH and Sample Temperature

T (°C)	K_W (mol^2 dm^6)	pH
0	0.114×10^{-14}	7.47
25	1.008×10^{-14}	7.00
50	5.476×10^{-14}	6.63
100	51.3×10^{-14}	6.14

- pH is *temperature dependent*
- Every solution will undergo a change in temperature in their pH value through changes in temperature
- To achieve highest accuracy, calibrate and measure at the same temperature.

https://www.westlab.com/blog/2017/11/15/how-does-temperature-affect-ph

pH Meter Calibration

- Before calibration or usage, make sure the electrode is in good condition.
- pH meter calibration is a necessary
- Regularly calibrating your pH meter will adjust your electrode based off any changes that may have occurred and ensures that your readings are accurate and repeatable.

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Aw

Water Activity (Aw)

Definition:

A parameter to characterize influence of water on food stability and properties.

Problem:

- Water is known to play an important role in determining food properties
- However, there is not a good correlation between total water content and food properties:
    - *Chemical reaction rates*
    - *Microbial growth rates*
    - *Physical properties*
- A new parameter was needed to describe waters behavior
    - **Water Activity**

UMASS Pilot Plant: 1988-1990

>130 million pounds today

Microbial stability: aw < 0.62
& Moisture migration control

Water Activity (Aw)

Table 1. **Common spoilage organisms and their a_w limits for growth.**

Microbial Group	Example	a_w	Products Affected
Normal bacteria	*Salmonella species* *Clostridium botulinum*	0.91	Fresh meat, milk
Normal yeast	*Torulopsis species*	0.88	Fruit juice concentrate
Normal molds	*Aspergillus flavus*	0.80	Jams, Jellies
Halophilic bacteria	*Wallemia sebi*	0.75	Honey
Xerophilic molds	*Aspergillus echinulatas*	0.65	Flour
Osmophllic yeast	*Saccharomyces bisporus*	0.60	Dried fruits

- Water Activity is the availability of water in the food.
- In food water is bound to other molecules or immobilized by the structure of the food
- Aw = Vapor Pressure of food/ Vapor Pressure of Pure Water
- It is a measure between 0 and 1, 0 meaning that there is no water available. This is temperature dependent
- Most foods have a water activity above 0.95 and that will provide sufficient moisture to support the growth of bacteria, yeasts, and mold.

Moisture content *versus* water activity

$$\boxed{MC = 100 \times \frac{m_{water}}{m_{sample}}}$$

Icing: MC= 15%

Cake: MC= 30%

Will water move from the cake to the icing ?

The answer is ......not sure

- because the moisture content does not predict water movement

Water Activity: Thermodynamic Definition

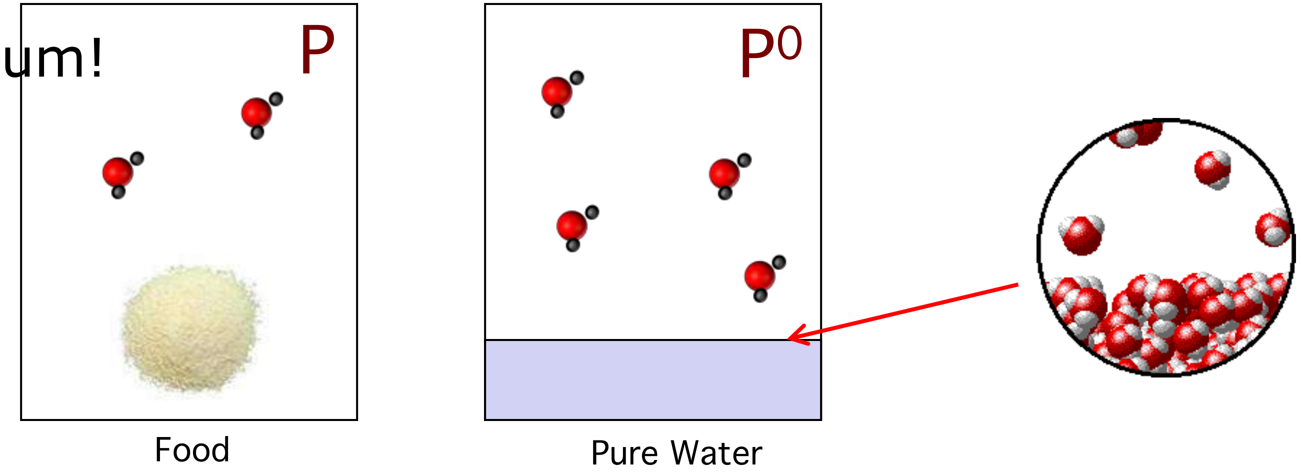
Thermodynamic Definition:

- Ideal Situation (Equilibrium)
  - a_w = water activity
  - f_w = fugacity (“escaping tendency”)
  - p_w = partial vapor pressure (“head space concentration”)

$$a_w = \left(\frac{f_w}{f_w^0}\right)_T = \left(\frac{p_w}{p_w^0}\right)_T$$

Problem:

- Most foods are not at equilibrium!

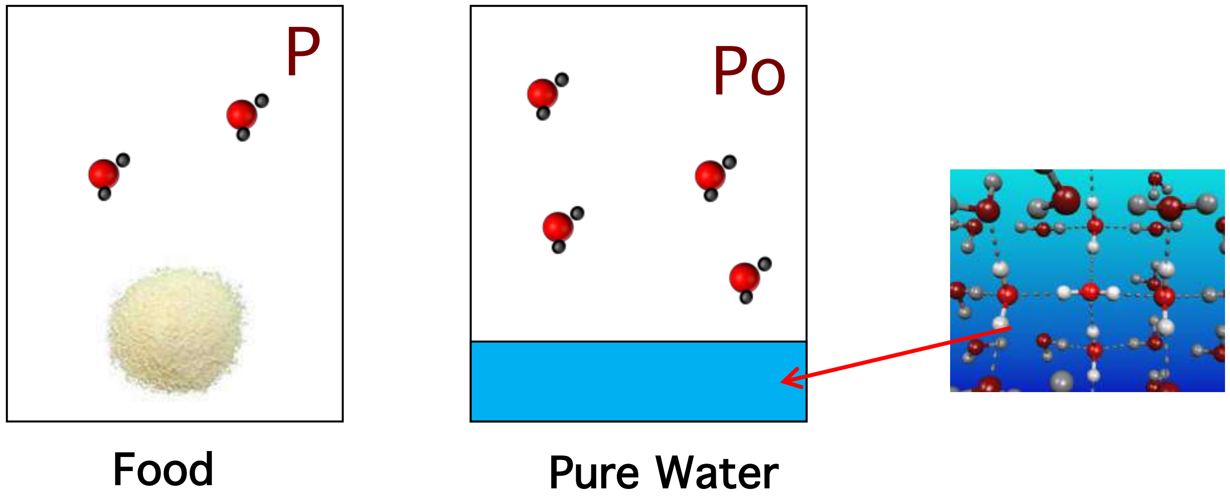


Water Activity: Practical Definition

Practical Definition:

- Real Situation (Non-Equilibrium)
- *RVP = Relative Vapor Pressure*
- p_w = partial vapor pressure

$$RVP = \left(\frac{p_w}{p_w^0} \right)_T$$

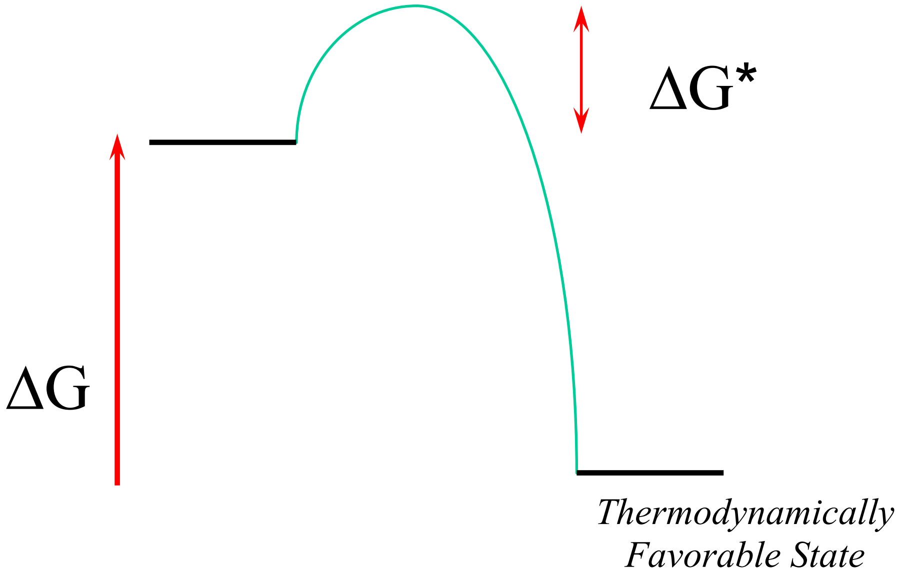


Water Activity: Approaches to controlling water migration

Raisin a_w = 0.55
Cereal a_w = 0.10

Water will tend to flow from raisins to cereal. To prevent:
(i) Change driving force: *e.g.*, add glycerol to lower a_w of raisin.
(ii) Create kinetic energy barrier: *e.g.*, coat raisins with a material that prevents water flow (*e.g.*, fat).

To prevent water-migration:
(i) **Thermodynamic approach:** Change driving force by equaling a_w. (DG ≥ 0)
(ii) **Kinetic approach:** create an activation energy (energy barrier, DG*) to inhibit movement.



Water Activity: Influence on Chemical, Biochemical and Microbial Reaction Rates

The water activity of a food influences many important kinetic processes in foods:

- Chemical Reaction Rates
- Microorganism growth
- Enzyme Activity

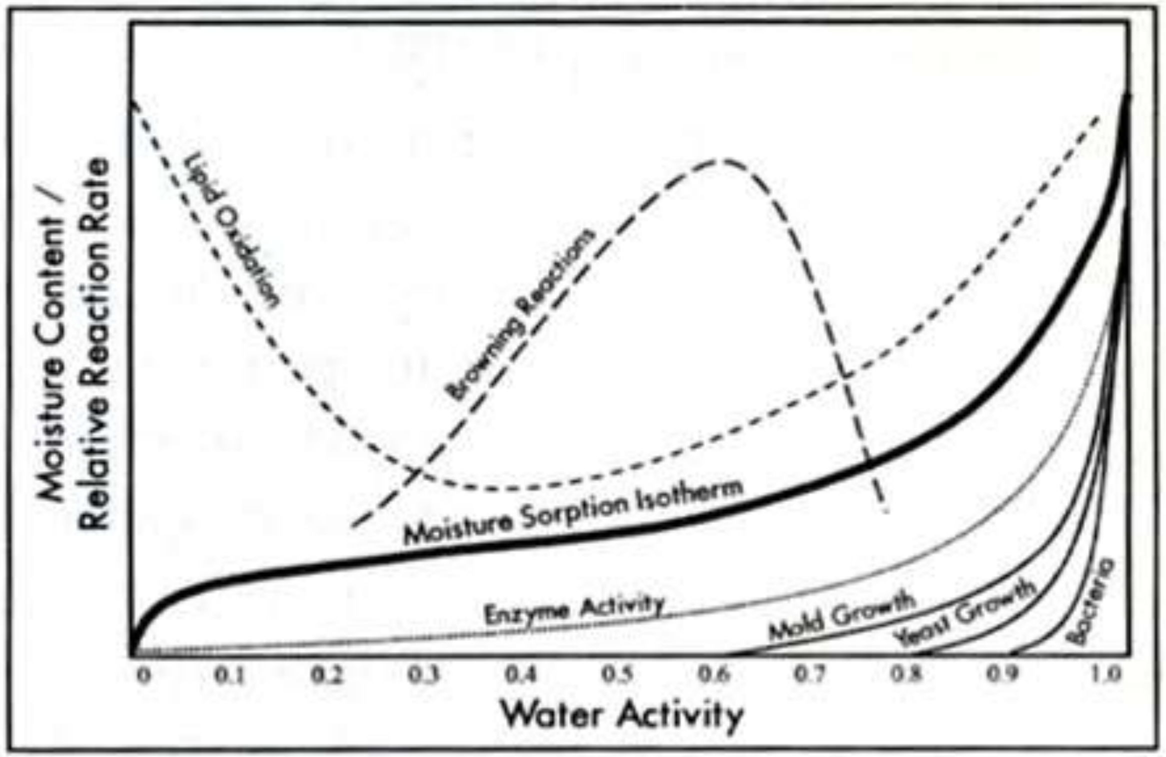
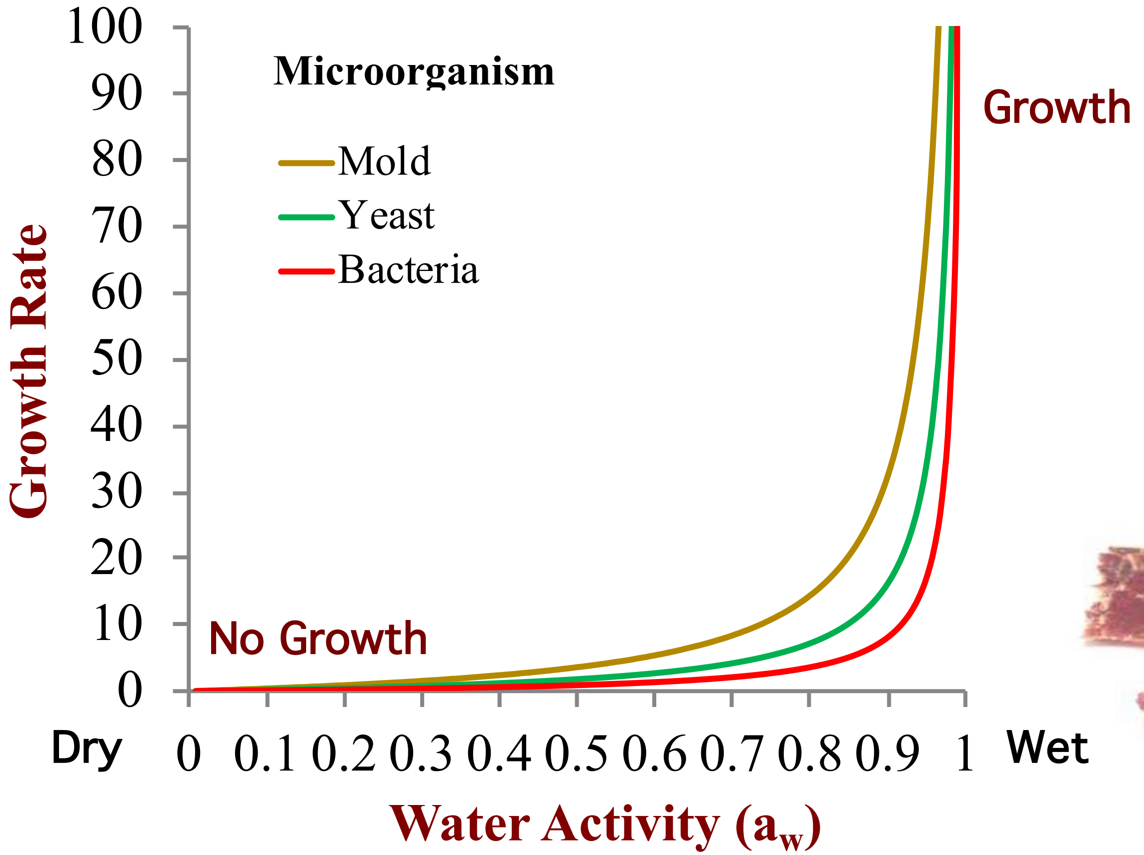


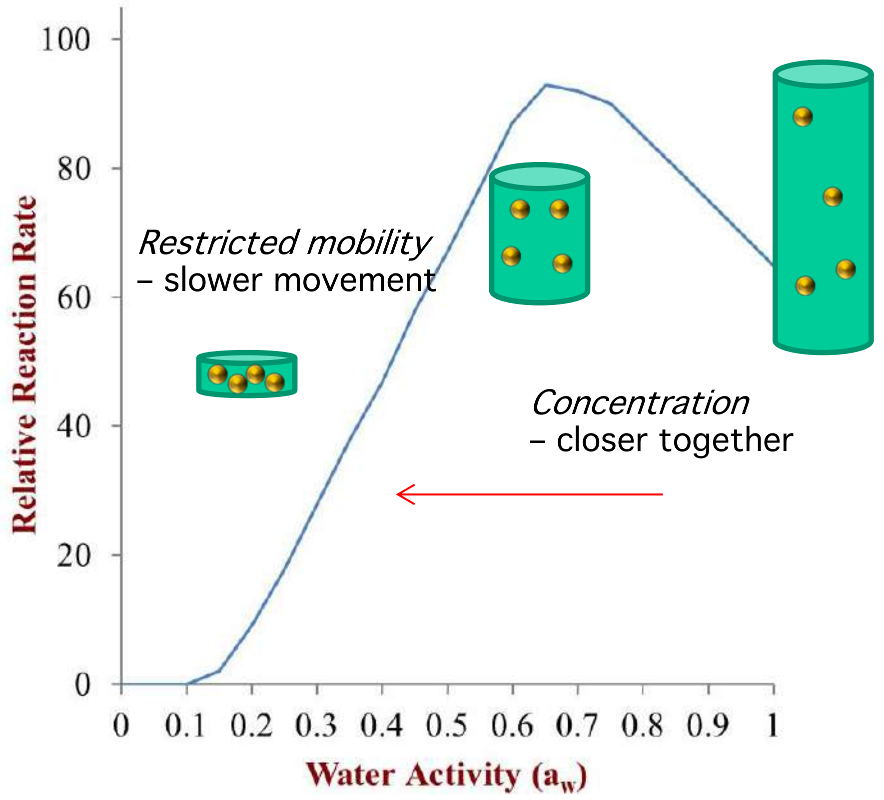
Figure 1. Water activity stability map. (Adapted from Labuza).[8]

Water Activity: Influence on Microbial Growth



Microbial growth requires a certain amount of available water, and only occurs above a critical water activity that depends on species and strain

Water Activity: Influence on Chemical Reaction Rates



The chemical reactivity of water-soluble reactants depends on the water activity:

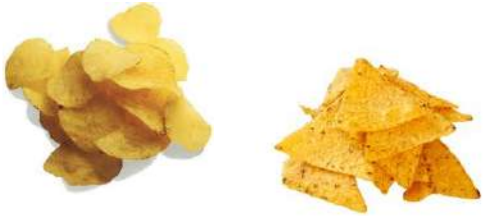
- Concentration – decreases distance between reactants
- High solute concentrations causes restricted molecular diffusion

Water Activity:
Influence on Physical Properties

Candy Floss

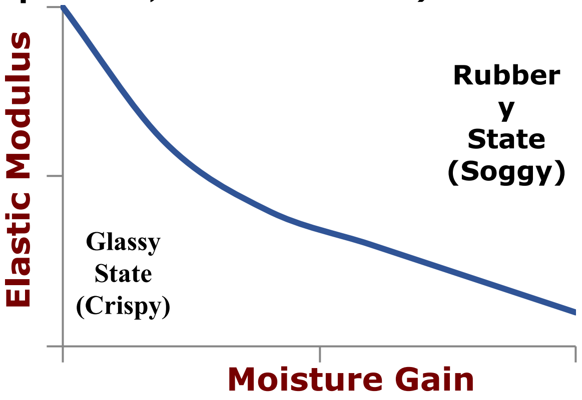
Cookies & Crackers

Cereals



Potato & Tortilla Chips

Water activity plays a major role in determining their physical properties, such as texture (crispiness, crunchiness)



Aw Measuring Guidance

- Calibrate the machine by utilizing a high and low water activity salt solution depending on the target result
- Put an amount of sample into the sample lid and place it inside the chamber
- Once you start the machine, the sample will automatically be calibrated to room temperature and the result should come out in 5 minutes.

Demonstration pH

How to Measure the pH of Liquid and Solid Foods

Equilibrated pH

Athiphunamphai, N, Cooley, H., Padilla-Zakour, O., How to Measure the pH of Liquid and Solid Foods, https://www.youtube.com/watch?v=QMfCYkZPvXg. The Northeast Center for Food Entrepreneurship, Cornell University, Published November 25, 2013.

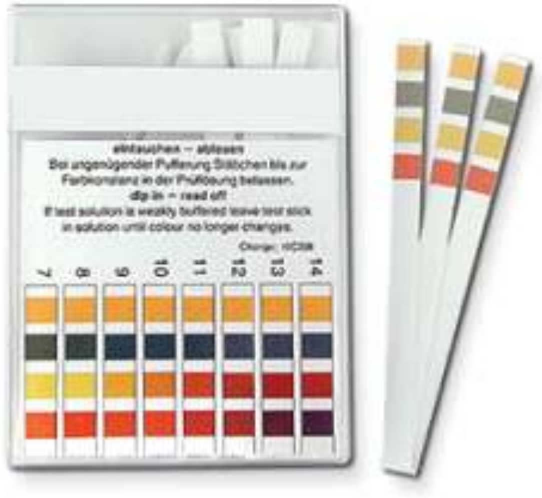
Demonstration Stations

Calibration

Equilibrated pH

Display Portable pH units

pH Strips (Litmus paper)



- Inexpensive
- Disposable
- Portable
- Highly variable!
- Regulations allow colorimetric monitoring for foods with pH levels below 4.0

http://www.modernistpantry.com/assets/images/ph-test-strips.jpg

Food Safety

Controls

pH Measuring Guidance

- Calibrate the probe by utilizing a buffer that has the closest pH to the product
- Rinse the reader with deionized water
- Blot with blotting wipes
- Measure the pH of the solids
- Rinse with deionized water and blot it
- Measure the pH of liquids
- Rinse with deionized water and blot it
- When measuring products with brine it is important to measure the pH of liquids and solids separate. Additionally, it is extremely to measure Equilibrium pH by blending equal parts of the solids and liquids and measuring the pH
- Repeat the procedure 3 times and take the average measurement.

Scheduled Process (pH)

- Required for
  - 21CFR113 – low acid, shelf stable foods
  - 21CFR114 – acidified, shelf stable foods

- Contains information about
  - Sizes allowed to produce
  - Processing method
  - Any relevant safety measures

School of Food and Agriculture 1865 THE UNIVERSITY OF MAINE

December 28, 2017

Ryan Claudino
100 Holdsworth Way
Amherst, MA 01003-9282
INVOICE # 3233

Dear Ryan:

Following are the results of the analyses performed on the samples sent to us for testing:

SAMPLE	pH	WATER ACTIVITY @ 25 C
1) Dill Relish	3.64	0.975
2) Dilly Beans	3.59	0.985

Test Results:
Based on the pH results, you met our recommendations of an overall product pH level of 4.20 or below for water bath processed products. You must follow our processing method changes and critical factors below to ensure the microbiological safety of your products.

Processing Methods:
You *must* follow Good Manufacturing Practices: http://www.fda.gov/Food/GuidanceRegulation/CGMP/default.htm.
You must also become familiar with the new FDA Food Safety Modernization Act changes to foods safety regulations, which will impact most businesses: http://www.fda.gov/Food/GuidanceRegulation/FSMA/. If you are processing food products, you must register your facility with the FDA: https://www.fda.gov/Food/GuidanceRegulation/FoodFacilityRegistration/ucm2006831.htm.

Please make the following changes to your processing methods, which can ensure your product safety:

Test Results:
Based on the pH results, you met our recommendations of an overall product pH level of 4.20 or below for water bath processed products. You must follow our processing method changes and critical factors below to ensure the microbiological safety of your products.

Process Control (Aw)

Critical Limits

- Hot fill: Time & Temperature
  - E.g. hot fill and hold at 185° F @ for 10 min
- Aw : < 0.85

Food Safety Controls - Aw

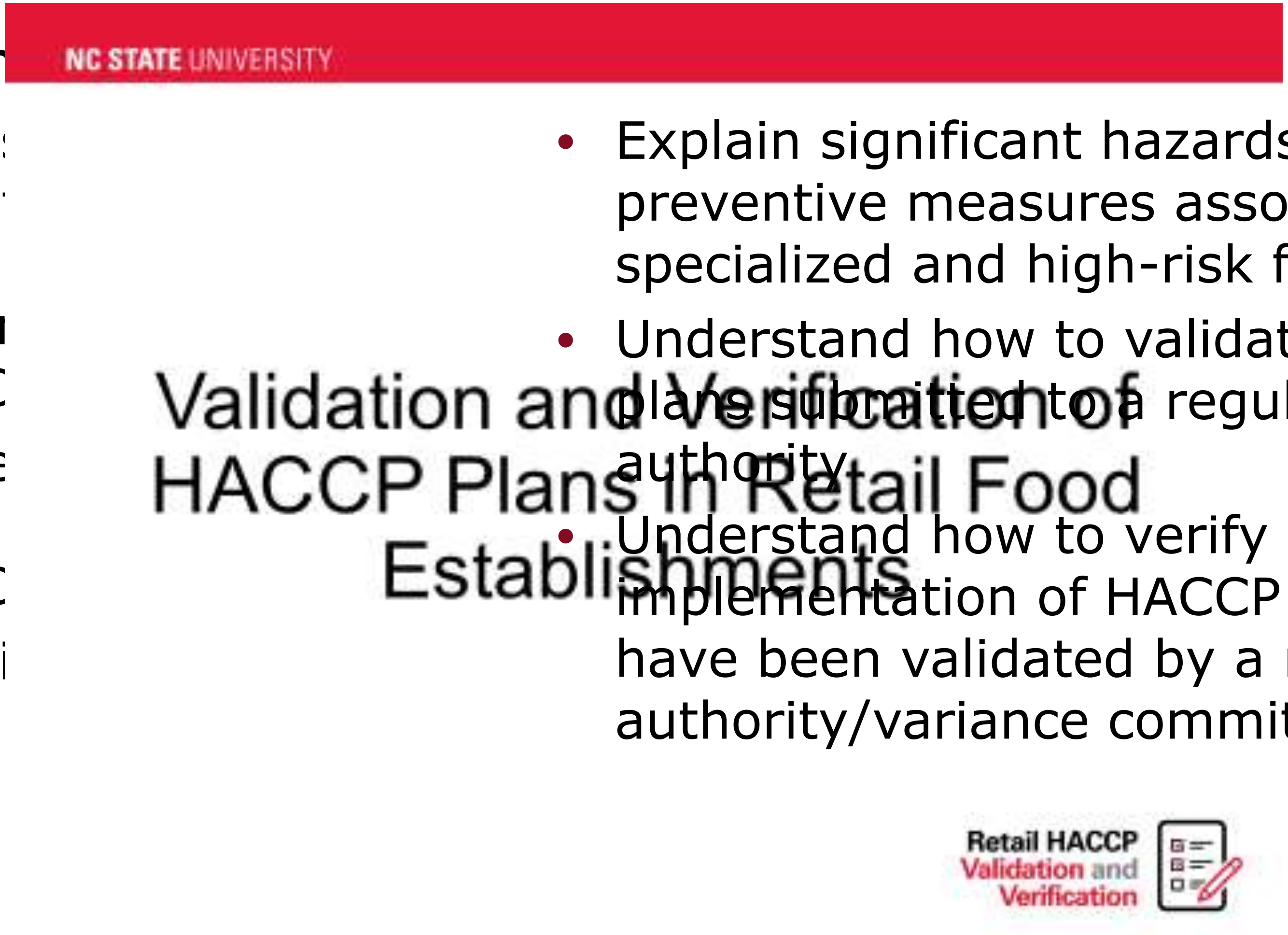
Table A4-1 Limiting conditions for pathogen growth

Organism	Temperature °F (°C)			pH			Water Activity (aw)			Max. % water phase salt
	Minimum	Optimum	Maximum	Minimum	Optimum	Maximum	Minimum	Optimum	Maximum	
Bacillus cereus	39 (4)	86-104 (30-40)	131 (55)	4.3	6.0-7.0	9.3	0.92	-	-	10
Campylobacter	86 (32)	108-109 (42-43)	113 (45)	4.9	6.5-7.5	9.5	>0.987	0.997	-	1.7
Clostridium botulinum • Proteolytic ABF	50 (10)	95-104 (35-40)	-118 (48)	4.6	-	9	0.935	-	-	10
• Non-proteolytic BEF	38 (3.3)	82-86 (28-30)	113 (45)	5.0	-	9	0.970	-	-	5
Clostridium perfringens	50 (10)	109-117 (43-47)	126 (50)	5	7.2	9.0	0.93	0.95-0.96	>0.99	7
Enterohemorrhagic *Escherichia coli* (EHEC)	44 (6.5)	95-104 (35-40)	121 (49.4)	4	6-7	10	0.95	0.995	-	6.5
L. monocytogenes	31 (-0.4)	99 (37)	113 (45)	4.4	7.0	9.4	0.92	-	-	10
Salmonella	41 (5.2)	95-109 (35-43)	115 (46.2)	3.7	7-7.5	9.5	0.94	0.99	>0.99	8
Shigella	43 (6.1)	-	117 (47.1)	4.8	-	9.3	0.96	-	-	5.2
Staph. aureus • growth (anaerobic)	45 (7)	99 (37)	122 (50)	4	6-7	10	0.83 (0.90)	0.98	>0.99	20
• toxin (anaerobic)	50 (10)	104-113 (40-45)	118 (48)	4	7-8	9.8	0.85	0.98	>0.99	10
Streptococcus group A	50 (10)	99 (37)	<113 (<45)	4.8-5.3	7	>9.3	-	-	-	6.5
Vibrio spp.	41(5)	99 (37)	114 (45.3)	4.8	7.6-8.6	11	0.94	0.91-0.99	0.998	10
Yersinia enterocolitica	30 (-1.3)	77-99 (25-37)	108 (42)	4.2	7.2	10	0.945	-	-	7

From FDA 2011. *Fish and Fishery Products Hazards and Controls Guidance.* 4th Edition and International Commission on Microbiological Specifications for Foods. 1996. *Microorganisms in Foods 5: Microbiological Specifications of Food Pathogens.* Blackie Academic and Professional, New York.

NC State – Retail HACCP

- 1-2 day worksh
  - Identify proces procedures tha HACCP plan or safety managei based on HACC
  - Understand pre for food safety based on HACC
  - Identify essenti of a HACCP pla



  - Explain significant hazards and preventive measures associated with specialized and high-risk food processes
  - Understand how to validate written plans submitted to a regulatory authority
  - Understand how to verify the effective implementation of HACCP plans that have been validated by a regulatory authority/variance committee

Summary

pH:

- Concentration of free H+ ions
- Measure of active acidity
- Affects reactions in foods

Aw:

- Measures “available water”
- Scale 0-1
- Influence on Chemical, Biochemical and Microbial Reaction Rates

Resources

- pH
  - Purchasing and Using a pH meter : https://foodsafety.wisc.edu/assets/pdf_Files/What_is_pH.pdf
  - Food Safety: Formulating Dressing, Sauces and Marinades (NCSU Extension)- https://fbns.ncsu.edu/extension_program/documents/acidified_formulating_dressings.pdf
  - The Guide to pH Measurement in Food & Drink: https://2ucloq3z4wn48w1h11mb5302-wpengine.netdna-ssl.com/wp-content/uploads/odb_guide_to_ph_measurement_in_food_v1-0.pdf

Resources

- Aw
  - Understanding the Water Activity of Your Food (VT Extension) - https://www.pubs.ext.vt.edu/content/dam/pubs_ext_vt_edu/FST/FST-59/FST-59NP_PDF.pdf
  - Water Activity (aw) in Foods (FDA): https://www.fda.gov/inspections-compliance-enforcement-and-criminal-investigations/inspection-technical-guides/water-activity-aw-foods

- Additional Resources - http://ag.umass.edu/food-science/resources

Thank you!

Wholesale Processing - FDA Regulations (21 CFR 113 & 114)

- A low-acid canned food is any food (other than alcoholic beverages) with a finished equilibrium pH greater than 4.6

Why?

The environment of pH below 4.6 inhibits the growth of harmful microorganisms and especially, growth of an extremely dangerous microorganism called Clostridium botulinum, which produces a potent toxin that causes the lethal disease botulism.

- The water activity level of 0.85 is used as a point of definition for determining whether a low-acid canned food or an acidified food is covered by the regulations.

Why?

Heat application of Aw above 0.85 is necessary to destroy vegetative cells of microorganisms of public health significance and spoilage microorganisms which can grow in a reduced Aw environment.