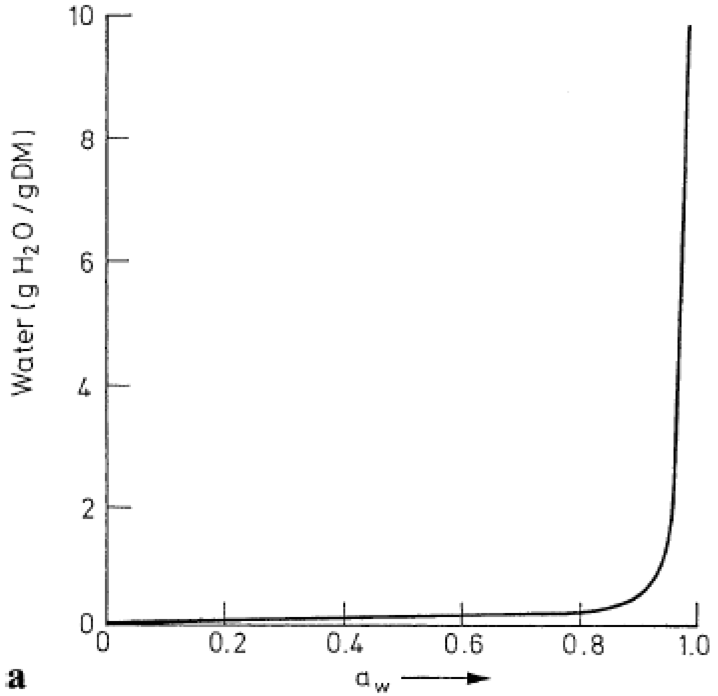
FDE 303
FOOD CHEMISTRY
WEEK-3

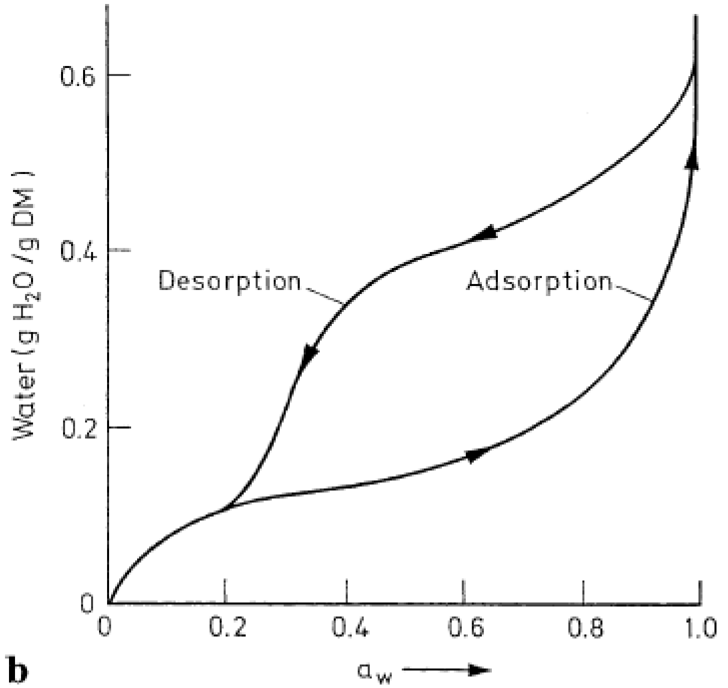
Water activity, Water sorption isoterms

Prof. Dr. Kezban Candoğan

(candogan@eng.ankara.edu.tr)

Moisture sorption isotherms





a-- Food with high moisture content
b-- Food with low moisture content (DM: Dry matter)

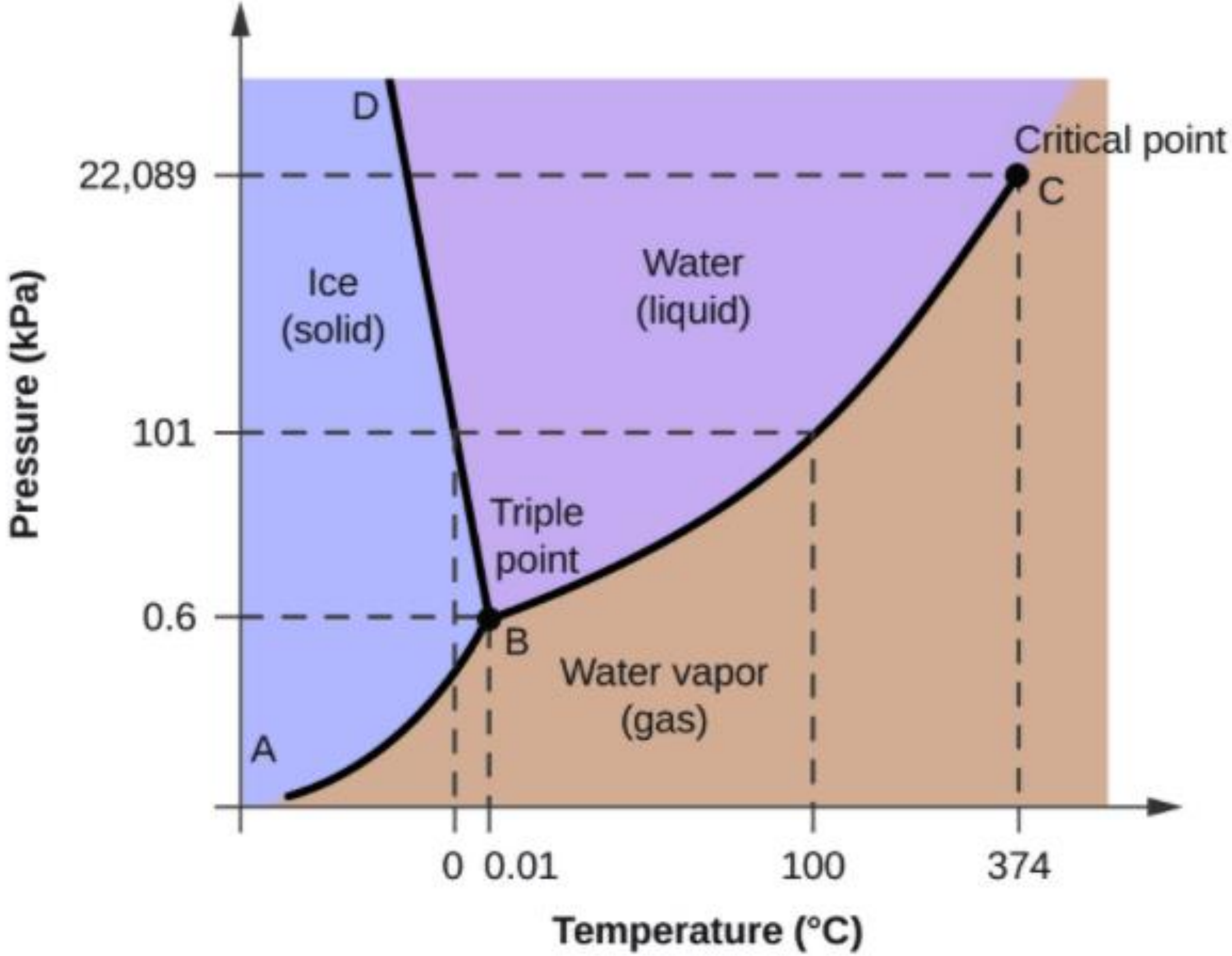
- ✓ At a low water content (<50%), even minor changes lead to major changes in water activity.
- ✓ For that reason, the sorption isotherm of a food with lower water content is shown with an expanded ordinate in «b», as compared with «a».
- ✓ Figure b: desorption isotherm, indicating the course of a drying process. The position of the hysteresis loop changes when adsorption and desorption are repeated with the same sample

Water Activity as an Indicator

- ✓ aw has limited use as an indicator for the storage life of foods with a low water content
  - Because aw indicates a state that applies only to ideal, i.e. very dilute solutions that are at a thermodynamic equilibrium.
- ✓ Foods with a low water content are non-ideal systems whose metastable (fresh) state should be preserved for as long as possible.
- ✓ During storage, such foods do not change thermodynamically, but according to kinetic principles.

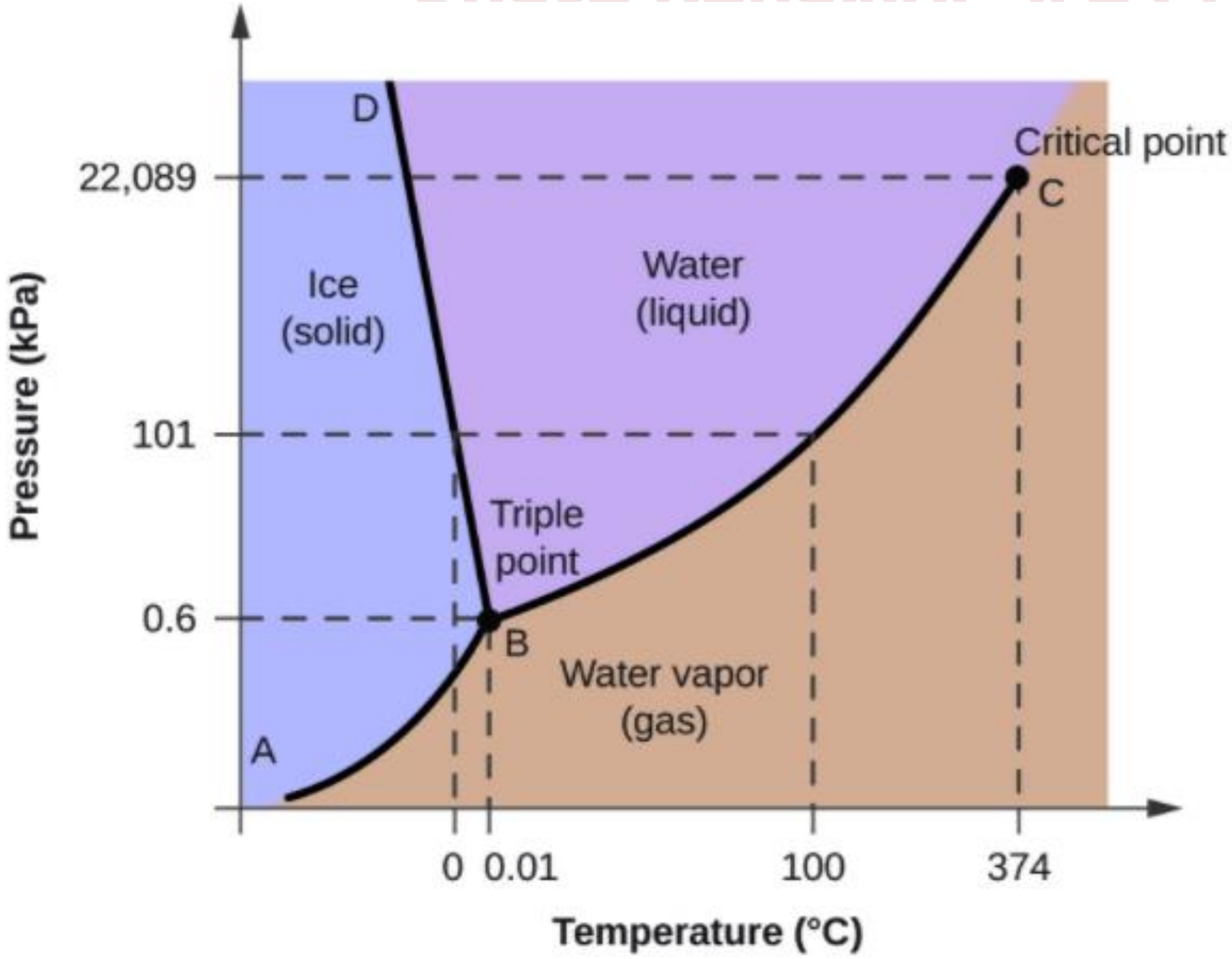
Phase Diagram

- ✓ A phase diagram describes the equilibrium behavior of water



- ➢ Three states of water:
  - –Solid (ice): low Entropy, strong interactions
  - –Liquid: medium Entropy, medium interactions
  - –Gas: high Entropy, weak interactions
- ➢ Temperature and pressure affect structural organizations and interactions.

Phase Behavior: Ice Crystallization



- **Importance of ice formation:**
  - **Preservation**
    - *Microbial, Chemical, Physical*
  - **Quality**
    - *Flavor, Texture, Appearance*

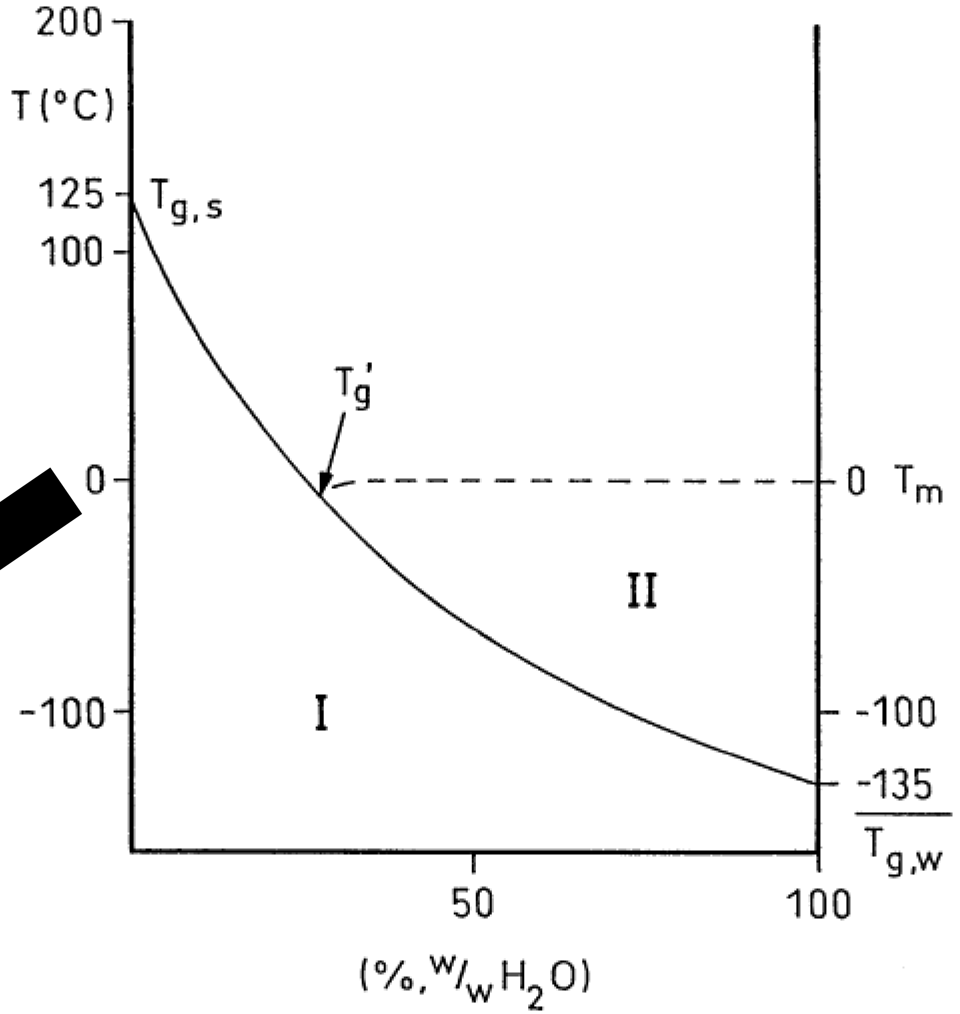
- **Liquid water-to-solid ice transition**
  - Why does it happen?
  - What factors affect it?

State Diagram

- The physical state of metastable foods is based on their composition, on temperature and on storage time.

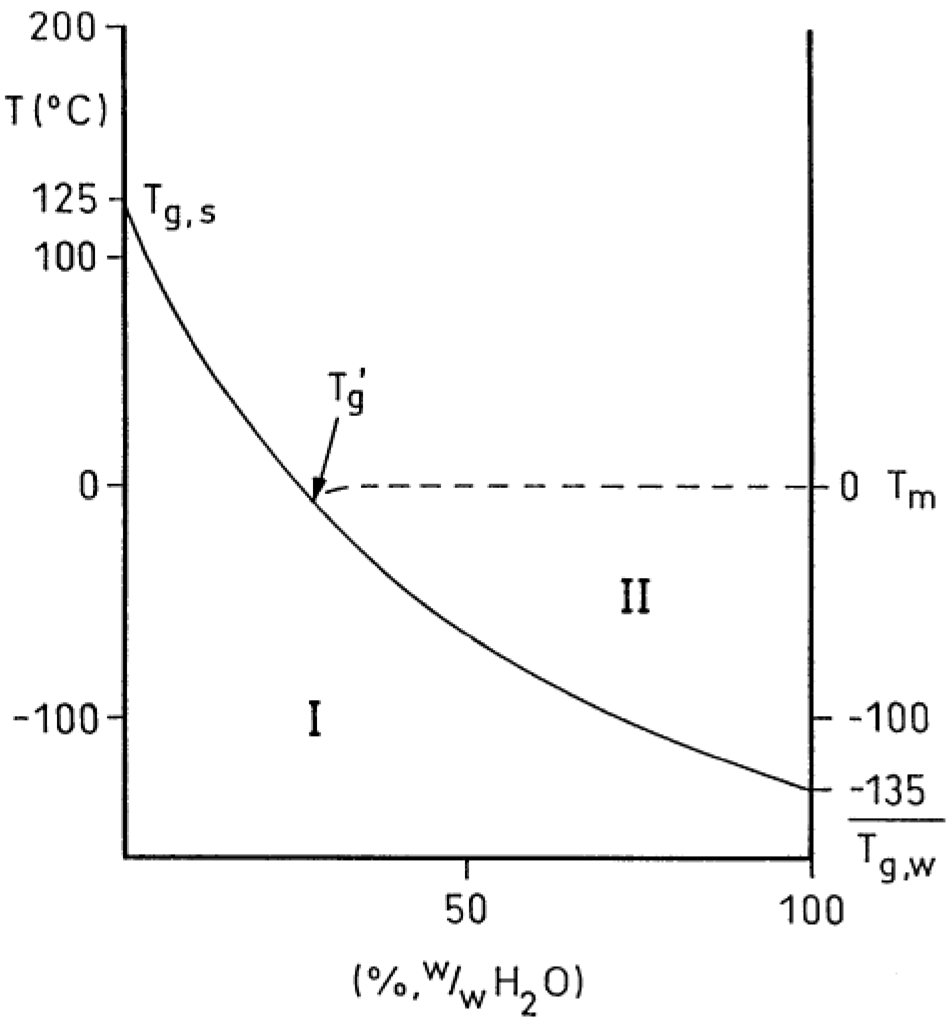
- For example, depending on the temperature, the phases could be ***glassy, rubbery or highly viscous***.

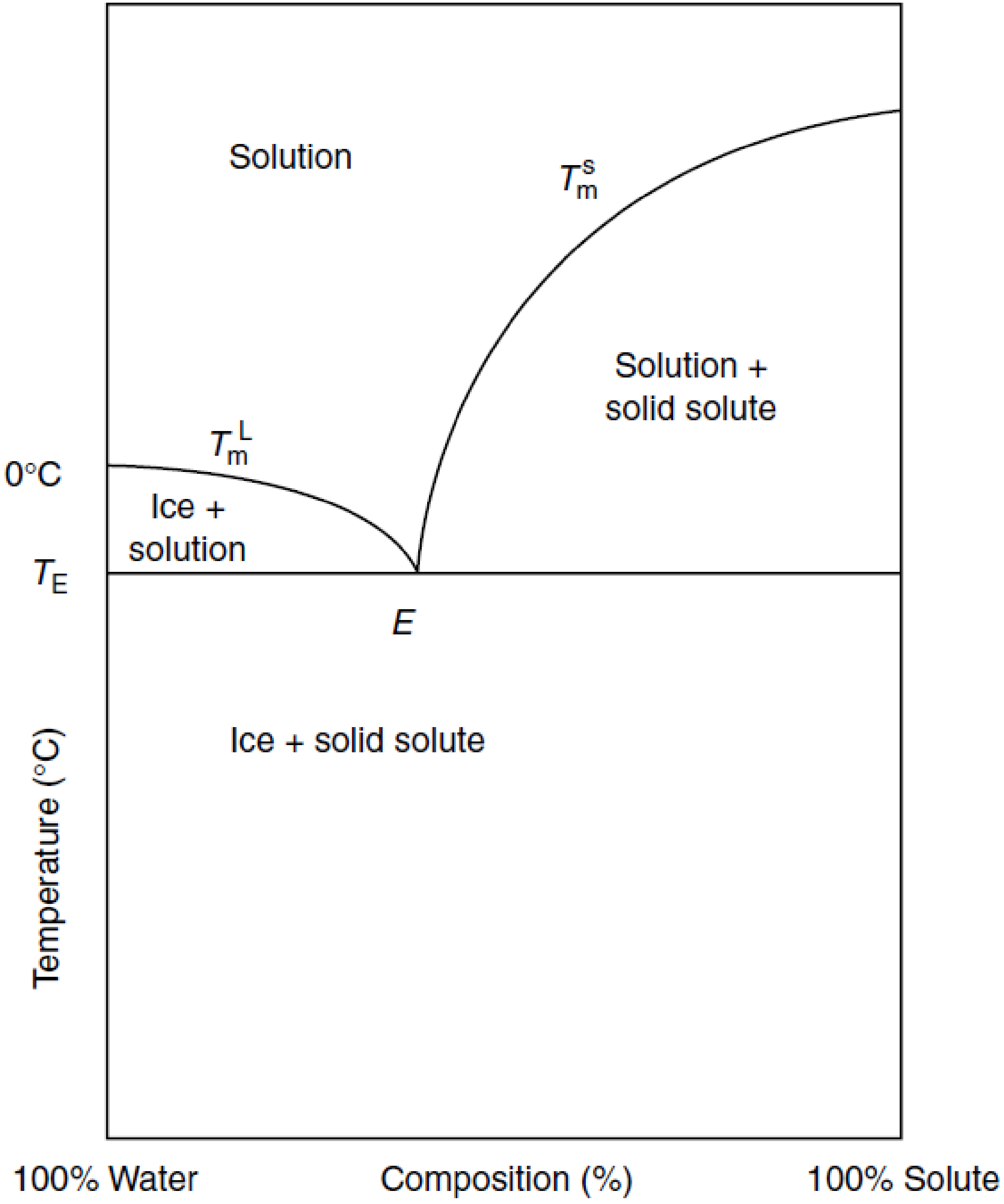
State diagram, showing the approximate T_g temperatures as a function of mass fraction, for a gelatinized starch-water system. States: I = glassy; II = rubbery; Tg,s and Tg,w = phase transition temperatures of dehydrated starch and water; Tm = melting point (ice)



State Diagram

- The kinetics of phase transitions can be measured by means of differential scanning calorimetry (DSC)
  - producing a thermogram that shows temperature Tg as the characteristic value for the transition from glassy to rubbery (plastic).
- Foods become plastic when their hydrophilic components are hydrated.
- Thus the water content affects the temperature Tg, for example in the case of gelatinized starch.



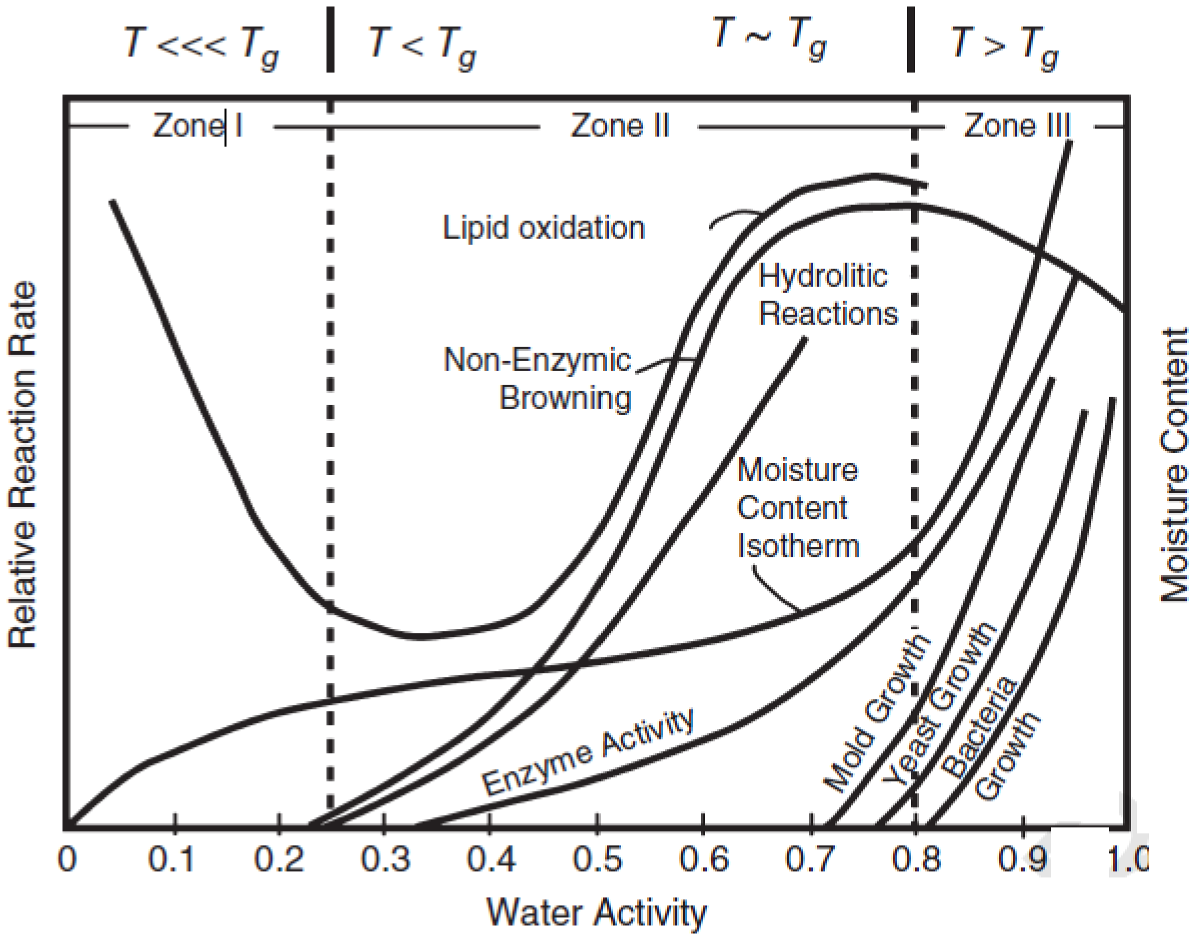


- ✓ Schematic binary phase diagram for a simple aqueous system
- ✓ It shows how the freezing point of a binary aqueous solution changes with concentration

How to Interpret the Three Sorption Zones

- The figure is divided into three zones that are separated by indistinct boundaries.

- ***Region I:*** ranges from 0 to 0.25 *aw*
- ***Region II:*** from 0.25 to 0.80 *aw*
- ***Region III:*** from 0.80 to 1.00 *aw*

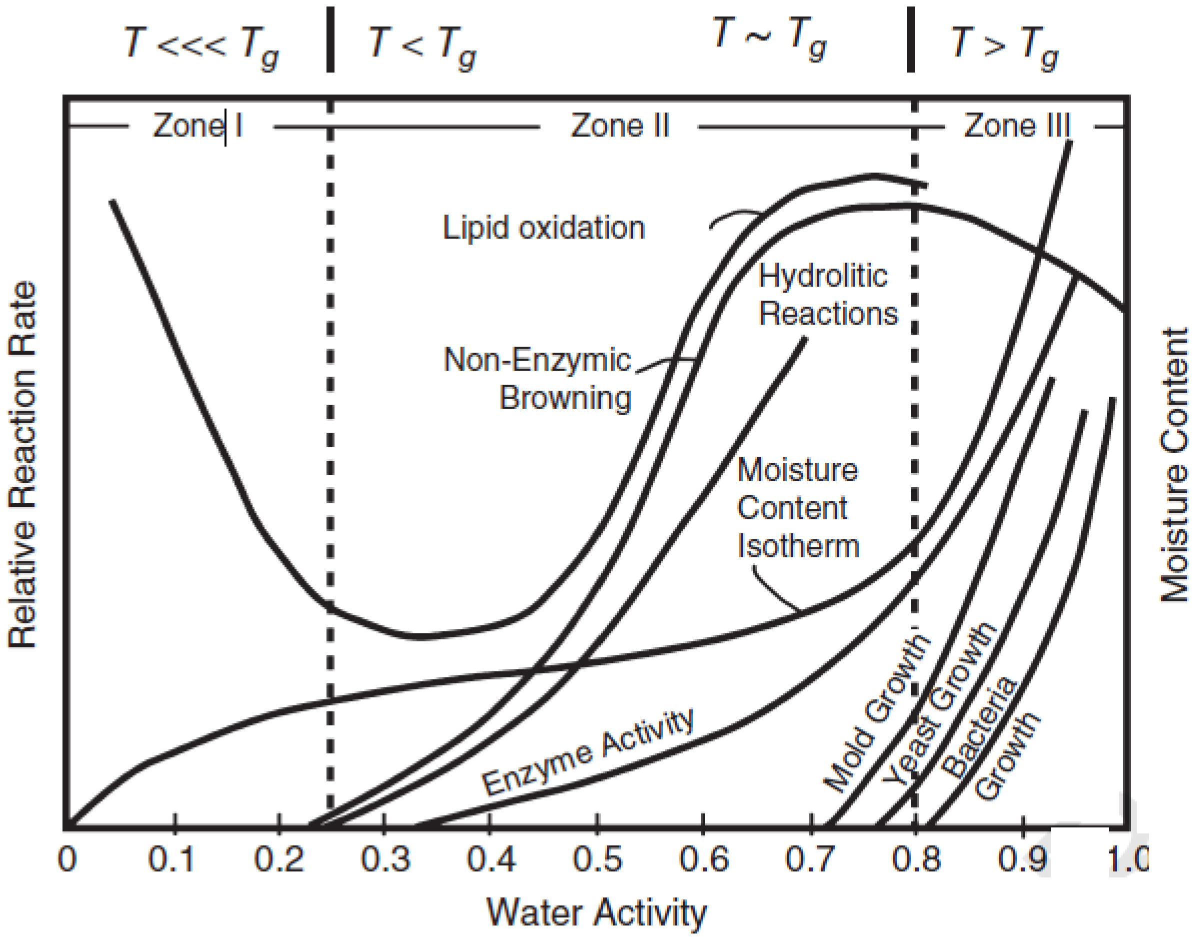


Relationship between water content and water activity - three zones of activity.

How to Interpret the Three Sorption Zones

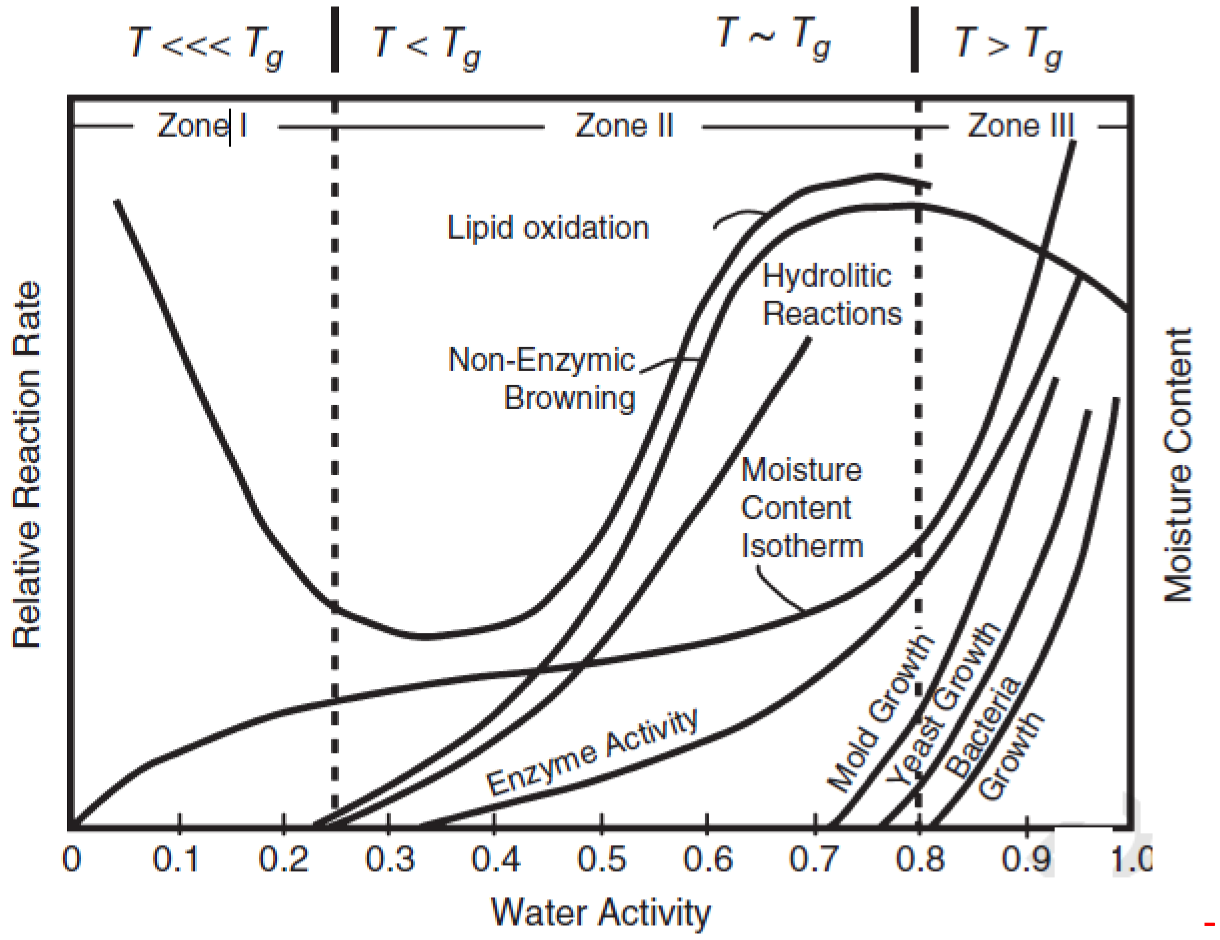
Water in Zone I:

- the most strongly adsorbed and the most immobile
- associates with the most polar, most accessible sites by means of strong water-ion or water-dipole bands
- has no solvent capacity, no plasticizing ability, is unfreezable down to a temperature of -40°C and exhibits an enthalpy of vaporization greater than that of pure water
- The boundary between Zones I and II represents the monolayer moisture value



How to Interpret the Three Sorption Zones

- Water is present in sufficient amount to cover, in a monolayer, all of the accessible polar sites on the dry food matrix.
- This water activity and the associated water content usually provides optimum stability for the food,
- If additional water is added to the sample, it occupies Zone II.

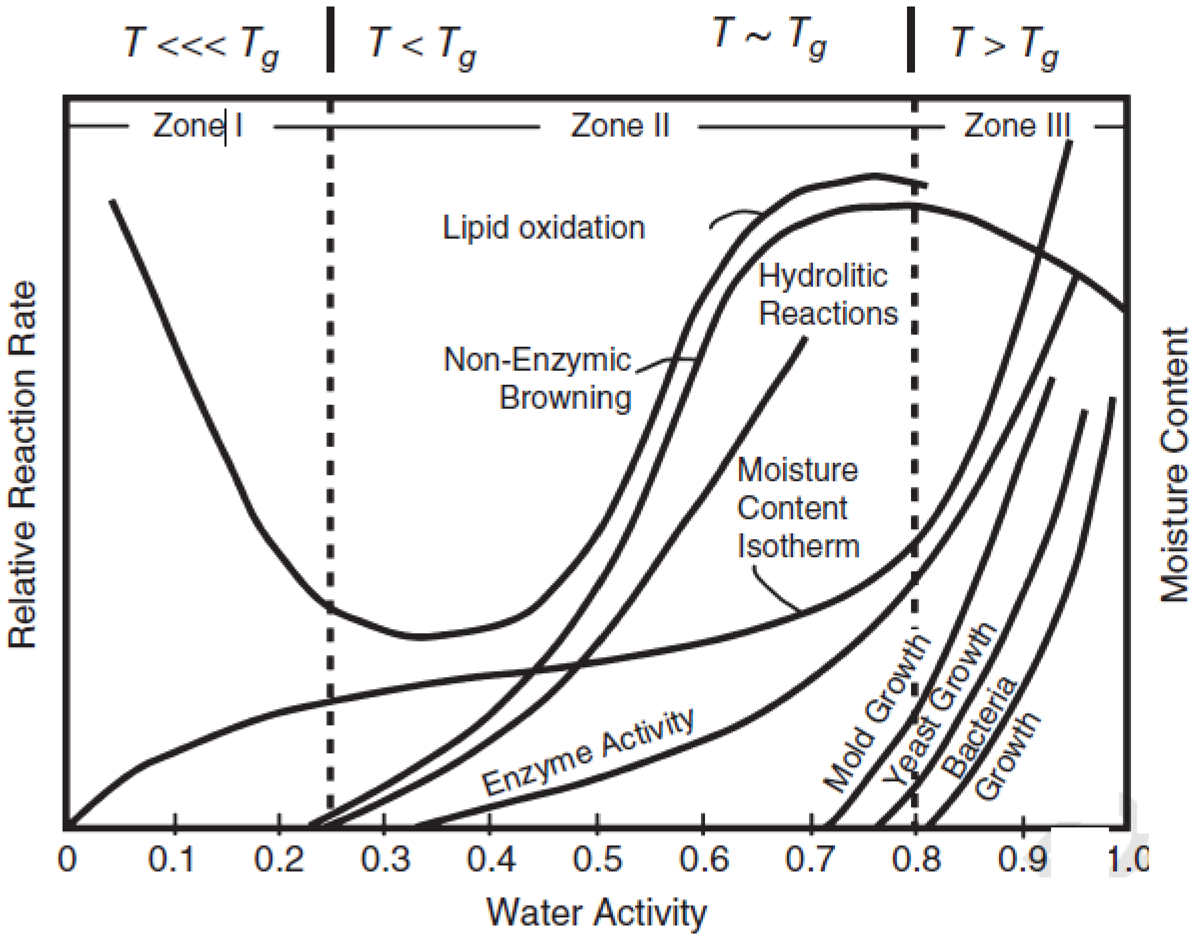


three zones of activity.

How to Interpret the Three Sorption Zones

Water in Zone II :

- Occupies the remaining accessible first-layer sites and also forms multilayers.
- Water-solute or water-water hydrogen binding are the primary means of intermolecular association.
- Zone II water exhibits a slightly elevated enthalpy of varporization compared to pure water, is largely unfreezable down to -40^{o}C

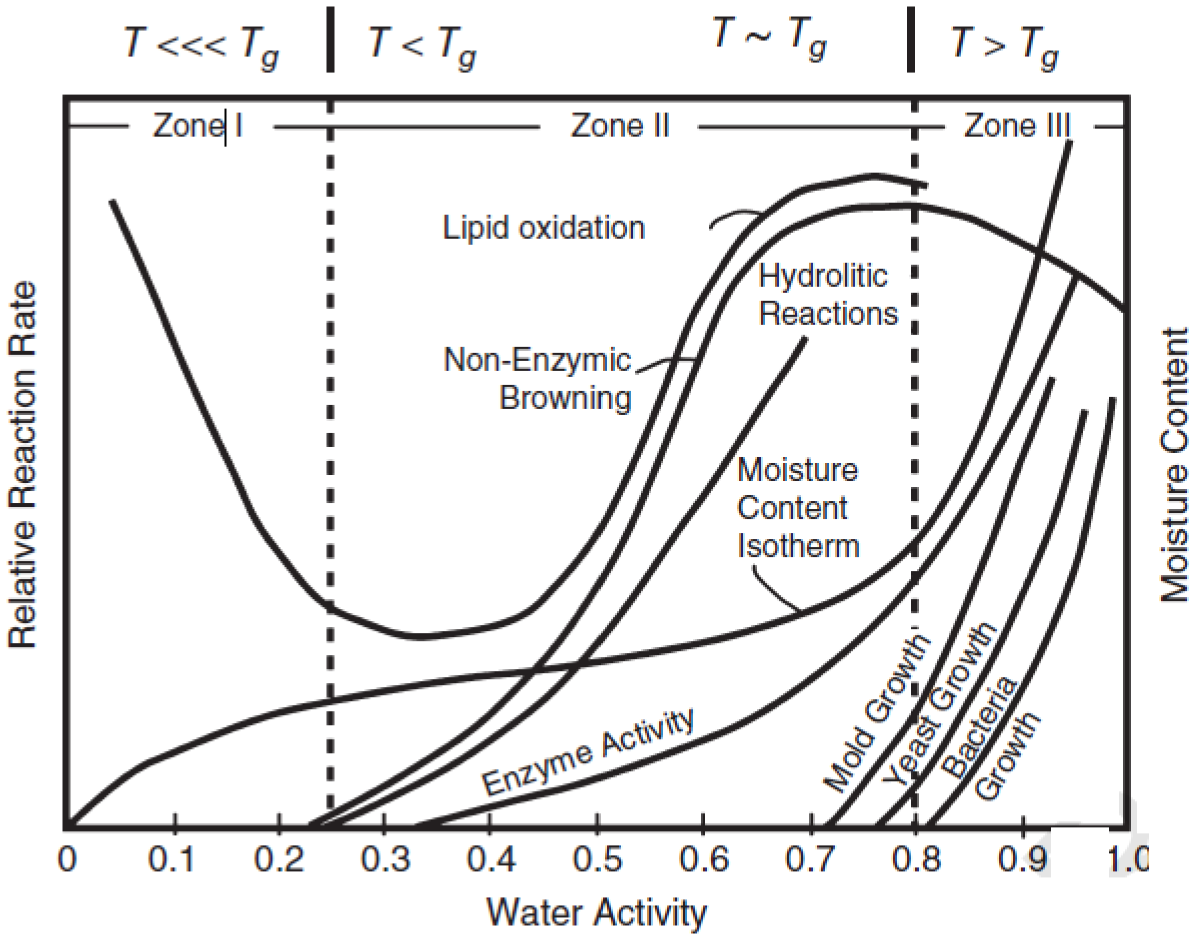


Relationship between water content and water activity - three zones of activity.

How to Interpret the Three Sorption Zones

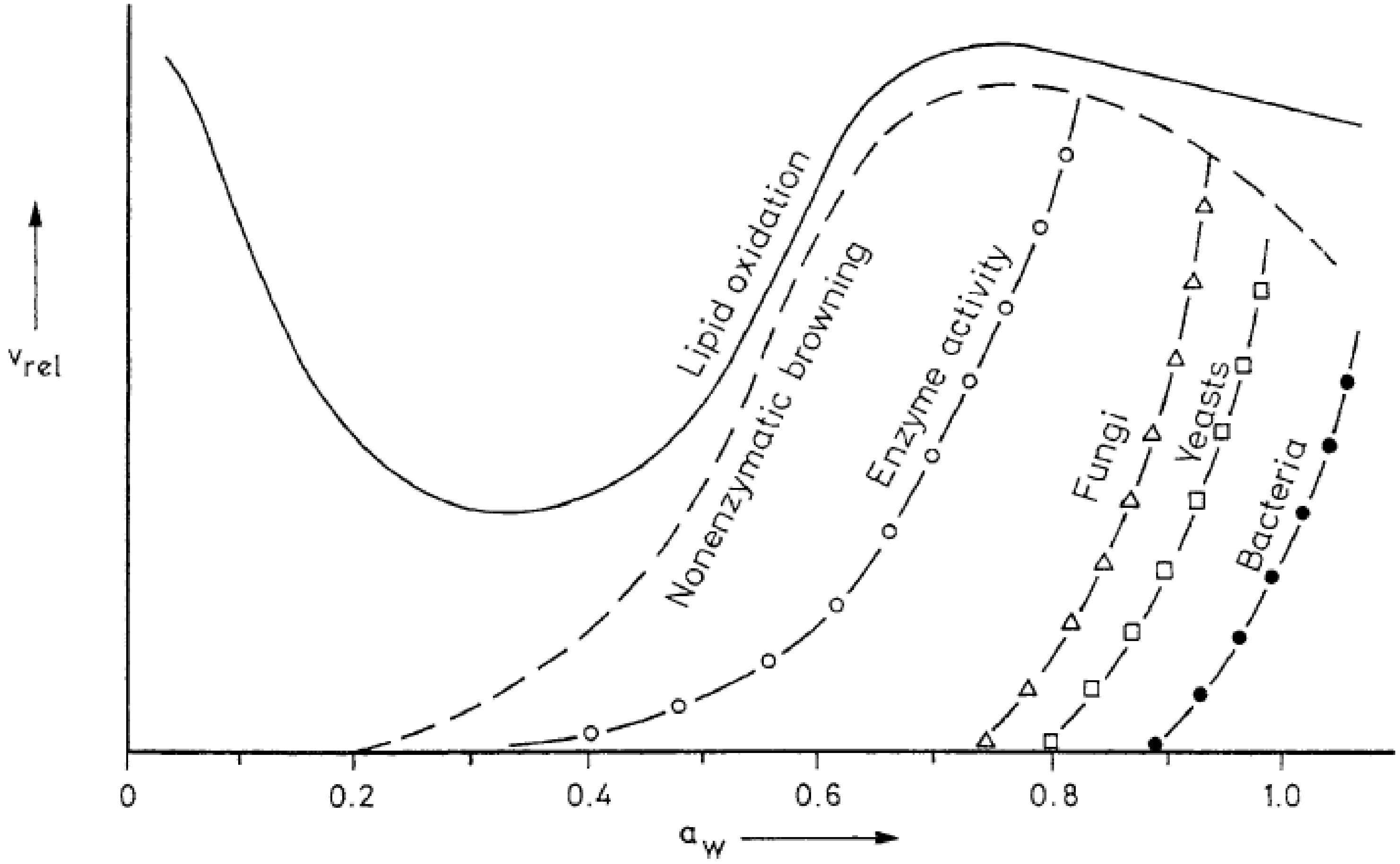
Zone III water:

- This water is the least strongly bound and most mobile of the three kinds of water.
- It is freezable, easily removable, available as a solvent and readily supports chemical reactions and growth of microorganisms.
- Sometimes referred to as bulk-phase water.
- In a high-moisture sample, Zone III water will constitute about 95% of the total water.



Relationship between water content and water activity - three zones of activity.

Food shelf life (storage stability) as a function of water activity

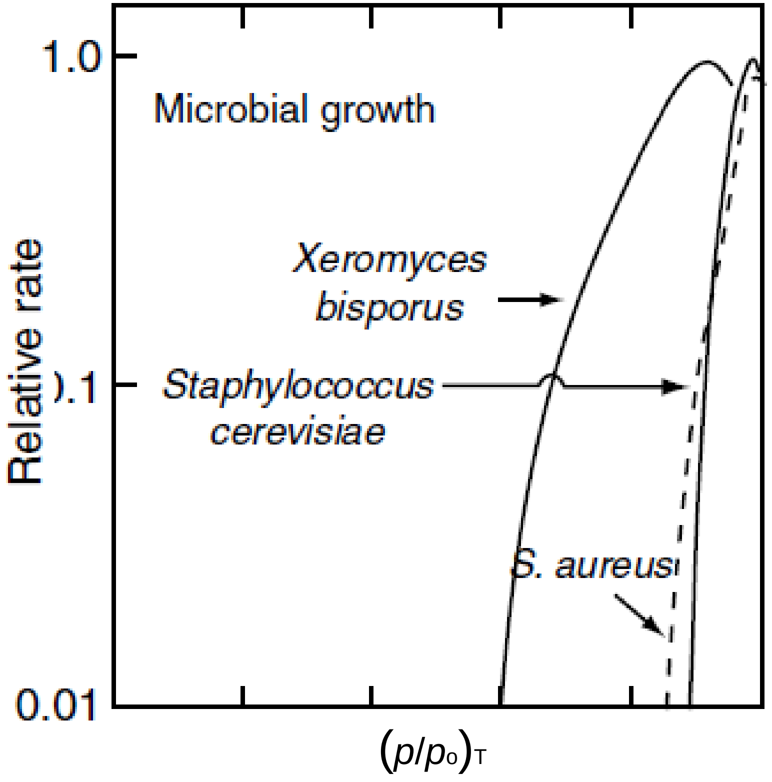


✓ Decreased a_w;

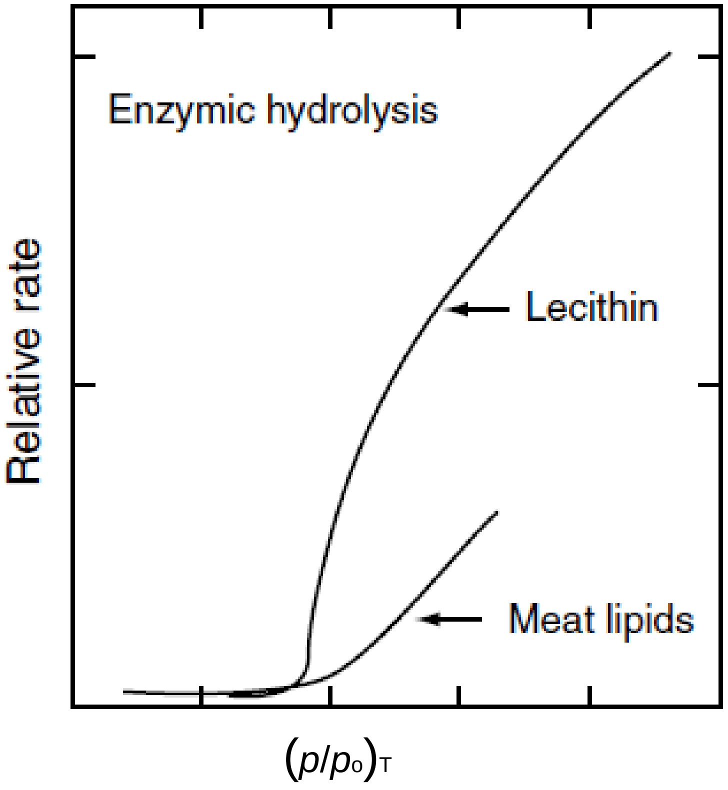
- retards the growth of microorganisms
- slows enzyme catalyzed reactions (particularly involving hydrolases)
- retards non-enzymatic browning
- in contrast, the rate of lipid autoxidation increases in dried food systems

- Foods with a_w values between 0.6 and 0.9 are known as “intermediate moisture foods”.
- These foods are largely protected against microbial spoilage.

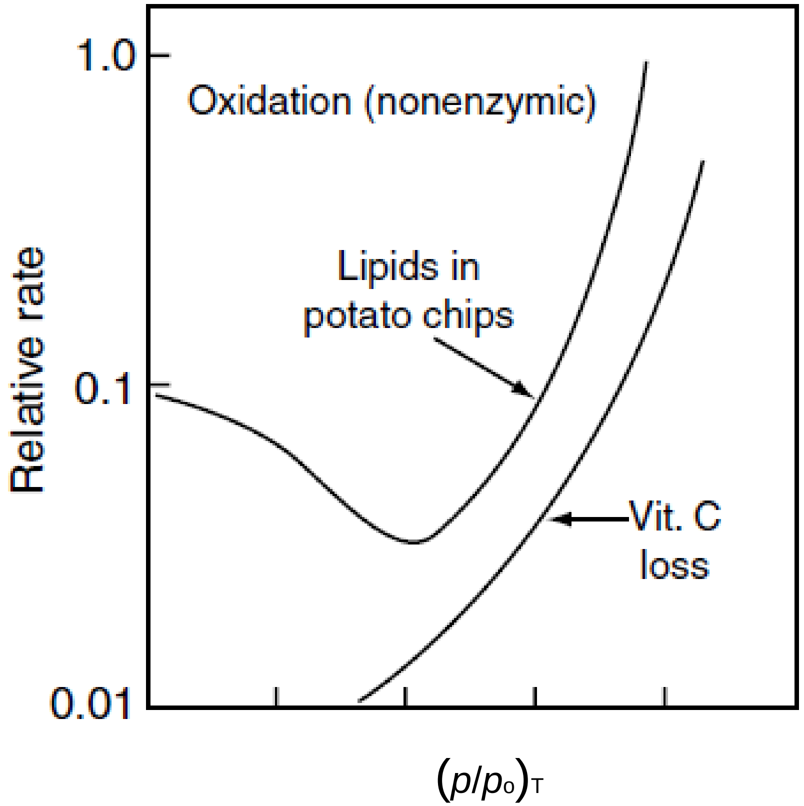
Relationships among relative water vapor pressure, food stability, and sorption isotherms



Microbial growth vs. (*p/po)*T

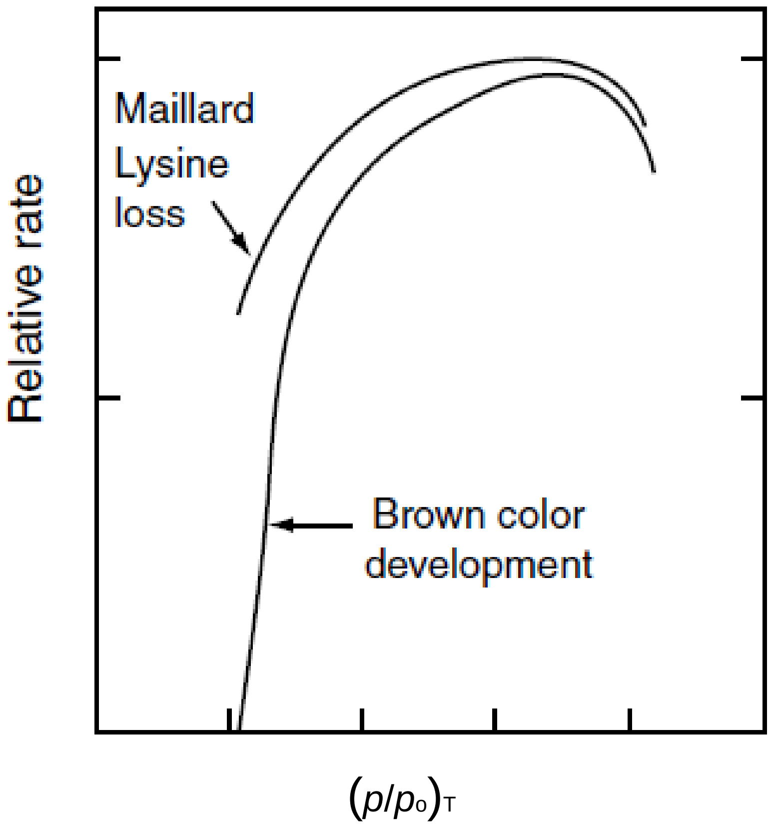


Enzymic hydrolysis vs. (*p/po)*T

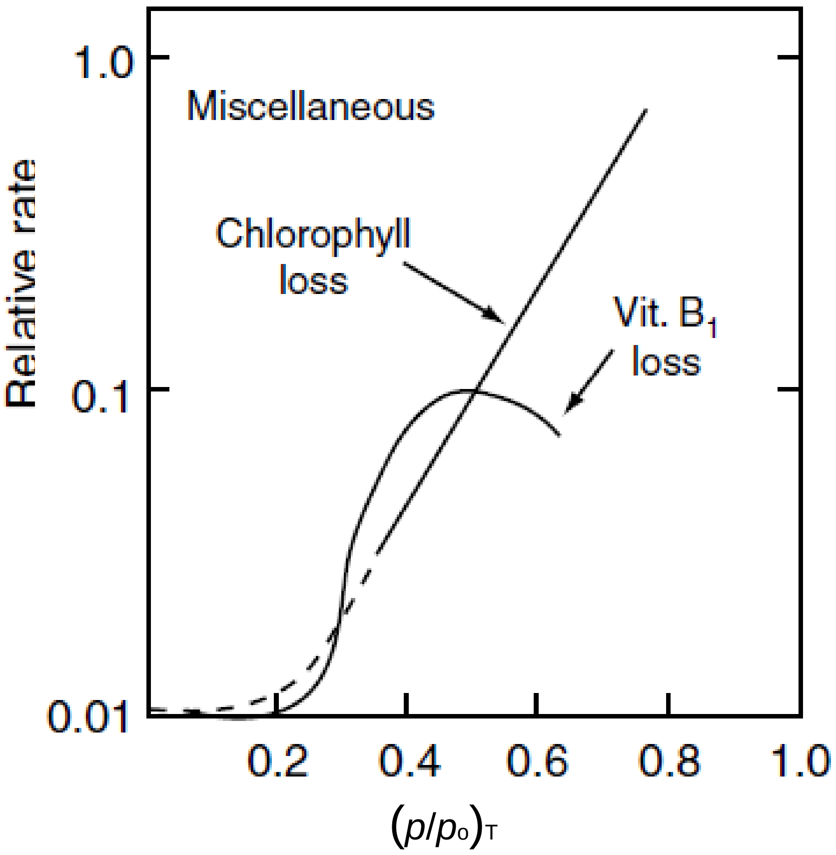


Oxidation (nonenzymic) vs. (*p/po)*T

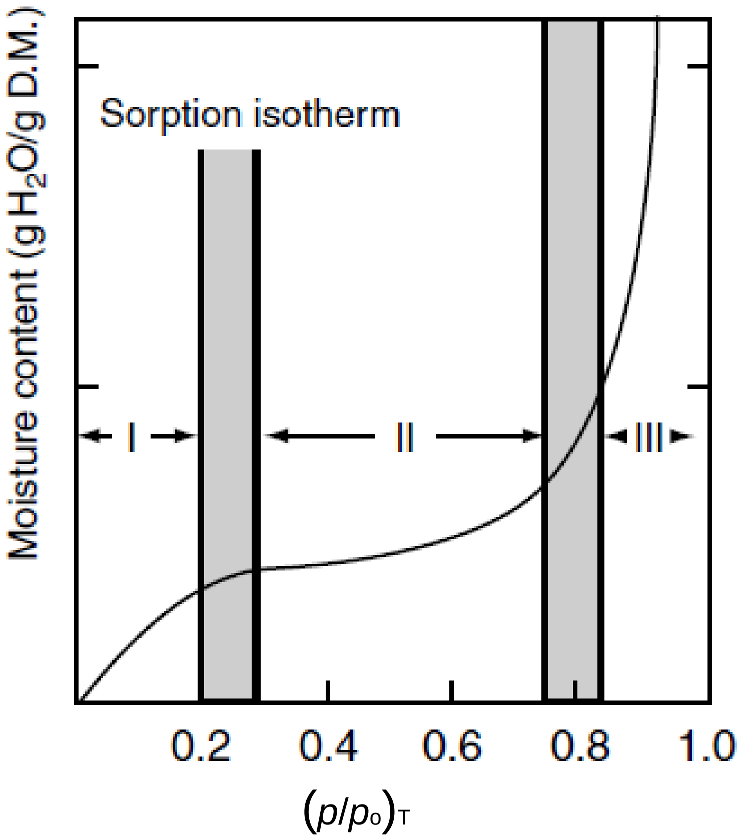
Relationships among relative water vapor pressure, food stability, and sorption isotherms



Maillard browning vs. (*p/po)*T



Miscellaneous reaction rates vs. (*p/po)*T



Water content vs. (*p/po)*T

Water migration

- In the case of multicomponent products, it may be necessary to separate the components or layers and measure each individually.

- Because *aw* is a driving force for moisture migration, it is necessary to know the *aw* values for the individual components or layers.

Water migration

- For example, in a flake cereal with fruit pieces, it is important to know the individual component water activities

- The *aw* values of cereal flakes and fruit pieces should be as close as possible to prevent moisture migration and, thus, to keep the flakes from becoming soggy and the fruit pieces from becoming hard and brittle

Water will tend to flow from dried fruits to cereal. To prevent:

- ➢ Change driving force: *e.g.*, add glycerol to lower a_w of raisin

- ➢ Create kinetic energy barrier: *e.g.*, coat raisins with a material that prevents water flow (*e.g.*, fat).

Raisin a_w = 0.55

Cereal a_w = 0.1

Water migration

- Control of initial *aw* and moisture migration is critical to the quality and safety of many foods

- Quality and safety factors that manufacturers must consider are

- For dry and semi-moist foods, shelf-life will depend on moisture content and *aw* of each domain.

- An example is the inner chocolate layer used to reduce moisture transfer from frozen ice cream to the baked cereal cone used for frozen novelties and prefrozen and filled ice cream cones.

Effects of Water Activity on Physical Properties

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