Water

Water

- Major Component of most foods
- Water has several effects on food stability, palatability, and overall quality
- Chemical reactions, enzymatic changes, and microbial growth may occur readily in foods with high water contents

Water Content of Foods

Food	Water Content (%)
Meat	
Pork, raw, composite of lean cuts	53-60
Beef, raw, retail cuts	50-70
Chicken, raw meat without skin	74
Fish, muscle proteins	65-81
Fruits	
Berries, cherries, pears	80-85
Apples, peaches, oranges, grapefruit	85-90
Rhubarb, strawberries, tomatoes	90-95
Vegetables	
Peas (green)	74-80
Beets, broccoli, carrots, potatoes	80-90
Asparagus, beans, cabbage, cauliflower, lettuce	90-95

Properties

- Solvent
  - Dielectric properties
- Mobility
  - Dissolve and mobilize substrate
- Reactant
  - Protons, hydroxyl, hydronium and water itself

General concepts

- Bound water: exists in the vicinity of solutes and other non-aqueous constituents, exhibit reduced mobility and properties differing significantly from "bulk water" in the same system and does not freeze at -40°C
  - Constitutional water: integral part of non-aqueous constituents
    - < 0.03% of total water
    - Interstitial regions of proteins; chemical hydrates
  - Vicinal water: Strongly interacts with specific hydrophilic sites by water-ion and water-dipole associations -
    - 0.5 ± 0.4 % of total water
    - Optimum overall stability at the Monolayer value
  - Multilayer water: occupies remaining first-layer sites and forms several layers around hydrophilic groups by w-w and w-s hydrogen bonds -
    - 3 ± 2 % of total water
    - Rates of reactions increase

General concepts

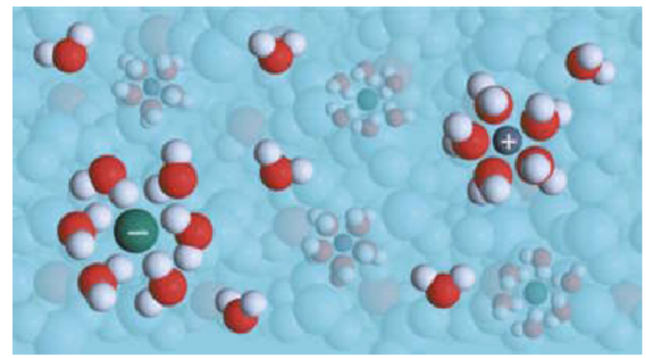
- "Water binding" and "hydration"
  - Tendency of water to associate with hydrophilic substances
- Water holding capacity
  - Ability of a matrix of molecules to entrap large amounts of water in a manner such that exudation is prevented

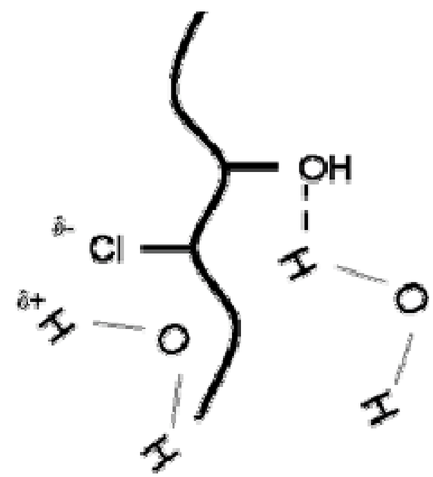
Forces acting in water

- Electrostatic – interactions between charges
- Hydrogen bonds – hydrogen shared between two electronegative atoms
- van der Waals – weak induced dipole interactions between any two atoms in close contact
- Hydrophobic interactions

Water Solute Interactions

- Water – Ionic groups: some of the most tightly bound water in food
  - Strong electrostatic attraction between the permanent charge of the ion and the dipole of water
- Water – Polar but uncharged solute
  - Weaker
  - Hydrogen bonding of dipole-dipole interactions
  - Allow polar components to dissolve



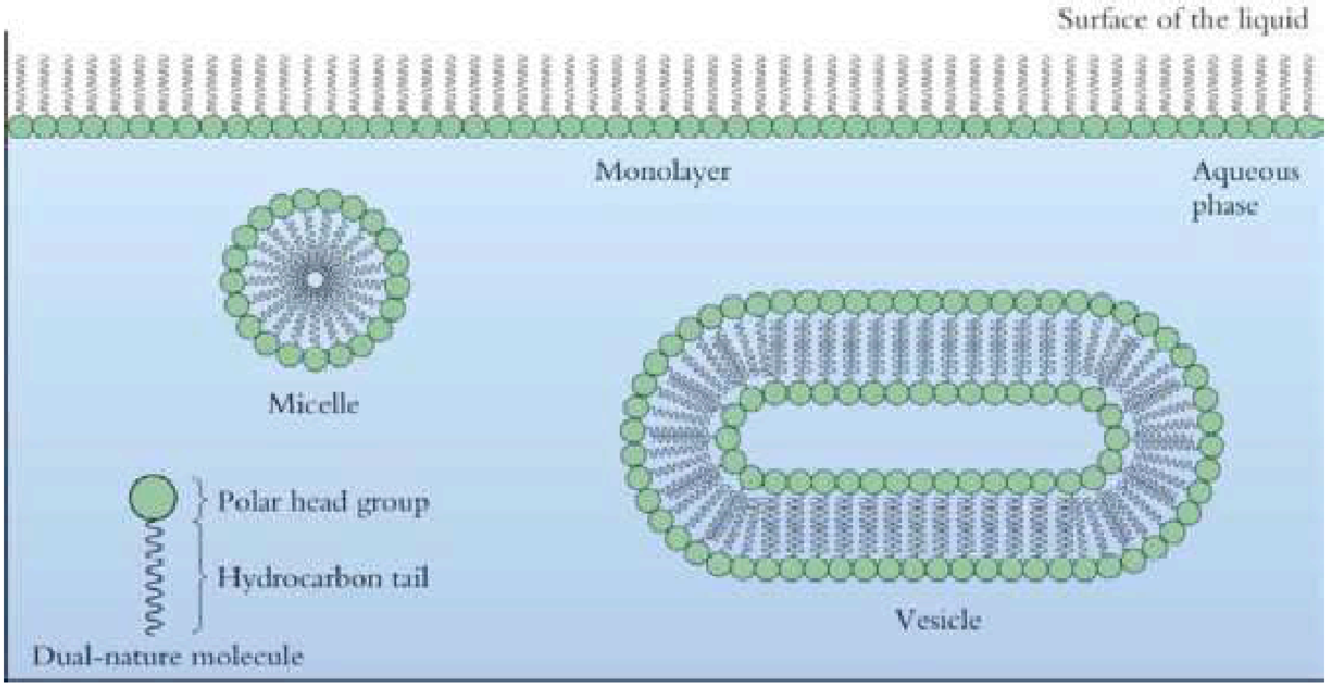


Water Solute Interactions

- Water – non-polar molecules
  - Thermodynamically unfavorable _ decrease in entropy
  - Formation of rigid ice-like clathrate at interface
  - Dipole – induced dipole
  - Hydrophobic interactions _ association of apolar and non-polar groups in aqueous environments

Water Solute Interactions

- Amphiphilic molecules



Water Activity

- Relationship between water and perishability
- Various foods with the same water content differ significantly in perishability
  - Water content alone is not reliable
- Importance of water associations with non-aqueous constituents to support deteriorative activities
- Rates of deteriorative changes and microbial growth at normal food storage conditions often depend on water content and a_w.

Water Activity

- Water activity is defined as the ratio of the vapor pressure of water in a material (p) to the vapor pressure of pure water (p_o) at the same temperature.
- The water activity (a_w) represents the ratio of the water vapor pressure of the food to the water vapor pressure of pure water under the same conditions
- $a_w = p/p_o$ = ERH (%) / 100

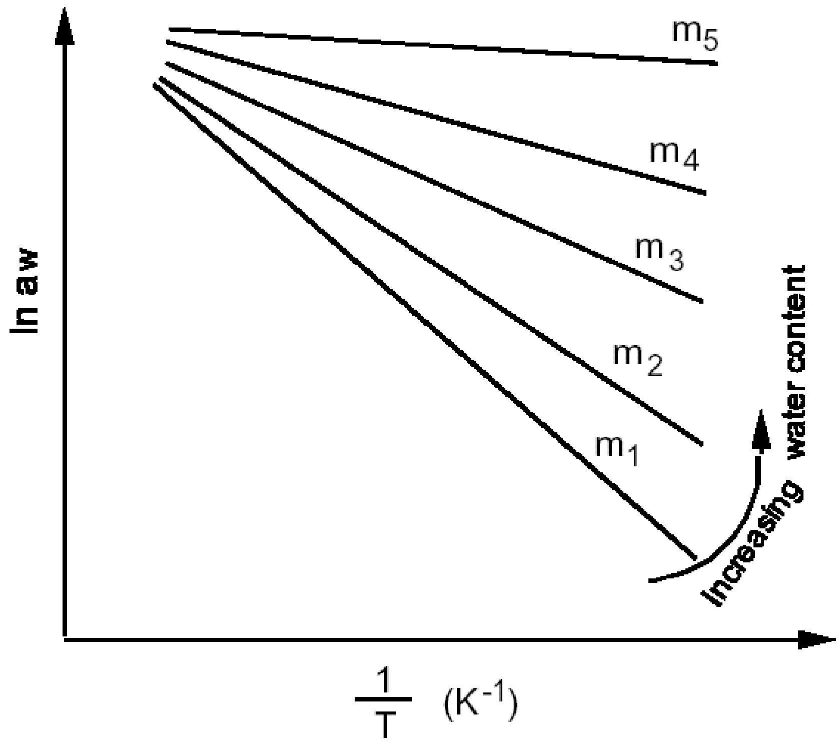
Temperature Dependence

Clausius-Clapeyron equation

$$\ln\left(\frac{P}{P}\right) = \frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T}\right)$$

Where: P is the vapor pressure
P° is a vapor pressure at a known temperature T°,
H is the heat of sorption (KJ/mol)
R is the ideal gas law constant, 8.2×10^{-3}
T is the temperature (in kelvins).

Clausius-Clapeyron relationship between a_w and Temperature



- The degree of °T dependance is a function of moisture content
- Water activity increases with increasing temperature

Sorption Isotherms

- Plots interrelating water content of a food with its water activity at constant temperature
- The curve is established using a microclimate method
  - Gas-tight jars where RH is fixed with saturated salt solutions
- Usefulness
  - Concentration and Dehydration processes
    - ease or difficulty of water removal
  - Assessing stability (shelf-life) of the food
  - Prevent caking and sticking of food powders
  - Determine moisture barrier properties of packaging materials
  - Formulation of food mixtures

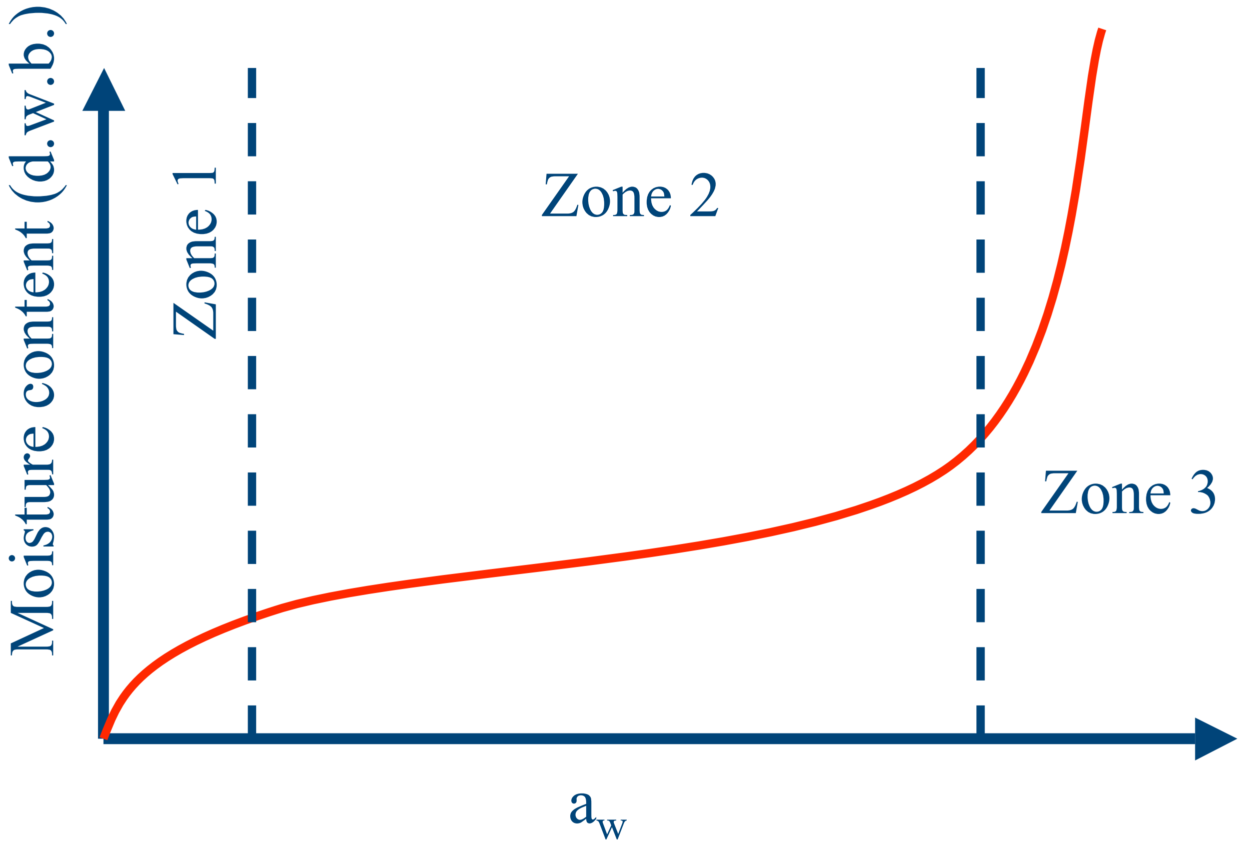
Equilibration process

- need pure salt solutions
- problem of volatile contamination
- large surface area to food
- must be slurry - need excess salt
- mixed type samples
- takes time 7 to 21 days
- vacuum fluxing
- toxicity of salts - eg lithium , nitrite, iodide, bromide

Saturated Salt Solutions

Saturated salt solution	a_w
$LiClH_2O$	0.12
CH_3COOK	0.23
$MgCl_26H_2O$	0.33
K_2CO_3	0.44
$Mg(NO_3)_26H_2O$	0.52
$NaCl$	0.75
$(NH_4)_2SO_4$	0.79
$CdCl_2$	0.82
Li_2SO_4	0.85
K_2CrO_4	0.88
KNO_3	0.94
K_2SO_4	0.97
Na_2HPO_4	0.98

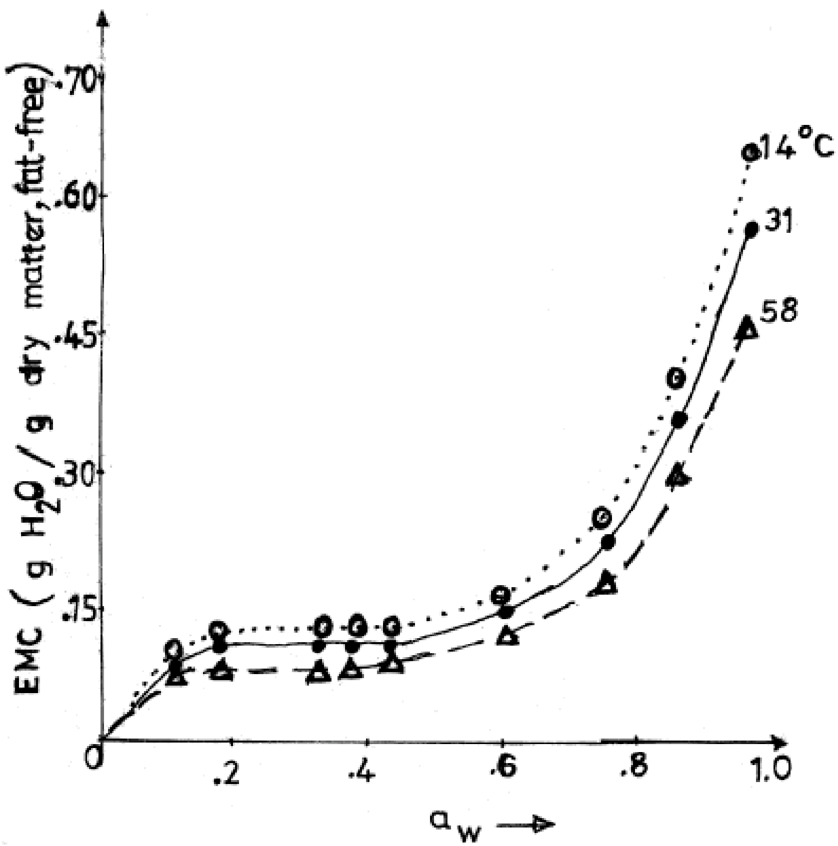
Zones of moisture



Water zones

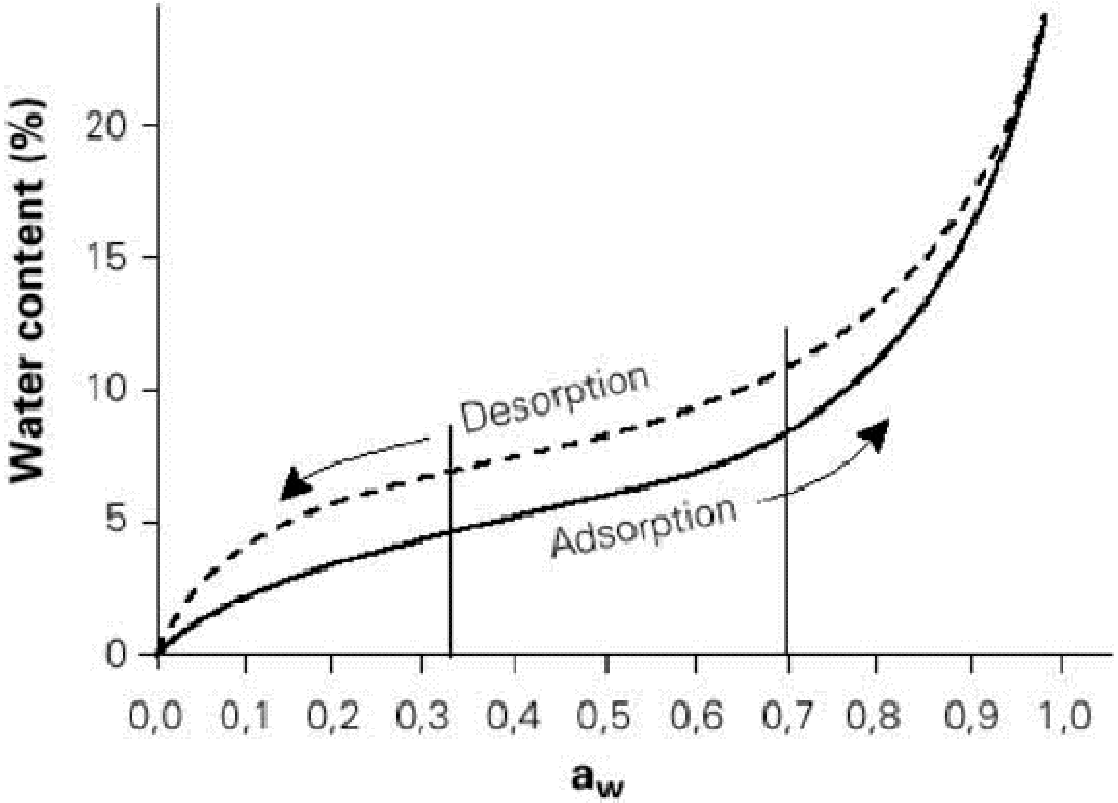
- Zone I
  - strongly absorbed
  - Not able to serve as solvent
  - Behaves as part of the solid
- Monolayer moisture
  - Boundary of zones I and II
  - Water that is strongly bound to the highly polar groups of dry matter
  - Constitutional and vicinal
- Zone II
  - Occupies the remaining layers around hydrophilllic groups
  - Multilayer water: associates with neighboring molecules by w-w w-s hydrogen bonding
- Zone III (Bulk-phase water)
  - Least strongly bound and most mobile (molecularly)
  - Freezable
  - Available as solvent
  - Allow chemical reactions & microbial growth
  - > 95% of total water

Moisture adsorption isotherms at different storage temperatures



At any given EMC, a_w increases with increasing temperature

Sorption Isotherms



Water Sorption Hysteresis

- Water sorption isotherms for desorption and adsorption differ
  - HYSTERESIS
- In desorption, water content at the same ERH is higher than in adsorption
- The magnitude of hysteresis depends on:
  - nature of food, physical changes during water removal, temperature, rate of desorption, degree of water removed during desorption.
- At any given a_w, the water content will be greater during desorption

λ ↑ Rates of lipid oxidation or loss of Vit. C during desorption compared to adsorption

λ To stop microbial growth, a product's a_w must be significantly lower if prepared by desorption than by adsorption

Controlling a_w in foods

- equilibration with atmosphere of known relative humidity
- water removal (e.g., dehydration)
- addition of solutes (humectants)
  - sugars
  - NaCl
  - polyhydric alcohols (glycerol, sorbitol)
  - propylene glycol
- loss or gain of moisture in packaged foods

Limitations on a_w lowering

- Solubility
- Organoleptic
- Crystallization in storage
- Reactivity
- Maillard reaction
- Toxicity
  - recent FDA action on propylene glycol

Calculating the Monolayer

- Water molecules are bonded to the product by strong H-bonds
- Higher Stability
- Brunauer, Emmett and Teller (BET) method

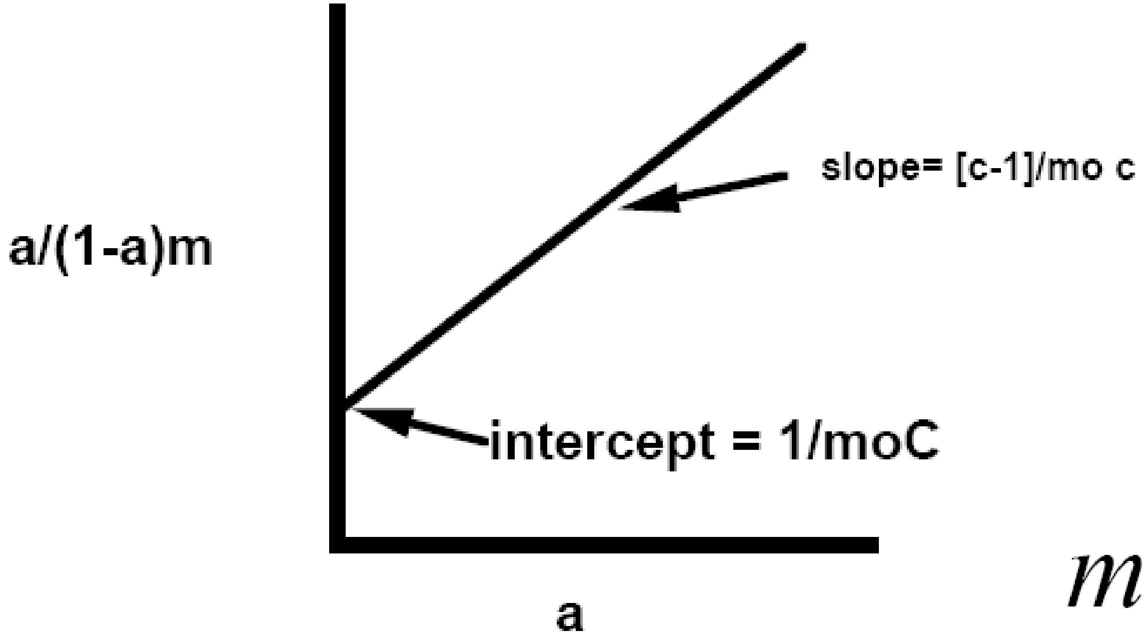
$$\frac{a_w}{(1-a_w)m} = \frac{1}{m_o c} + \left[\frac{c-1}{m_o c}\right] a_w$$

m = water content (dry basis)
m_o = water content at monolayer
c = constant related to adsorption heat

$$c = e^{\frac{Q_s}{RT}}$$

Q_s = heat capacity of the monolayer

BET Monolayer Determination



$$m_0 = \frac{1}{I + S}$$

Limitation - only use up to 0.55 maximum

GAB isotherm equation

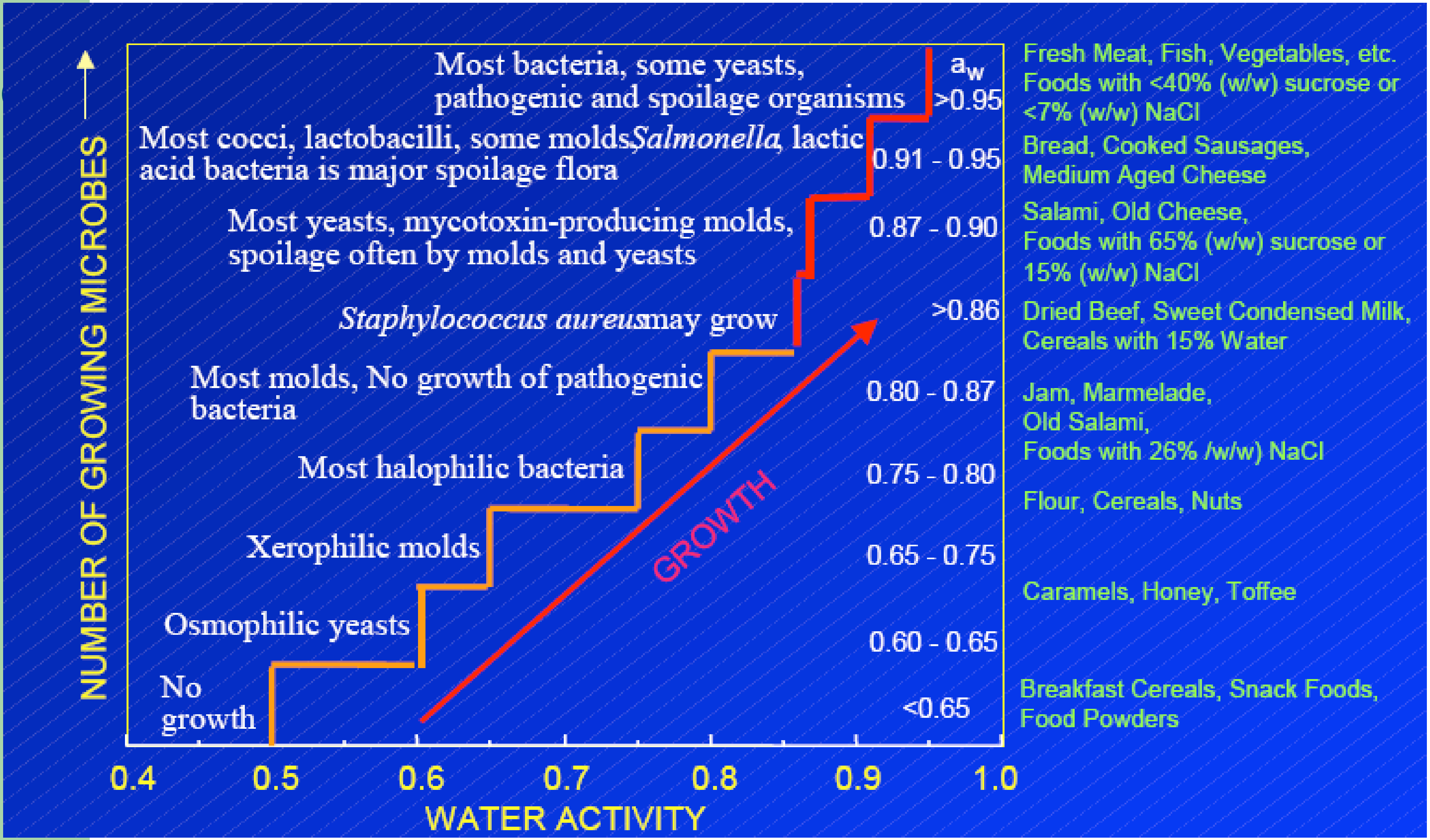
- improved BET accounts for multilayer adsorption

$$m = \frac{m_0 k_b c a}{[1 - k_b a][1 - k_b a + c k_b a]}$$

polynomial solution - stepwise regression

$$\frac{a}{m} = \frac{k_b}{m_o}\left[\frac{1}{c} - 1\right]a^2 + \frac{1}{m_0}\left[1 - \frac{2}{c}\right]a + \frac{1}{m_0 k_b c}$$

a_w and Growth of Microorganisms



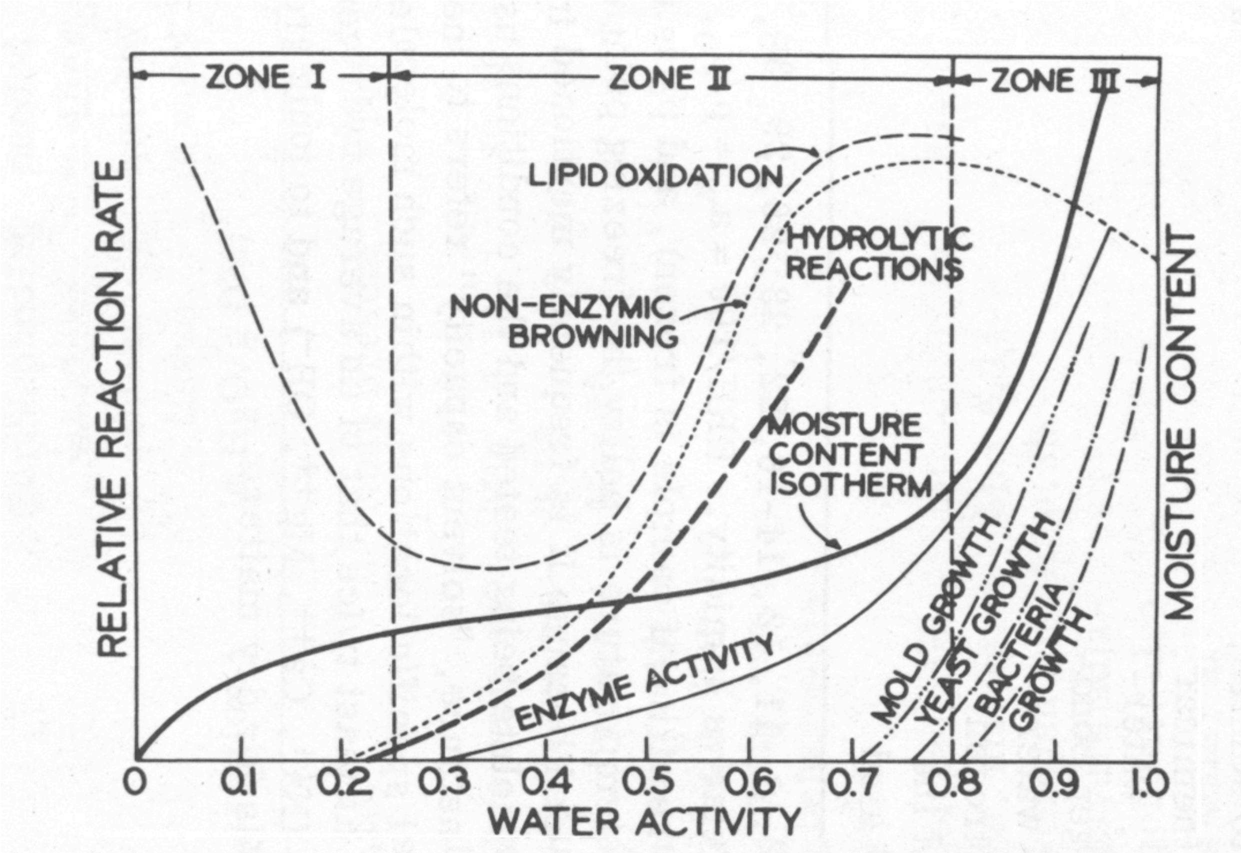
Minimum a_w for some microorganisms

Bacteria	
Staphylococcus aureus	0.86
halophilic bacteria (*Halobacterium* spp.)	0.75
Molds	
Aspergillus flavus	0.78
Chrysosporium fastidium	0.69
Xeromyces bisporus	0.61
Yeasts	
Debaryomyces hansenii	0.83
Torulopsis spp.	0.70
Zygosaccharomyces bailii	0.80
Zygosaccharomyces rouxii	0.62

Predicting Food Spoilage

- The a_w of a solution may dramatically affect the ability of heat to kill a bacterium at a given temperature.
  - a population of *Salmonella typhimurium* is reduced tenfold in 0.18 minutes at 60°C if the a_w of the suspending medium is 0.995.
  - If the a_w is lowered to 0.94, 4.3 min are required at 60°C to cause the same tenfold reduction.
- The regulations (21 CFR 113.3(e) (1) (ii)) state that commercial sterility can be achieved by the control of water activity and the application of heat.
  - The risk of food poisoning must be considered in low acid foods (pH > 4.5) with a water activity greater than 0.85 a_w.

Influence of a Product's Water Activity on Types of Reactions



From Principles of Food Science, Part I,Food Chemistry, by Owen R.Fennema, 1976

Water Content Determination

Moisture Measurement

- **Air Oven**
  - Options:
    - 16 hr @ 100° C
    - 8-10 hr @ 110° C
    - 2-4 hr @ 120° C
  - (precision ~ + 0.25 % moisture)
- Vacuum Oven
  - Drying under reduced pressure (25-100 mm Hg) allows a more complete removal of water and volatiles without decomposition within 3-6 hr drying time.

Moisture Measurement

- Microwave Oven
  - Rapid
  - Microwave energy penetrates deeply into food products and can reduce process time by 90%
  - standardize the drying procedure and ensure that the microwave energy is applied evenly across the sample

Practical Considerations

- The rate and extent of moisture removal depends on the size and shape of the sample, and surface area.
- Clumping and surface crust formation.
- Elevation of boiling point, slower rate of moisture loss
- Water type: interaction with the other components
- Decomposition of other food components: Sugars
- Volatilization of other food components
- Temperature and power level variations

Moisture Analysis - Chemical

Karl Fischer titrations are based on the reaction of elemental iodine with water, in the presence of sulfur dioxide

The Karl Fischer reaction

$I_2 + SO_2 + 2H_2O \text{--->} 2HI + H_2SO_4$

Moisture Analysis - Spectroscopic

- NMR
  - Hydrogen atoms
  - Distinguish between free and bound water
- NIR
  - Absorption of water at different λs (1950, 1450 and 977 nm)
  - Non-destructive
  - Rapid

Water Activity Measurements

Chilled-mirror Dew-point Temperature method

- Temperature at which saturation of water is observed and the the exact point at which condensation first appears
- Measurement is based on temperature determination
  - calibration is not necessary, but measuring a standard salt solution checks proper functioning of the instrument

Capacitance Hygrometer

- Sample placed in a tight measuring chamber at controlled temperature
- use a sensor made from a hygroscopic polymer and associated circuitry that gives a signal relative to the ERH
- the sensor must be calibrated with known salt standards
- A_w range of 0.15 – 0.85