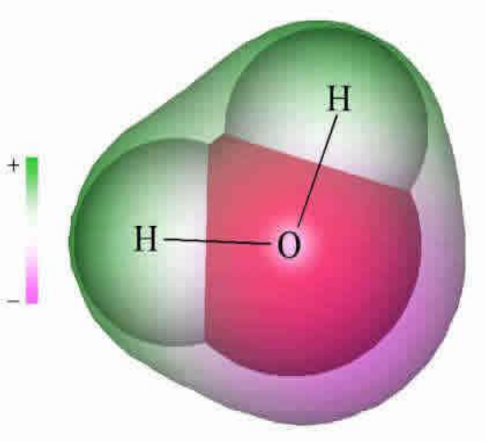
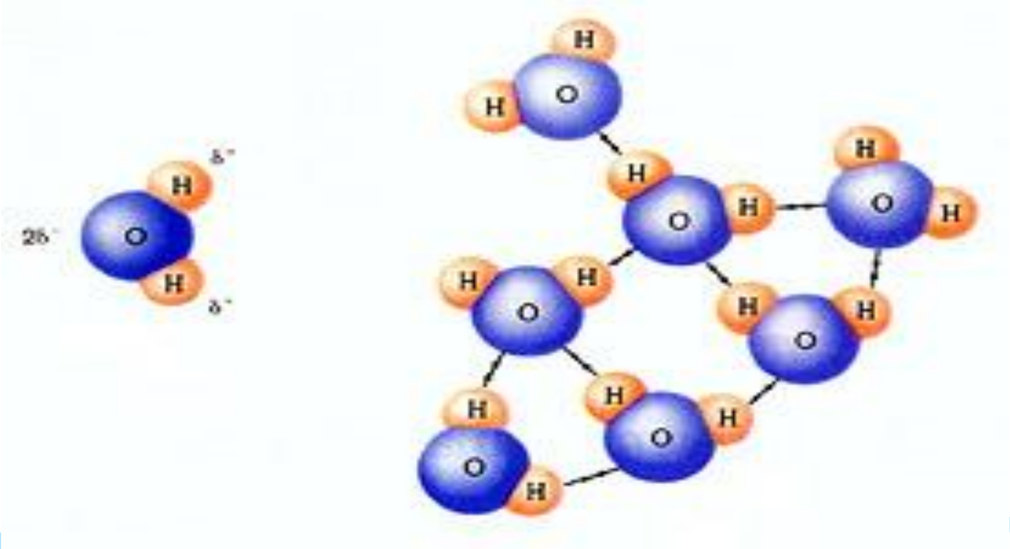
Kimia Air dalam Pangan

Course 2

Water in Foods: Physicochemical Properties and its Role in Food Safety and Quality

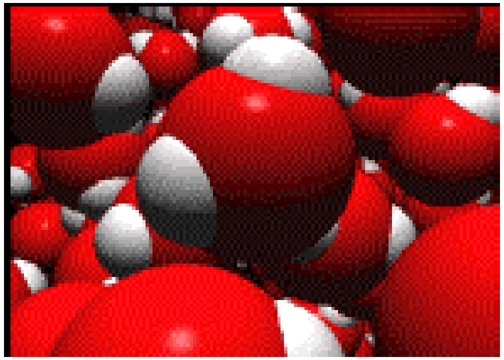




Outline

- Introduction
- Chemical Structures and Physical Properties
- Water Activity and MSI Curve
- Role of Water
    - Microbiological Safety
    - Chemical Reaction
    - Physical Properties of Foods
- Conclusion

Water in Foods



- Unique molecule - abundant in all 3 phases
- Essential for Life
- Water affects taste, structure, & susceptibility to spoilage
- Fresh foods (meat, fruit, veg.) contain large amount of water
- Need to control water in food for safety, quality, and storage

Moisture Contents of Foods

Food	Moisture Content (%)	Food	Moisture Content (%)
Tomato	94	Fried fish	38
Watermelon	93	Beef	66
Broccoli	92	Bread	36
Pineapple	85	Dried fruit	28
Mungbean	88	Milk powder	14
Milk	90	Wheat flour	12

Foods According to Their Perishability

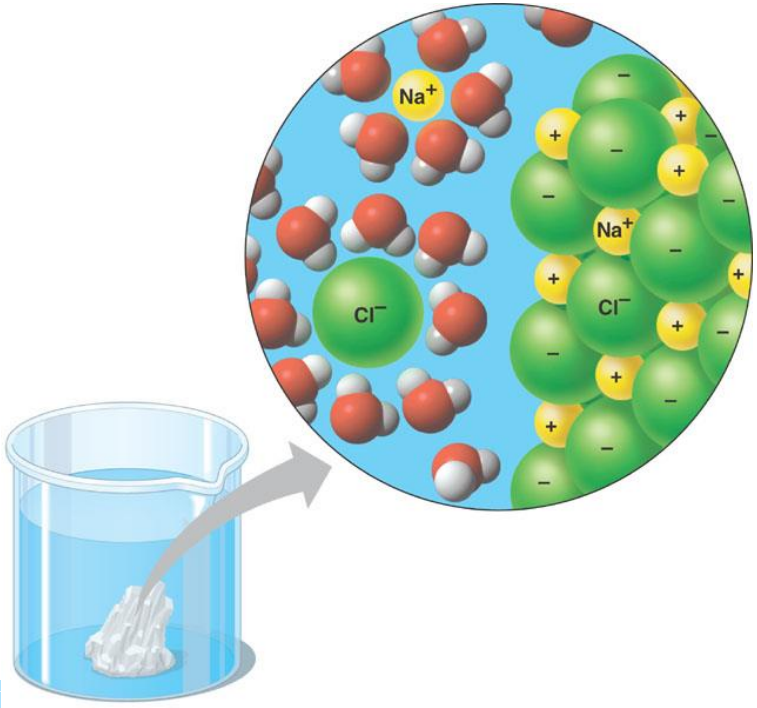
- Vervy perishable: beef, chicken, fish, milk, egg
- Moderately perishable: vegetable, fruits, bread, cake
- Non-perishable: bean, legume, sugar

Role of Water in Food System

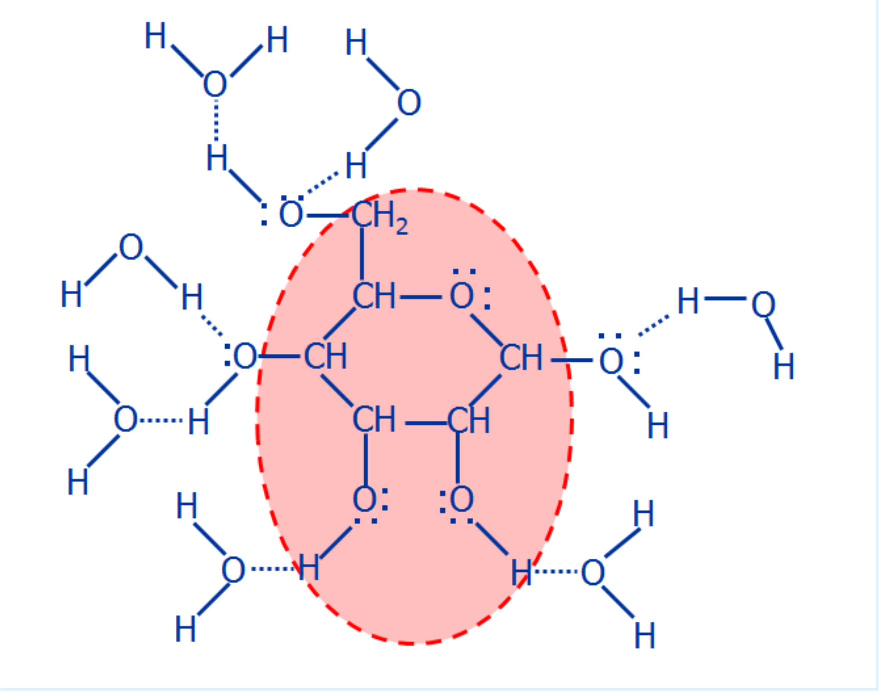
- Universal solvent (salt, vitamin, sugar, pigment)
- Ionizable (H_3O^+, OH^-)
- Chemical reaction (exp. protein hydrolysis= n amino acids) and enzyme activity
- Microbiological growth → food safety and stability
- Heat transfer medium

Water as a Solvent

Salt dissolution in water

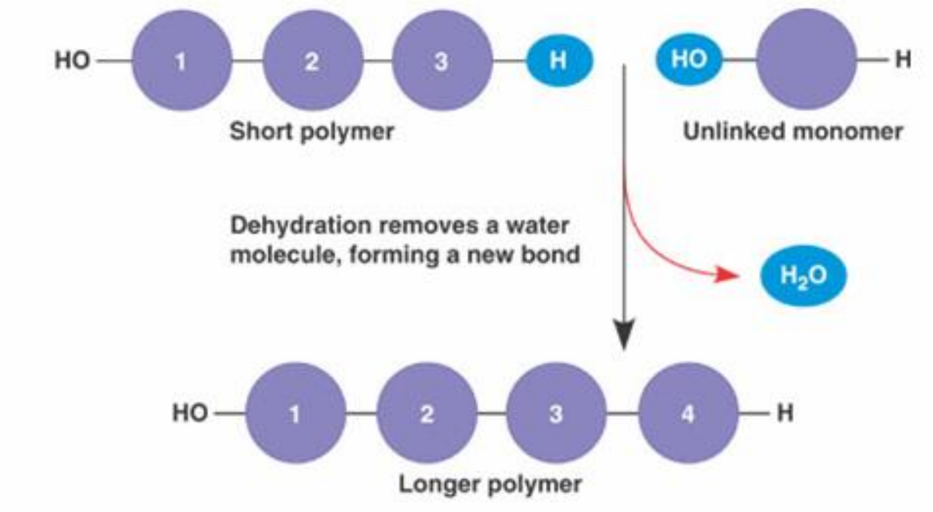


Glucose solubility in water

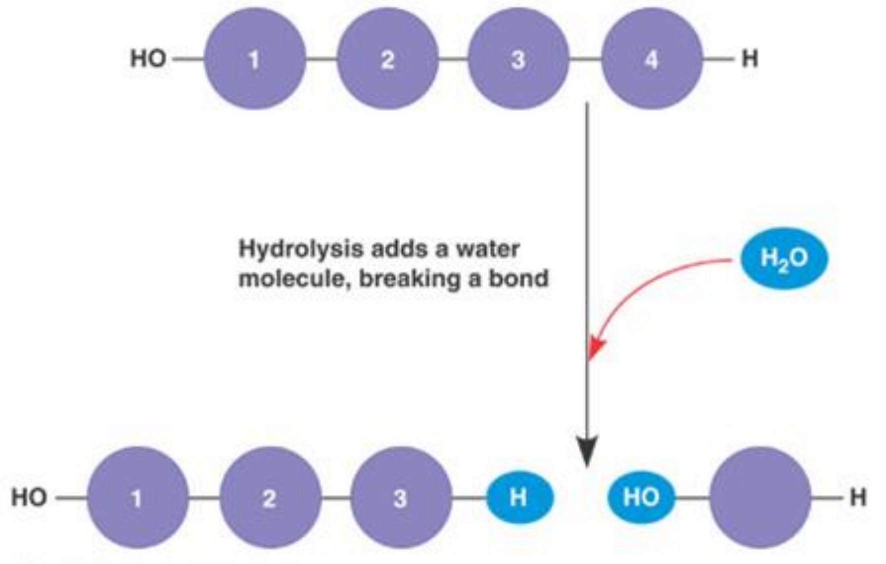


Water Involvement in Chemical Reaction

Dehydration Reaction in the Synthesis of a Polymer

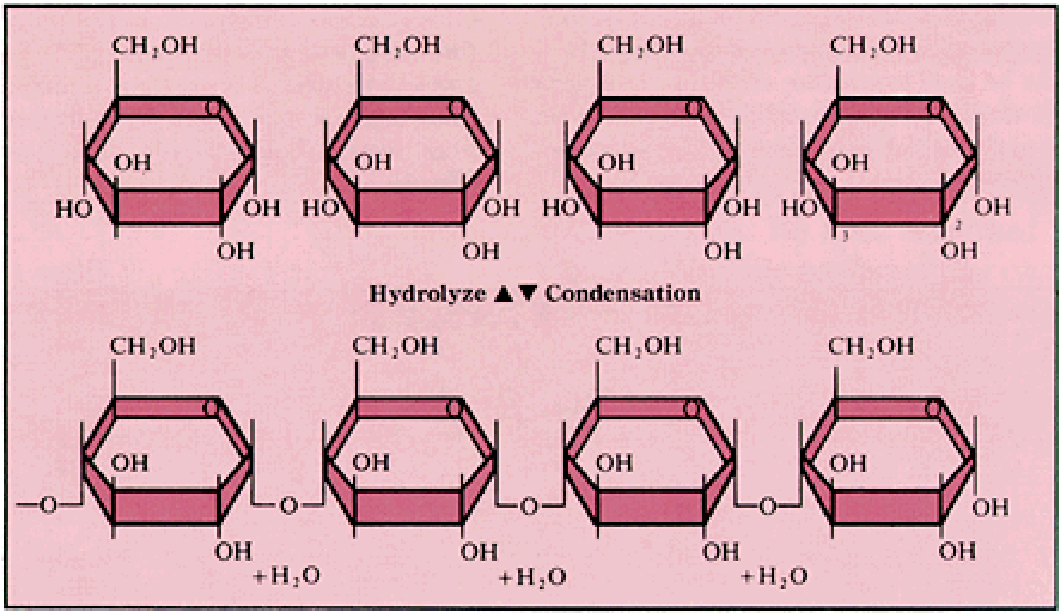


Hydrolysis Reaction of a Polymer



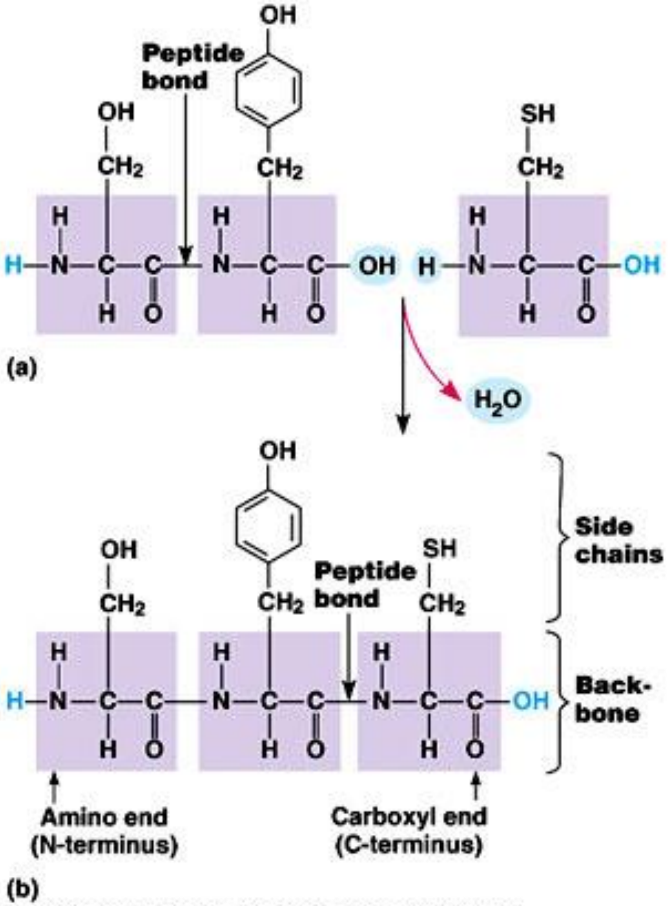
Water involvement in starch-glucose polymerization

Figure 2

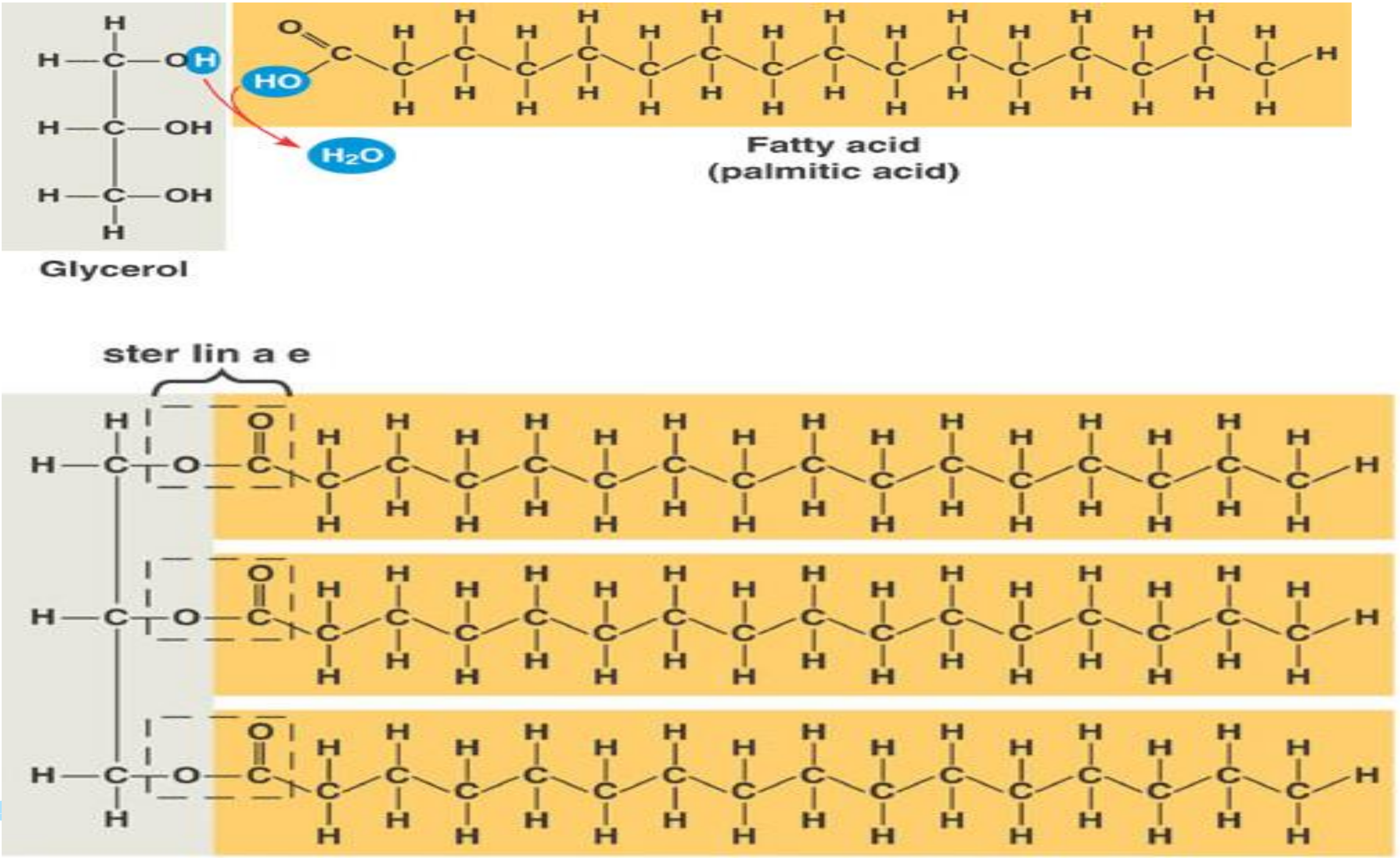


Starch — glucose polymer

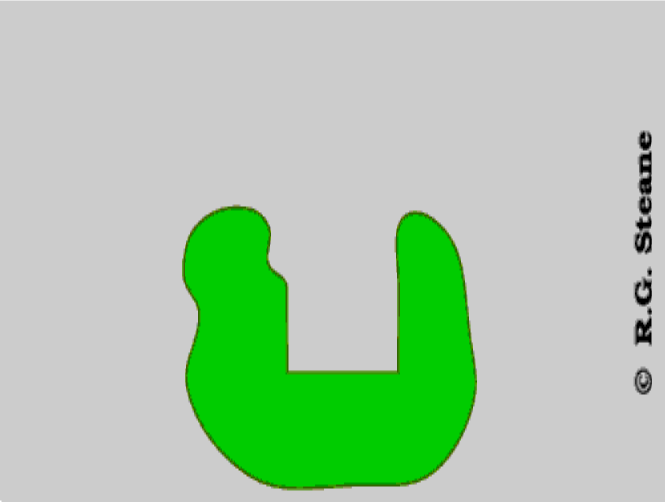
Water involvement in peptide synthesis



Water Involvement in Lipid Synthesis

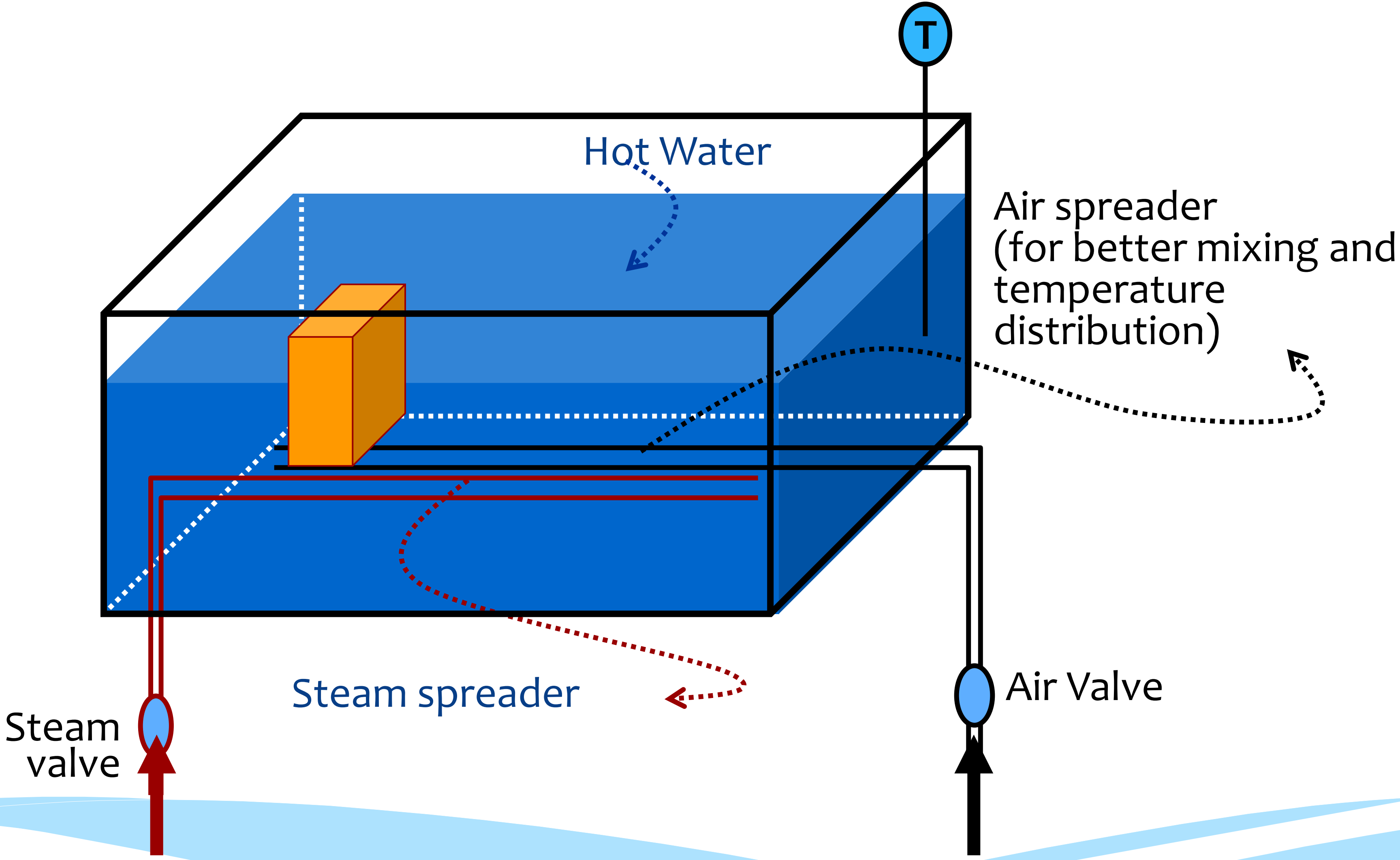


Water in Enzyme Activity



- The green one is enzyme. Unchanged at the end of the reaction
- The orange one is substrate molecules acted on by the enzyme. Changed to products.
- The blue one is water. Involved in the reaction.

Water as Heat Transfer Medium:
Batch Pasteurization (example)



Roles of Water in Food

Role	Moisture Range	Mechanism of Effect	Quality Attribute Affected
Solvent	All -excluding bound water	Solution	All
Reaction Medium	All -excluding bound water	Facilitation of chemical change	All
Reactant	All	Hydrolyzing agent	flavour, texture
Antioxidant	Low	Hydration and precipitation of metal catalysts, bonding to peroxides and functional groups of proteins and carbo-hydrates, promotes free radical recombination.	Flavour, colour, texture, nutritive value
Prooxidant	Medium	Reduction in viscosity increases mobility of reactants and catalysts. Swelling of solid matrices exposing catalytic surfaces and oxidizable groups	Flavour, colour, texture, nutritive value

Roles of Water in Food

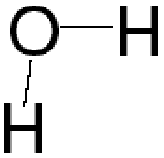
Role	Moisture Range	Mechanism of Effect	Quality Attribute Affected
Structural-intramolecular	All	Maintains the integrity of proteins molecules	texture and attributes affected by enzymes
Structural-intermolecular	Low	Hydrogen bonding to surface groups on macromolecules Hydrogen bonding to cross-linking sites of macromolecules	Viscosity Texture - in dehydrated foods
Structural-intermolecular	Medium and High	Influence on structure of emulsions (i.e. binding to surface lipids). Influence the interactions and conformation of gel forming polysaccharides and proteins.	Rheological properties of emulsions and textural properties of gels.

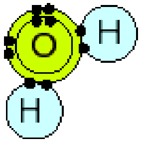
Physicochemical Properties of Water

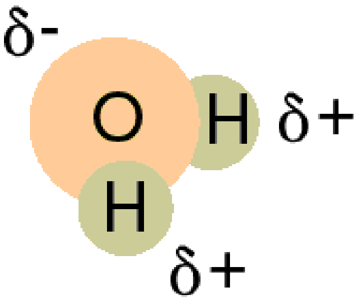
pH (pure water	7.0
Molecular weight	18.0153
Melting point at 1 atm	0.0°C
Boiling point at 1 atm	100°C
Heat of fusion at 0°C	6.012 kJ (1.436 kcal)/mol
Density	1 g/ml
Heat of vaporization at 100°C	40.657 kJ (9.711 kcal)/mol
Heat of sublimation at 0°C	50.91 kJ (12.16 kcal)/mol

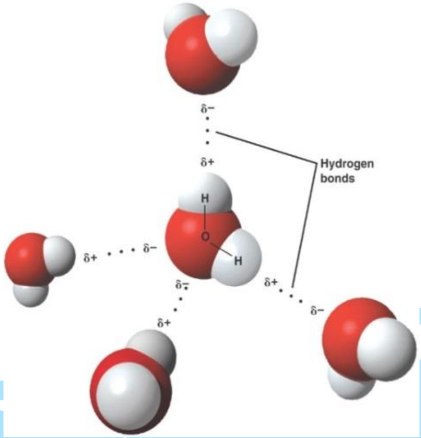
Water Molecule

- Chemical formula: H_2O
- H and O atoms are connected by covalent bonds
- Polar:
  - H : positive (δ^+)
  - O : negative (δ^-)

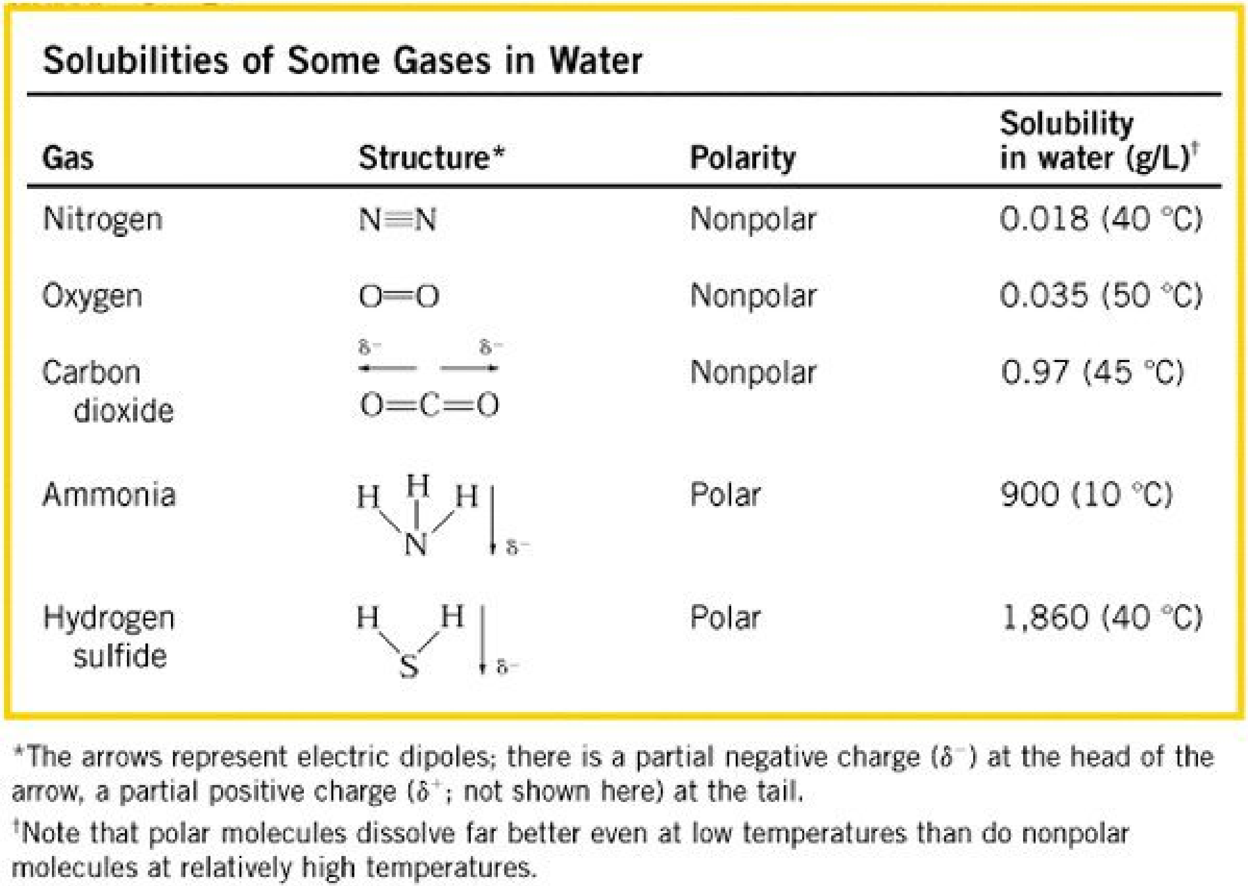








Water/solute interactions



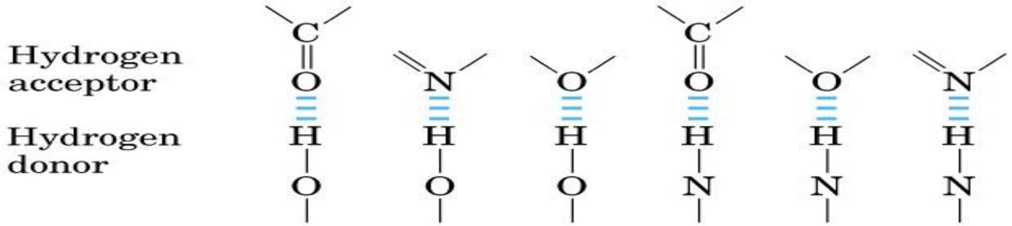
Solubilities of Some Gases in Water

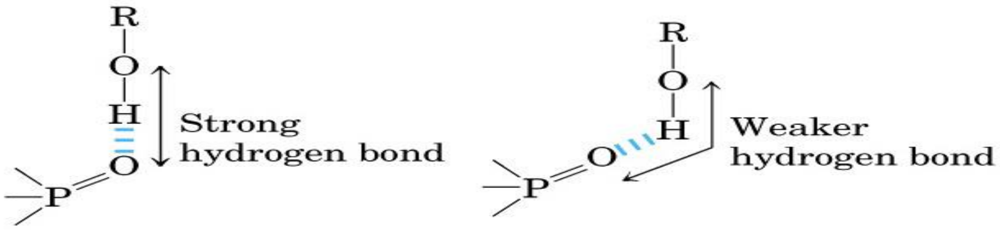
Gas	Structure*	Polarity	Solubility in water (g/L)†
Nitrogen	$N{\equiv}N$	Nonpolar	0.018 (40 °C)
Oxygen	$O{=}O$	Nonpolar	0.035 (50 °C)
Carbon dioxide	$\overset{\overset{\delta^-}{\longleftarrow}\quad\overset{\delta^-}{\longrightarrow}}{O{=}C{=}O}$	Nonpolar	0.97 (45 °C)
Ammonia		Polar	900 (10 °C)
Hydrogen sulfide		Polar	1,860 (40 °C)

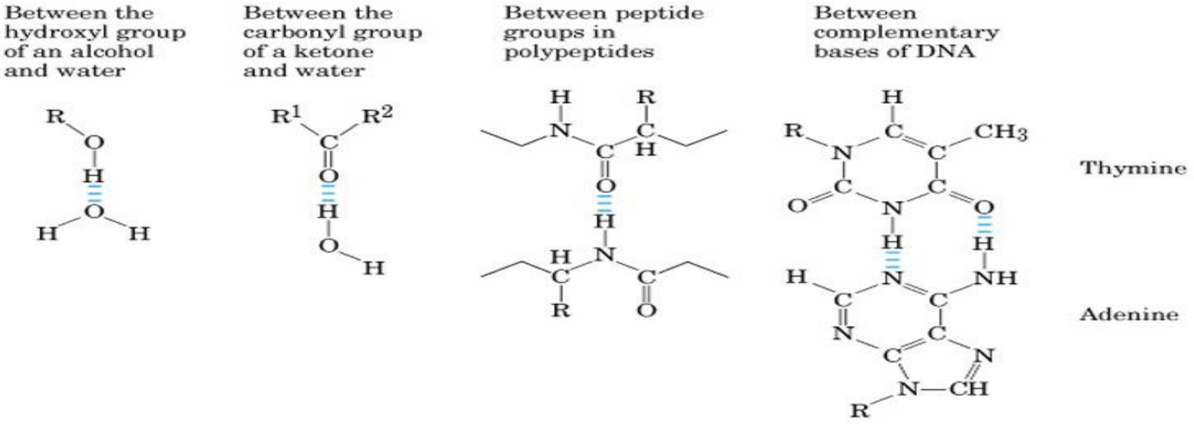
*The arrows represent electric dipoles; there is a partial negative charge (δ^-) at the head of the arrow, a partial positive charge (δ^+; not shown here) at the tail.

†Note that polar molecules dissolve far better even at low temperatures than do nonpolar molecules at relatively high temperatures.

Hydrogen Bonds

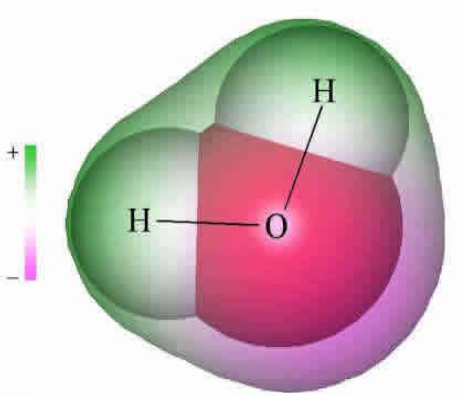


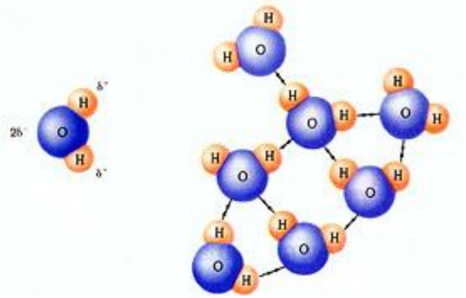


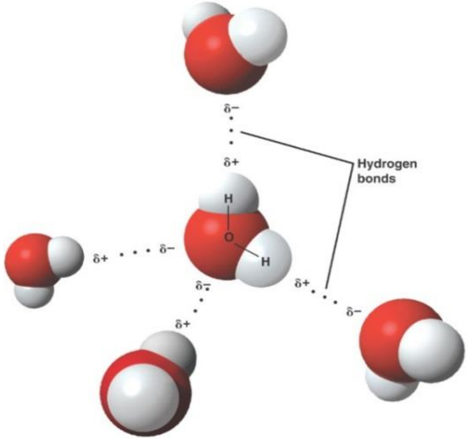


Hydrogen Bond in Water

- Hydrogen bond: as a result of electropositive of H and electronegative of O
- 10% of of H-O covalent bond (10 Kcal/mole).
- H bonds: high boiling point (100°C at 1 atm) and flowable







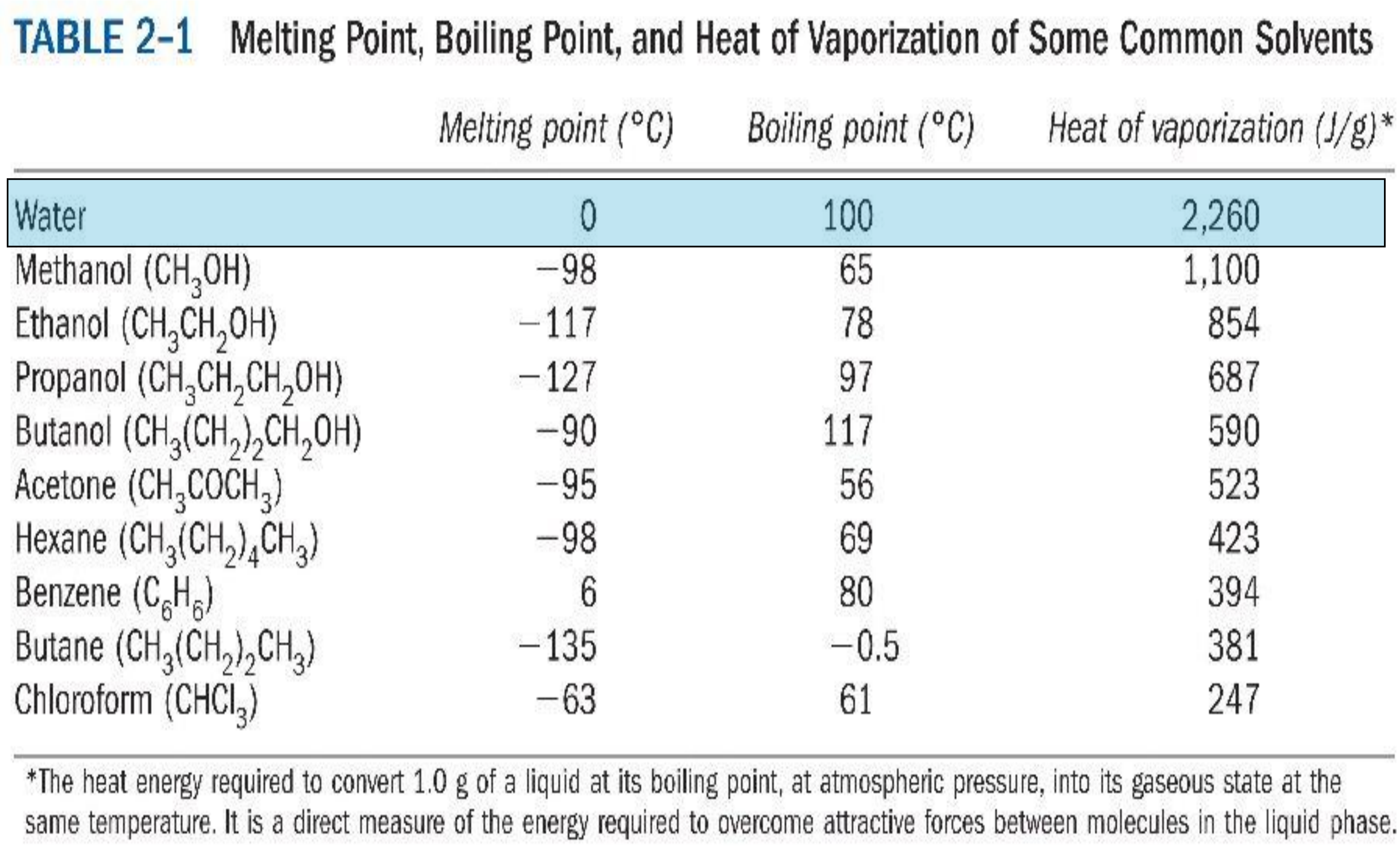
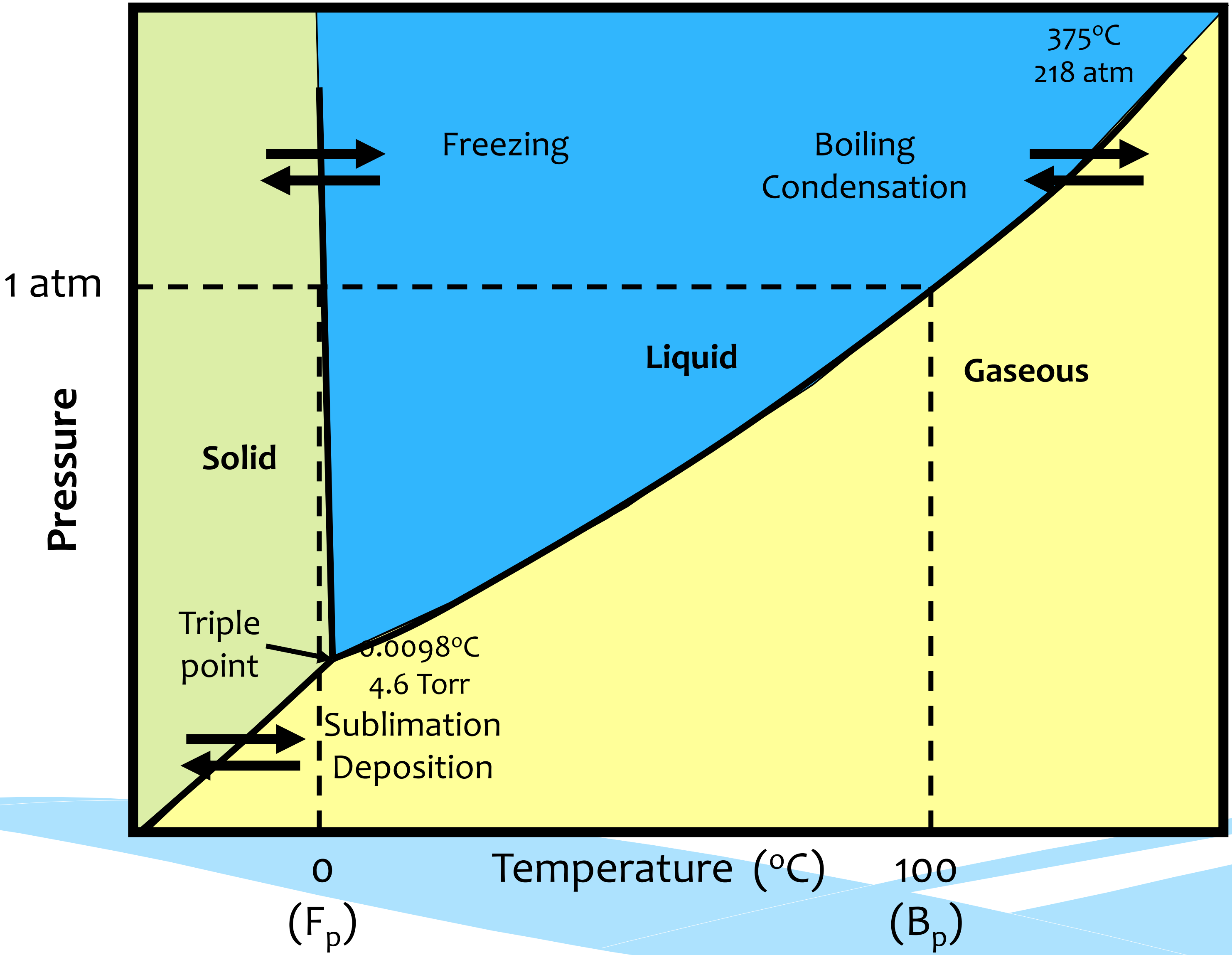


TABLE 2-1 Melting Point, Boiling Point, and Heat of Vaporization of Some Common Solvents

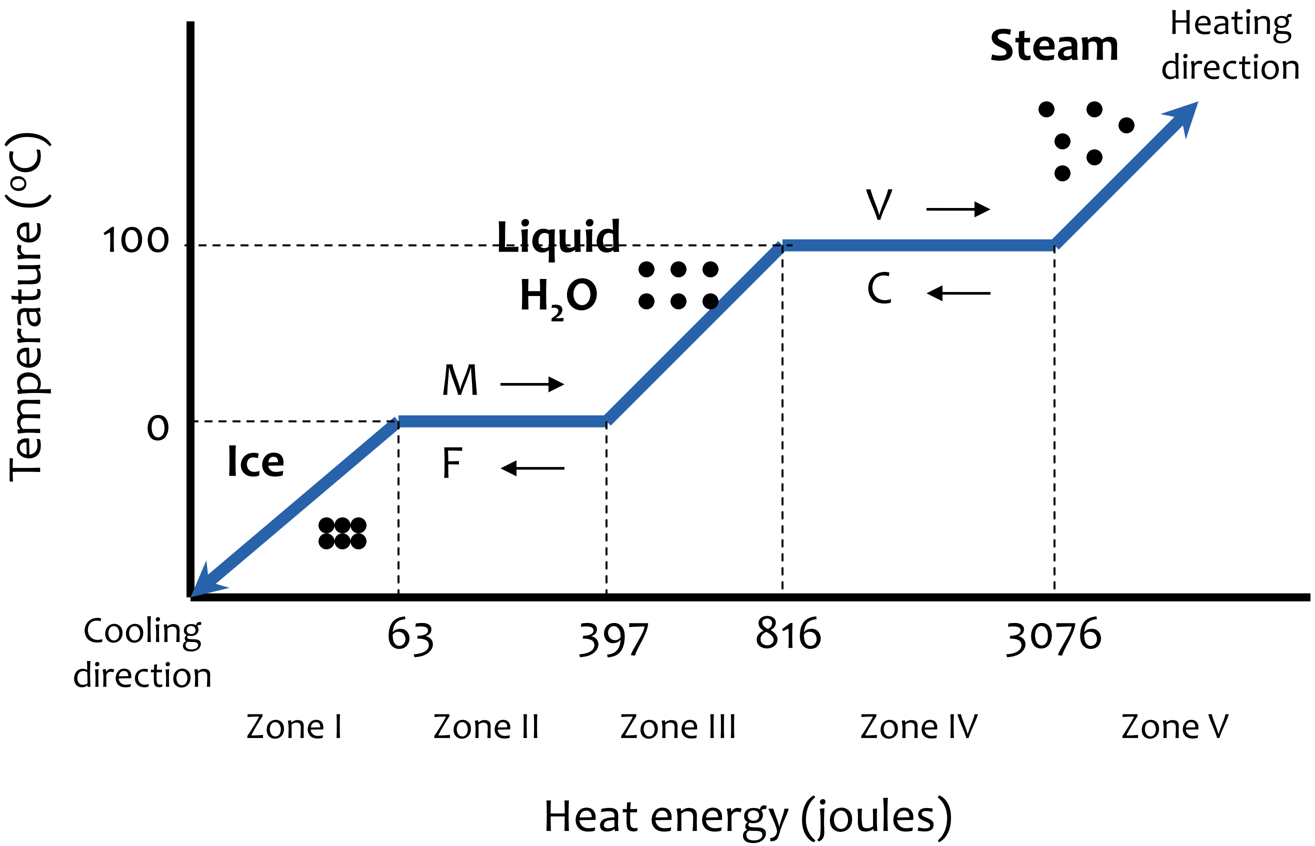
	Melting point (°C)	*Boiling point (°C)*	*Heat of vaporization (J/g)**
Water	0	100	2,260
Methanol (CH_3OH)	−98	65	1,100
Ethanol (CH_3CH_2OH)	−117	78	854
Propanol ($CH_3CH_2CH_2OH$)	−127	97	687
Butanol ($CH_3(CH_2)_2CH_2OH$)	−90	117	590
Acetone (CH_3COCH_3)	−95	56	523
Hexane ($CH_3(CH_2)_4CH_3$)	−98	69	423
Benzene (C_6H_6)	6	80	394
Butane ($CH_3(CH_2)_2CH_3$)	−135	−0.5	381
Chloroform ($CHCl_3$)	−63	61	247

*The heat energy required to convert 1.0 g of a liquid at its boiling point, at atmospheric pressure, into its gaseous state at the same temperature. It is a direct measure of the energy required to overcome attractive forces between molecules in the liquid phase.

Phase Diagram of Water



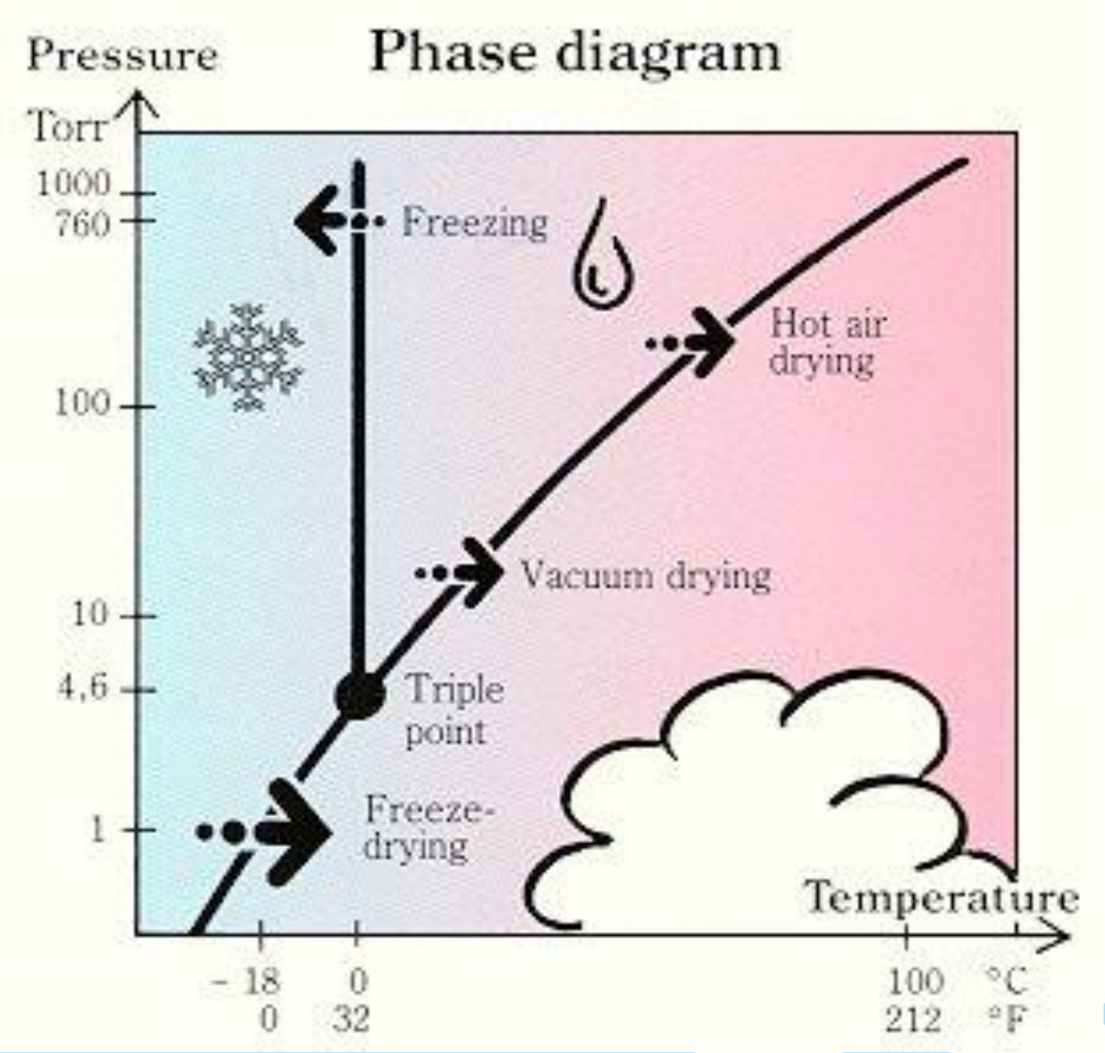
Latent and Sensible Heating and Cooling Curves for Water



Sensible heat : Heat energy due to temperature change

Latent energy : heat energy due to change of state

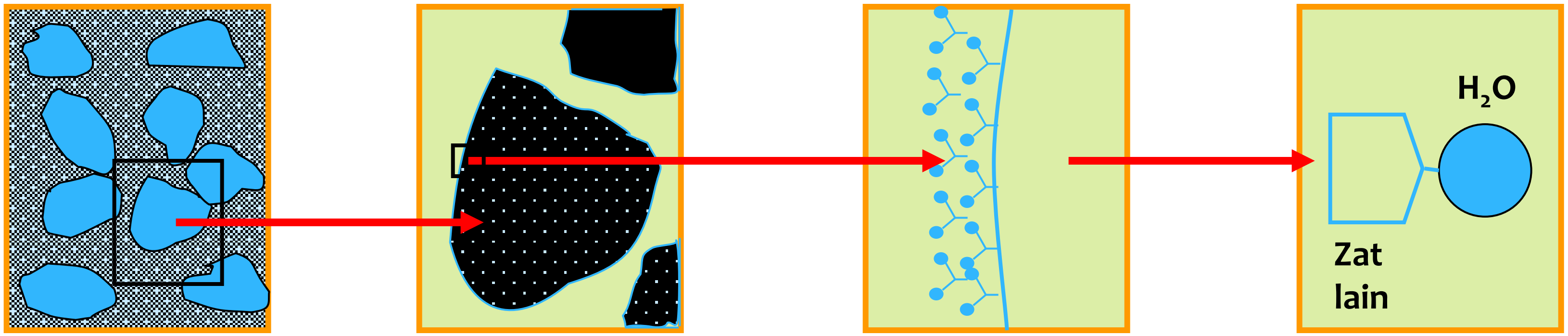
Drying Process in Food Processing



Defining Water

- ***Moisture content:*** The total amount of water in food system (in percentage). It does not describe water activity.
- ***Relative humidity (RH):*** Amount of water in air (in percentage).
- ***Water activity (a_w):*** Degree of water activity in food system (chemical and biological properties). Value: 0 – 1 (no uit). A_w=1 (pure water)

Jenis Air Dalam Pangan



Air kapiler
(ERH>98%)

Air terlarut
(ERH:24-100%

Air adsorpsi
(ERH:15-68%)

Air konstitusi/
Air kristal
(ERH:0-34%)

Air Dalam Bahan Pangan

Tipe 1:

- Air terikat yang sebenarnya
- Molekul air yang terikat pada molekul lain melalui ikatan hidrogen.
- Molekul air membentuk hidrat dengan molekul-molekul lain yang mengandung atom O dan N, seperti karbohidrat, protein dan garam.
- Tidak dapat membeku, sebagian dapat dihilangkan dengan pengeringan.

Air Dalam Bahan Pangan

Tipe 2:

- Molekul-molekul air membentuk ikatan hidrogen dengan molekul air lain, terdapat pada mikrokapiler.
- Sifatnya berbeda dari air murni.
- Lebih sukar dihilangkan dibandingkan air bebas.
- Apabila dihilangkan, kadar air bahan akan mencapai 3-7%

Air Dalam Bahan Pangan

Tipe 3:

- Air yang secara fisik terikat dalam jaringan matriks bahan, seperti membran, kapiler, serat, dll.
- Bersifat sebagai air bebas.
- Mudah diuapkan dan dapat dimanfaatkan untuk pertumbuhan mikroba dan media bagi reaksi-reaksi kimiawi.
- Apabila dihilangkan, kadar air bahan akan mencapai 12-25% dengan Aw ~ 0.8

Tipe 4:

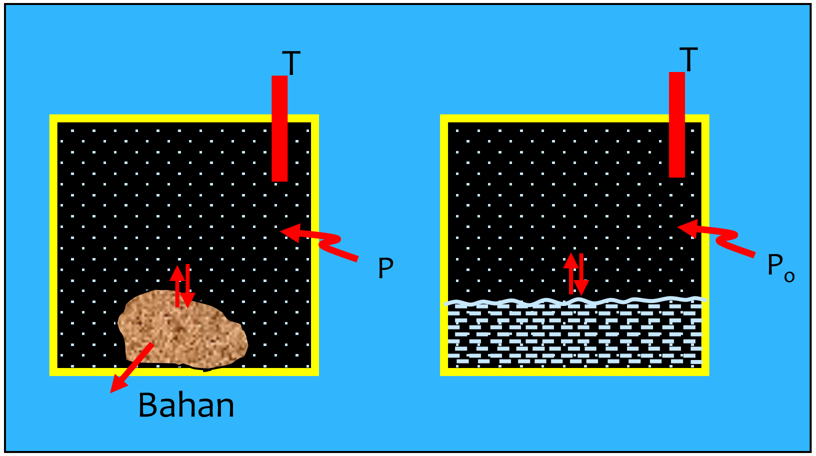
- Air yang tidak terikat dalam jaringan suatu bahan.
- Bersifat air murni (air biasa) dengan keaktifan penuh.

Aktifitas Air (A_w)

- Aktifitas air paling umum digunakan sebagai kriteria untuk keamanan pangan dan kualitas pangan.
- Air tidak terdistribusi secara merata (homogen) dalam bahan pangan: derajat keterikatan berbeda-beda
- Aktifitas air merupakan indeks yang lebih baik dari kadar air untuk pertumbuhan mikroba, karena mikroba hanya dapat menggunakan air bebas untuk pertumbuhannya.
- Nilai A_w: 0.0 - 1.0 (tanpa satuan). A_w=0 (absolutely dry); A_w=1 (pure water)

Pengertian Aktifitas Air (Aw)

- Apabila air murni disimpan dalam ruangan tertutup, maka akan terbentuk kesetimbangan dengan udara sekitar. Tekanan udara adalah P_o.
- Apabila air berisi garam disimpan dalam ruangan tertutup:
    - Tekanan udara akan menurun (P)
    - Molekul air akan lebih sulit berubah fase dari cair ke uap (kenaikan titik didih) dan dari cair ke es (penurunan titik beku)
- Garam yang berbeda memiliki kelarutan yang berbeda: besarnya perubahan tekanan (P) berbeda



$$A_w = P/P_o = ERH/100$$

ERH = equilibrium Relative Humidity

P = Tekanan uap bahan

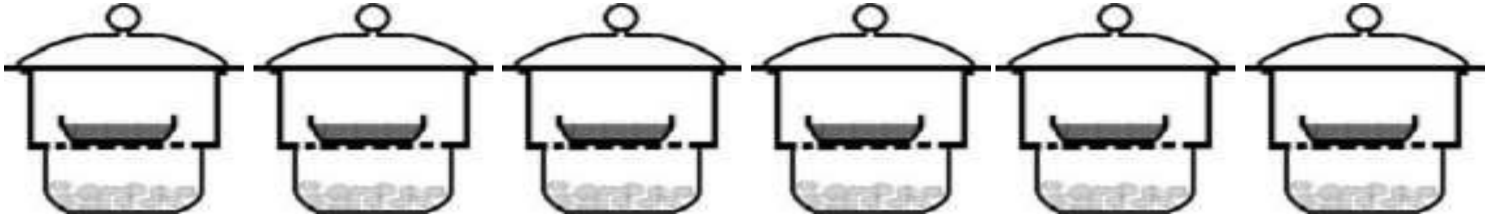
Po = Tekanan uap air murni

Menentukan aktifitas Air

- *Equilibrium Relative Humidity* (ERH) adalah persentase dari rasio P dan P_o
- Apabila bahan pangan disimpan dalam desikator berisi larutan garam jenuh, maka kadar air dan Aw-nya akan berubah sehingga mencapai kondisi kesetimbangan.
  - Bila A_w produk > ERH, air akan dilepaskan ke udara (kadar air menurun)
  - Bila A_w produk < ERH, air dari udara akan masuk ke bahan pangan (kadar air meningkat)

Aktivitas air dari berbagai larutan garam jenuh pada suhu yang berbeda

Larutan garam jenuh	20°C	25°C	30°C
NaOH	0.0698	0.0695	0.0687
LiCl	0.1114	0.1115	0.1116
$KC_2H_3O_2$	0.2310	0.2260	0.2200
$MgCl_2$	0.3030	0.3273	0.3238
NaI	0.3918	0.3775	0.3625
$Mg(NO_3)_2$	0.5447	0.5286	0.5133
KI	0.6986	0.6876	0.6785
$NaNO_3$	0.7513	0.7379	0.7275
NaCl	0.7542	0.7532	0.7521
KBr	0.8177	0.8071	-
KCl	0.8531	0.8432	0.8353
Na_2SO_4	0.8690	0.8595	0.8640
K_2CrO_4	0.8660	0.8640	0.8630
$BaCl_2$	0.9069	0.9026	-
$NH_4H_2PO_4$	0.9220	0.9270	0.9110
K_2SO_4	0.9720	0.9690	0.9660



0.11	0.33	0.38	0.75	0.86	0.97
$LiCl$	$MgCl_2$	NaI	$NaCl$	K_2CrO_4	$K_2Cr_2O_7$

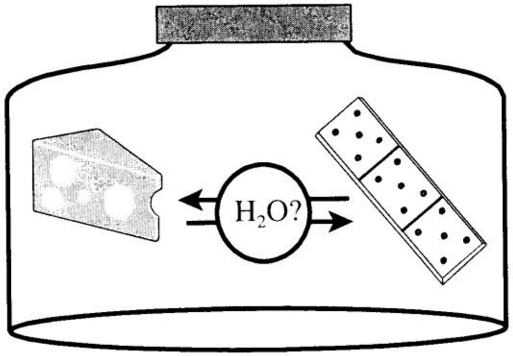
- Bahan pangan yang disimpan pada larutan garam jenuh yang berbeda akan memiliki kadar air dan A_w yang berbeda.
- A_w pangan akan membentuk kesetimbangan dengan RH lingkungannya.
- Kondisi kesetimbangan tercapai apabila kadar air bahan tidak berubah lagi (tidak ada perpindahan air lagi), sehingga tercapai A_w=ERH/100

Measuring Water Activity

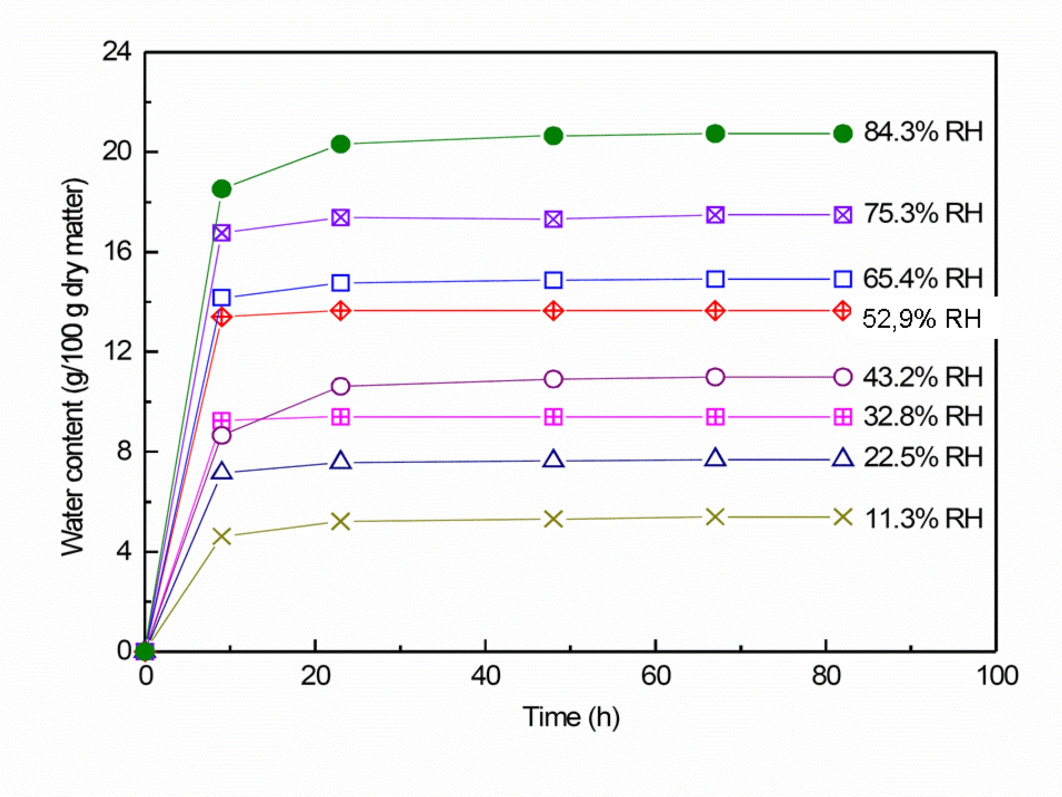
Kadar air kesetimbangan: Kadar air bahan pangan ketika tekanan uap air dari bahan tersebut dalam kondisi setimbang dengan lingkungannya dimana produk sudah tidak mengalami perubahan atau pengurangan bobot produk.

Kurva Sorpsi Isotermis Air

- Sejumlah contoh (produk pangan) yang diketahui beratnya (tanpa kemasan) dimasukkan ke dalam beberapa chamber yang berisi larutan garam jenuh, kemudian chamber ditutup rapat. Chamber disimpan ke dalam inkubator yang diatur suhunya (misalnya 30°C).
- Chamber diamati secara periodik (misalnya setiap 5 jam) dan ditimbang. Peningkatan berat dicatat sehingga diperoleh berat konstan.



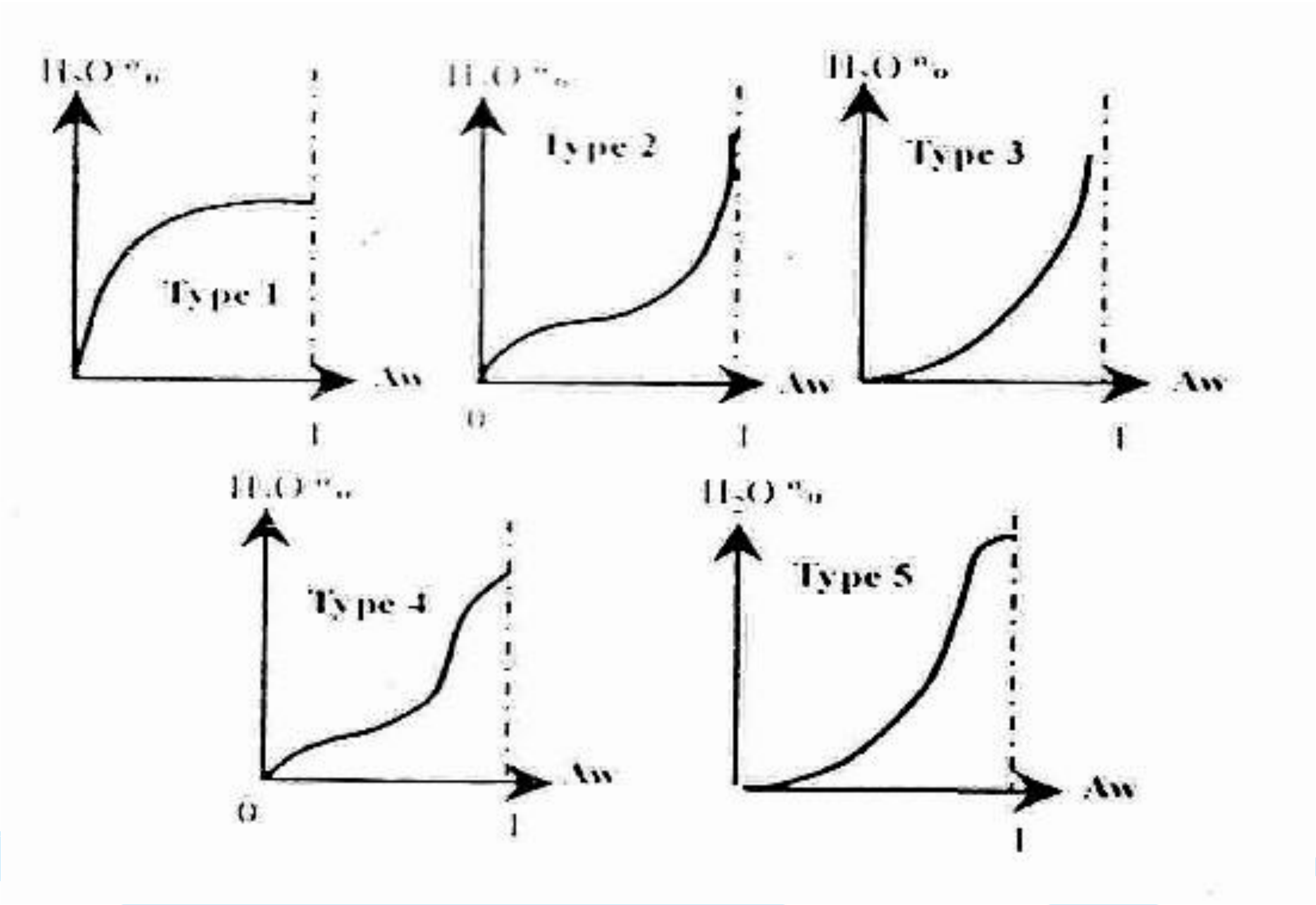
Kurva Kenaikan Kadar Air Menuju ke Kadar Air Kesetimbangan Selama Penyimpanan Pada Berbagai Kondisi RH



Model Persamaan Sorpsi Isotermis

- Dilakukan untuk mendapatkan kemulusan kurva sorpsi isotermis.
- Model-model yang banyak digunakan:
  - * Model Hasley : $a_w = exp\ [-P1/(Me)^{P2})$
  - * Model Chen-Clayton: $a_w = exp[-P1/exp(P2 * Me)]$
  - * Model Henderson: $1 - a_w = exp\ (-KMe^n)$
  - * Model Caurie: $\ln Me = \ln P1 – (P2 * a_w)$
  - * Model Oswin: $Me = P1 * [a_w/(1 – a_w)]^{P2}$
  - * Model GAB: $M = Xm.C.K.a_w/(1\text{-}K.a_w)(1\text{-}K.a_w+C.K.a_w)$

Tipe-Tipe Kurva Isothermis
(Mathlouthi dan Roge dalam Fauzi, 2006)



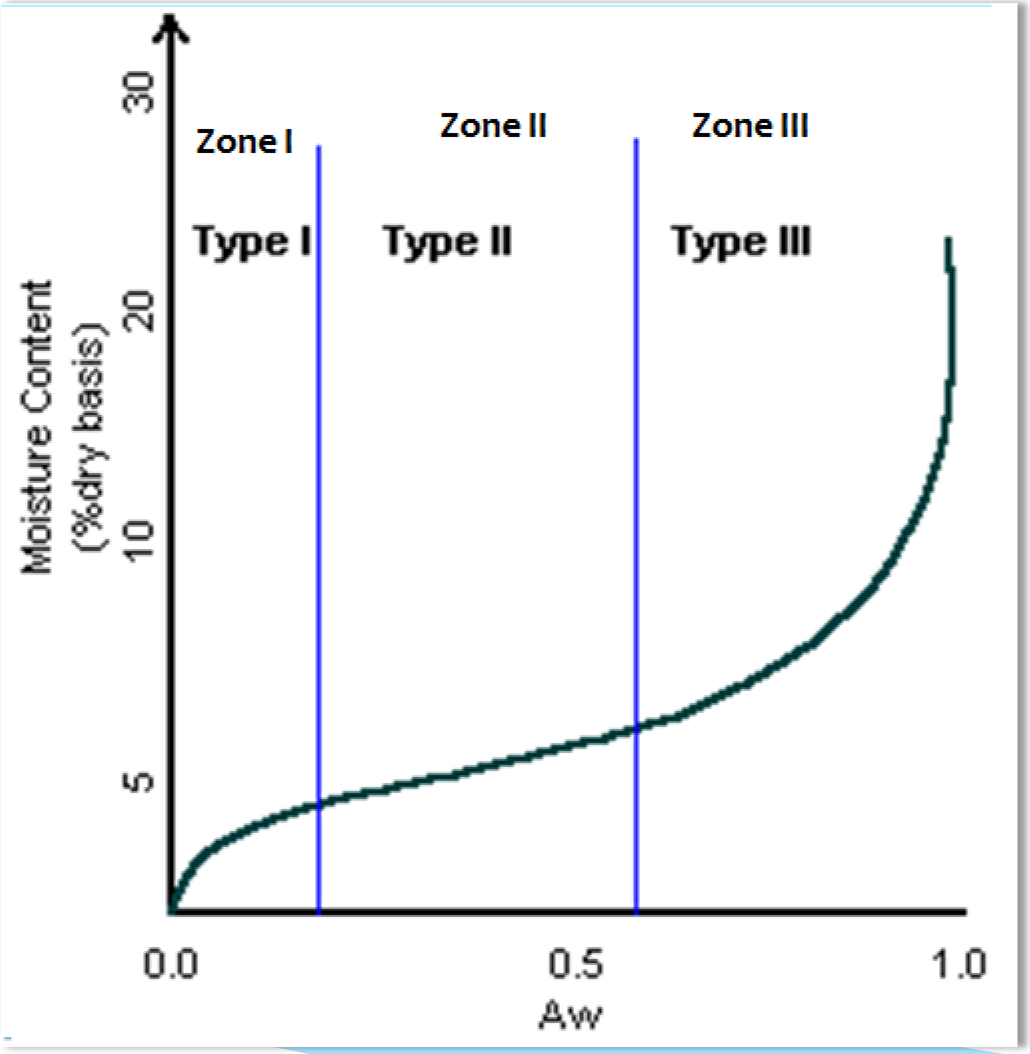
Hubungan A_w dengan Kadar Air

- Peningkatan Aw selalu diikuti peningkatan kadar air, tetapi tidak linear.
- Hubungan antara aktifitas air dan kadar air digambarkan dengan **Moisture Sorption Isotherm** (MSI). Kurva ini dibuat secara eksperimental. Kurva MSI umumnya berbentuk sigmoidal.
- Kurva MSI spesifik untuk setiap produk pangan dan dipengaruhi oleh suhu.
- Untuk produk pangan yang sangat higroskopis (seperti permen), kurva MSI tidak berbentuk sigmoid pada A_w tinggi, karena akan terus menyerap air dan larut (tidak mencapai kadar air kesetimbangan

Kadar Air dan aktifitas Air pada Beberapa Bahan Pangan

Pangan	Kadar air (%)	A_w
Es pada 0^oC	100	1.00
Daging segar	70	0.985
Roti	40	0.96
Tepung	14.5	0.72
Makaroni	10	0.45
Potato chips	1.5	0.08

Adsorption Isotherm for Water in Foods

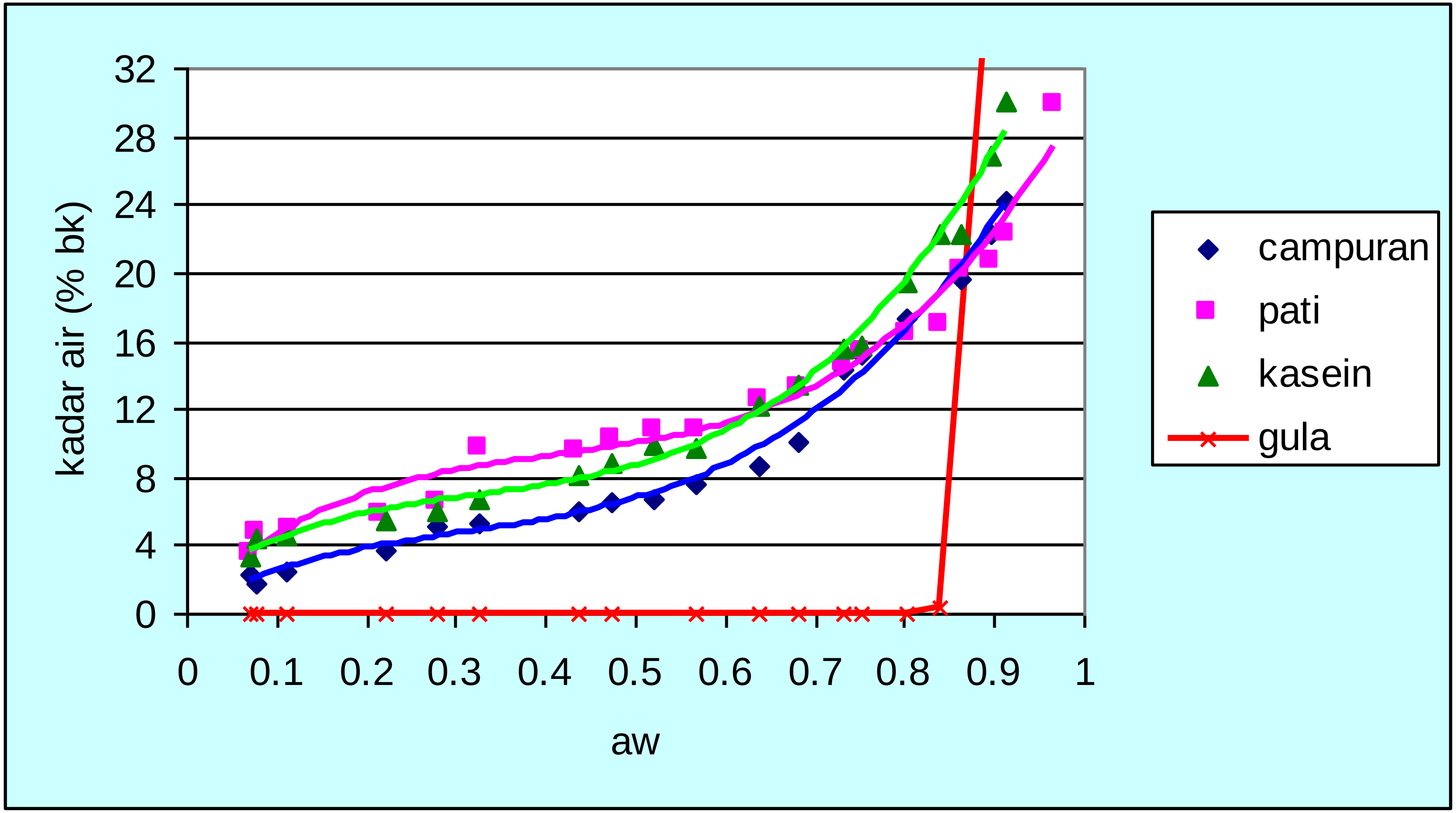


Type I. Bound Water
Here water is adsorbed on the surface of macromolecular colloids. This I is knows as the water of hydration. The adsorption forces include both hydrogen bonding and Van der Waals forces.

Type II. Monolayer Moisture Content
In this case the monolayer is adsorbed and the first multilayers are added.

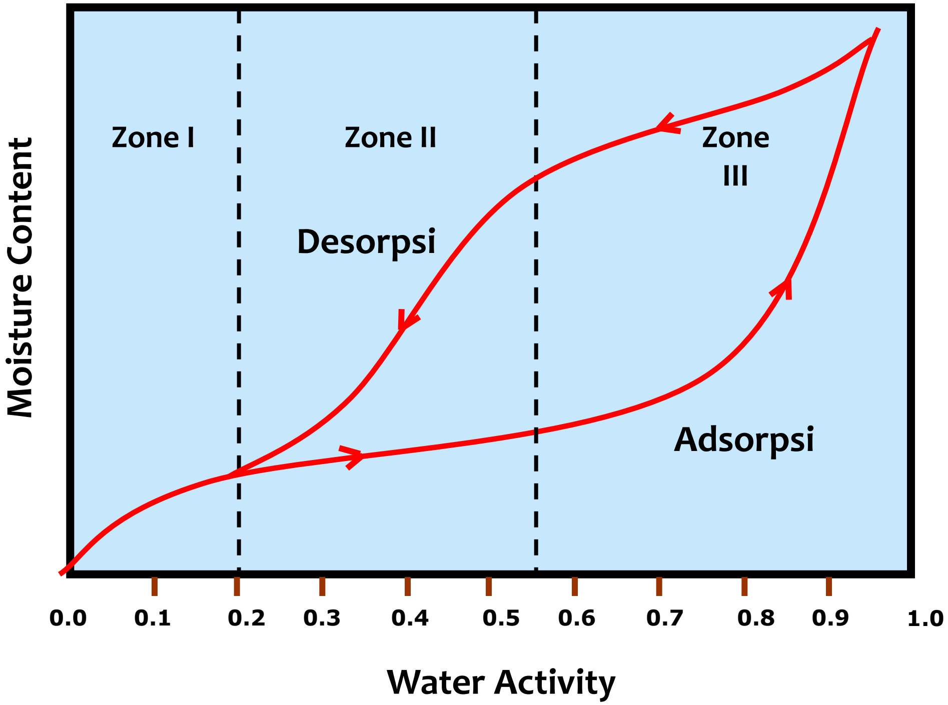
Type III. Free Water
Here water fills the intergranular spaces and the spaces within the pores. This water is mobile and retains the properties of water. Thus, its is a dispersing agent as well as a solvent.

Model Kurva Sorpsi Isotermis Air



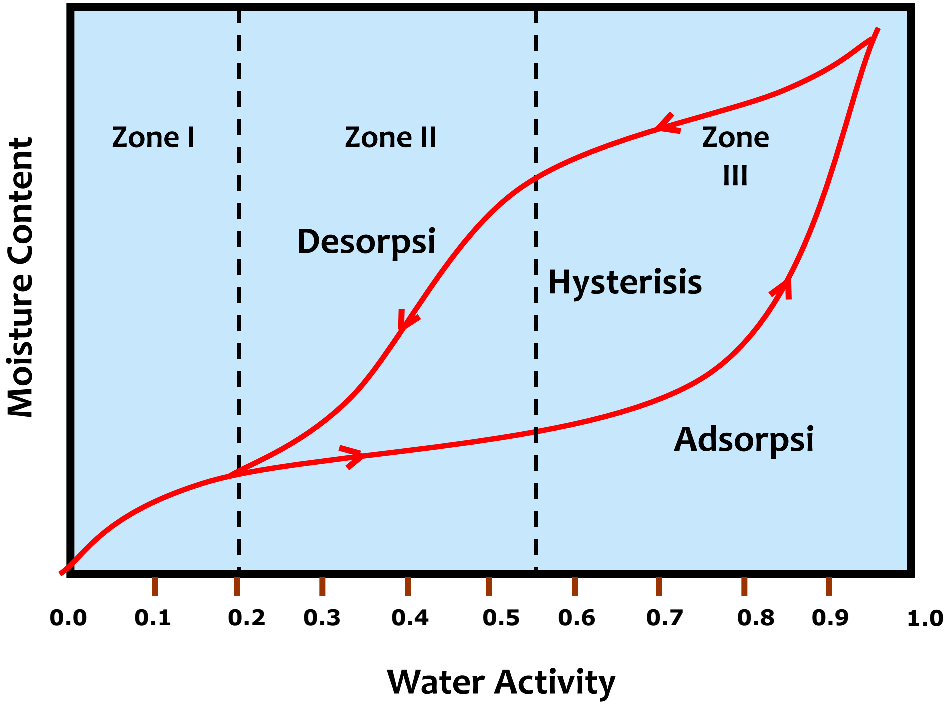
Adawiyah, 2006

Desorpsi vs Adsorpsi



- **Kurva MSI Adsorpsi:** Kurva dimulai dari kondisi kering hingga kondisi basah (misal: proses rehidrasi/penyerapan air).
- **Kurva MSI desorpsi:** Kurva dimulai dari kondisi basah ke kondisi kering (misal: proses dehidrasi/proses pengeringan).

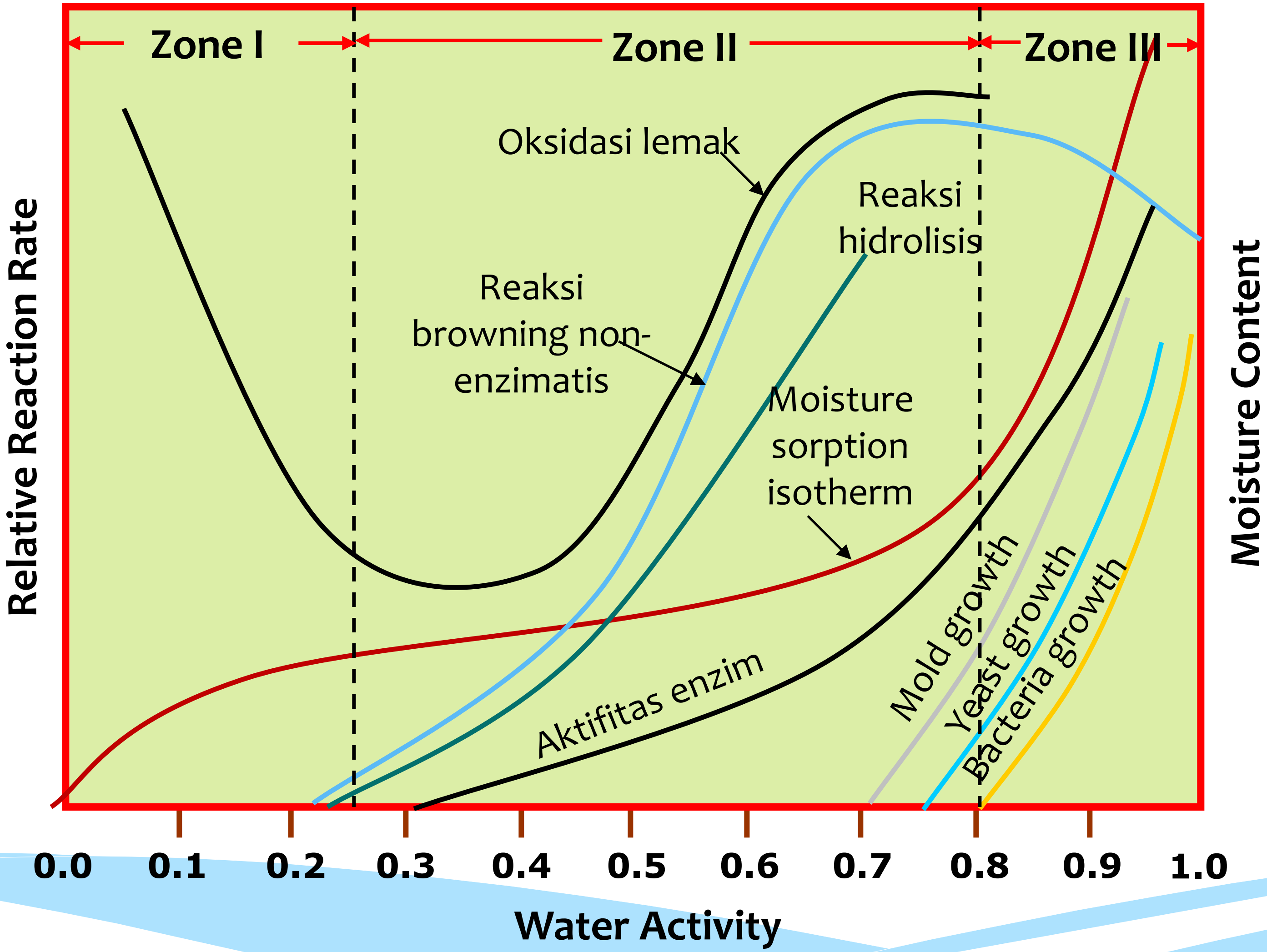
Desorpsi vs Adsorpsi



- Kurva MSI Adsorpsi dan kurva MSI Desorpsi tidak melalui garis yang sama
- Fenomena perbedaan kurva MSI dari proses adsorpsi dengan proses desorpsi disebut **moisture sorption hysteresis.** Secara umum terjadi pada bahan pangan.

Mengapa A_w penting?

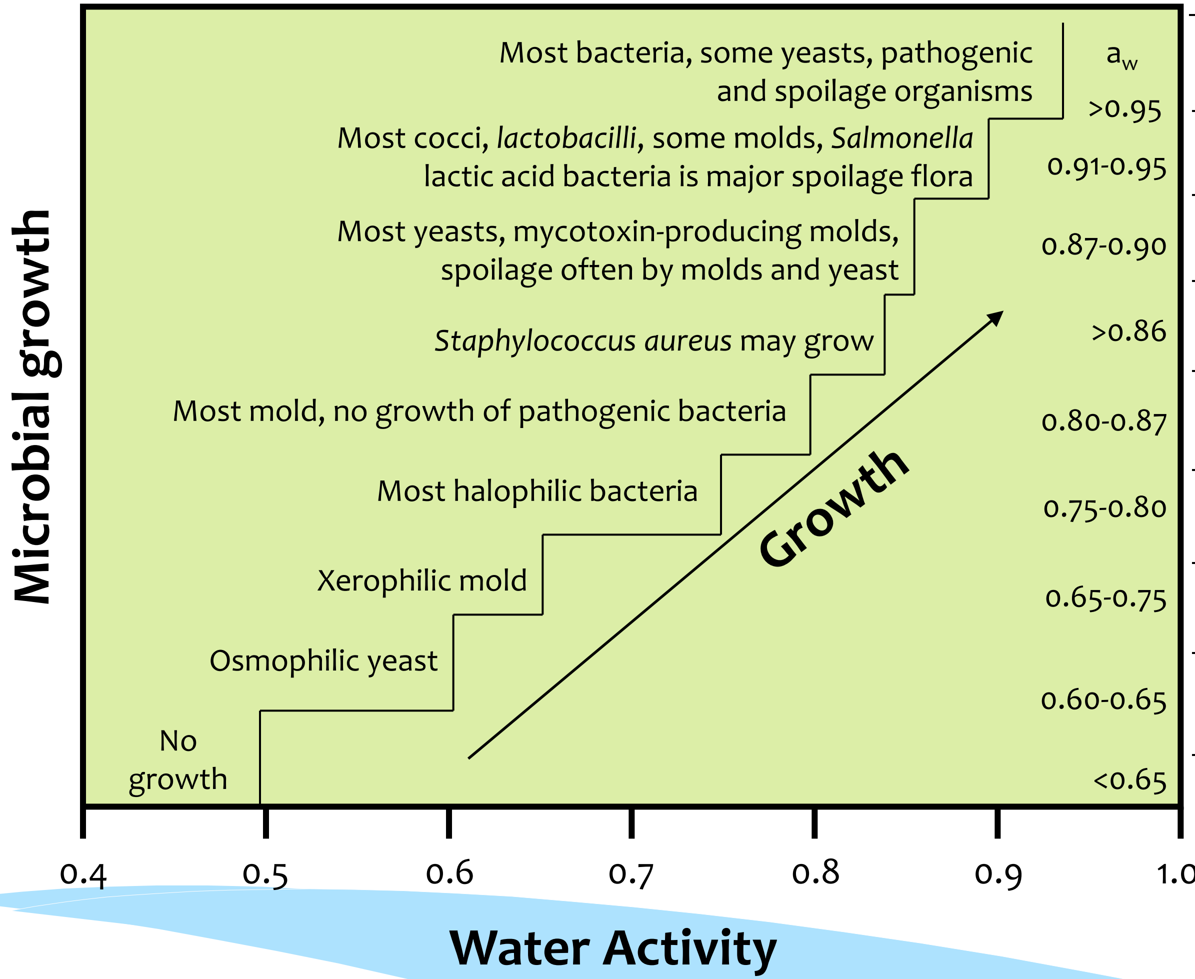
Laju Reaksi pada Produk Pangan Akibat Perubahan Aktifitas Air



Pentingnya aktifitas Air (A_w)

- Mempengaruhi pertumbuhan mikroba
  - Pada A_w rendah (<0.6): Menghambat pertumbuhan mikroba
  - Pada A_w tinggi (>0.6): mikroba tumbuh (semakin tinggi A_w, semakin mudah mikroba tumbuh)
- Mempengaruhi keawetan produk pangan
  - Produk pangan dengan A_w>0.95 mudah rusak
- Mempengaruhi tingkat resiko keamanan produk pangan
  - Semakin tinggi A_w, semakin beresiko

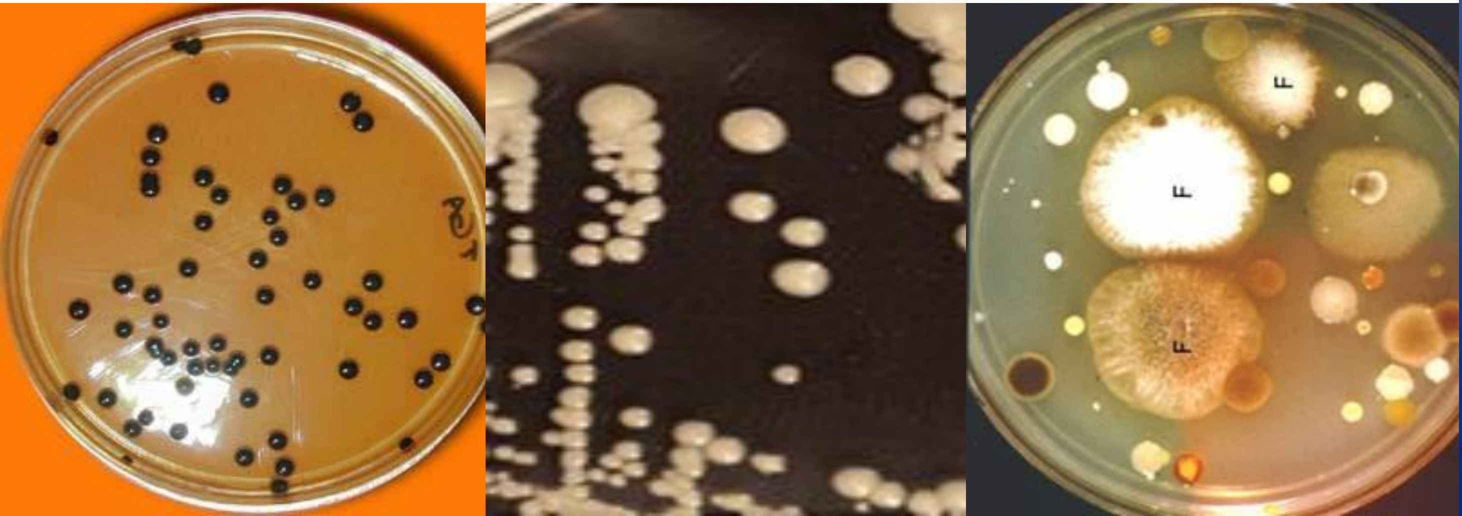
Hubungan Antara aktifitas Air Dengan Pertumbuhan Mikroba Pada Berbagai Produk Pangan



	a_w	
Most bacteria, some yeasts, pathogenic and spoilage organisms	>0.95	**Fresh meat, fish, vegetables, etc. Foods with <40% (w/w) sucrose or <7%(w/w) NaCl**
Most cocci, *lactobacilli*, some molds, *Salmonella* lactic acid bacteria is major spoilage flora	0.91-0.95	**Bread, cooked sausages, medium aged cheese**
Most yeasts, mycotoxin-producing molds, spoilage often by molds and yeast	0.87-0.90	**Salami, old cheese, foods with 65% (w/w) sucrose or 15% NaCl**
Staphylococcus aureus may grow	>0.86	**Dried beef, sweet condensed milk, cereals with 15% water**
Most mold, no growth of pathogenic bacteria	0.80-0.87	**Jam, marmalade, old salami, foods with 26% (w/w) NaCl**
Most halophilic bacteria	0.75-0.80	**Flour, cereals, nuts**
Xerophilic mold	0.65-0.75	**Caramels, honey**
Osmophilic yeast	0.60-0.65	**Breakfast cereals, snack foods, food powders**
No growth	<0.65	

Aktifitas Air vs Pertumbuhan Mikroba

- Bakteri (0.91)
  - Bakteri halofilik (0.75)
- Khamir (0.88)
  - Khamir osmofilik (0.60)
- Kapang (0.80)
  - Kapang Serofilik (0.65)



Faktor yang mempengaruhi pertumbuhan mikroba

Mikroorganisme	Suhu (^oC)	pH	A_w
Vibrio cholerae O1	8 - 42	6 - 9.6	>0.95
Vibrio parahaemolyticus	12.8 - 40	5 - 9.6	> .94
Clostridium perfringens	6 - 52	5.5 - 8	> .93
Bacillus cereus	10 - 49	4.9 - 9.3	> .95
Escherichia coli	2.5 - 45	4.6 - 9.5	> .935
Streptococcus pyogenes	> 10 - < 45	4.8 - < 9.2	NR

A_w vs pH

- Aw kritis: 0.85
- pH kritis: 4.6

Clostridium botulinum

- Resiko bahan pangan:
  - Resiko rendah (*low risk*): pH<4.6, A_w<0.85

    Contoh: Produk kering dengan pH rendah
  - Resiko sedang (*medium risk*): pH<4.6, A_w>0.85 atau pH>4.6, A_w<0.85

    Contoh : Asinan, daging kering, ikan asin, biskuit
  - Resiko tinggi (*high risk*): pH>4.6, A_w>0.85 (*low acid food*): ***Potentially Hazard Foods***

    Contoh: Mie basah, daging/ayam segar, bakso, susu

Pentingnya aktifitas Air (A_w)

- Mempengaruhi tekstur (crispiness, crunchiness), misal produk chips, cracker
  - The sound produced by 'crunching' breakfast cereal disappearing above about A_w = 0.65
- Mempengaruhi kecepatan penggumpalan (aglomerasi) produk yang mudah menyerap air, misal susu bubuk

Pentingnya Aktifitas Air (A_w)

- Mempengaruhi reaksi kimia
  - Oksidasi lemak
  - Reaksi kecoklatan non-enzimatis (reaksi Maillard)
  - Reaksi enzimatis

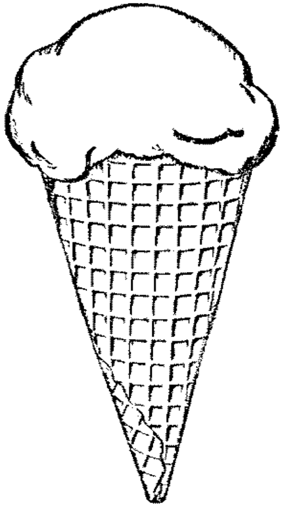
Pentingnya Aktifitas Air (A_w)

- Dalam pengolahan pangan
  - Proses pengeringan
  - Proses pemekatan
  - Proses rehidrasi
  - Penentuan umur simpan: *Accelerated testing method (ASLT)* Metode Kadar Air Kritis

Effect of Water on Physical Properties of Foods

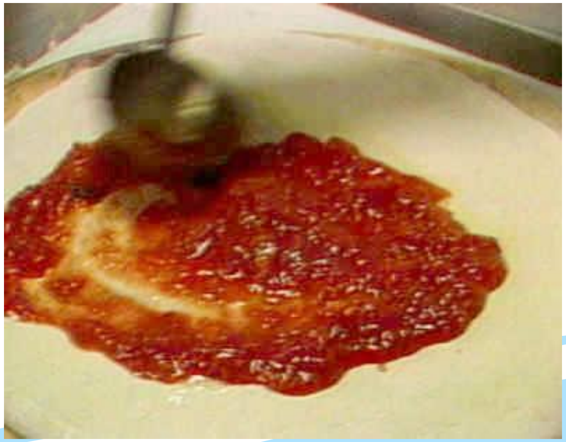
- Physical Properties
  - Texture
  - Moisture migration
  - Powder Flow Properties
  - Caking and Clumping of powders

Physical Properties

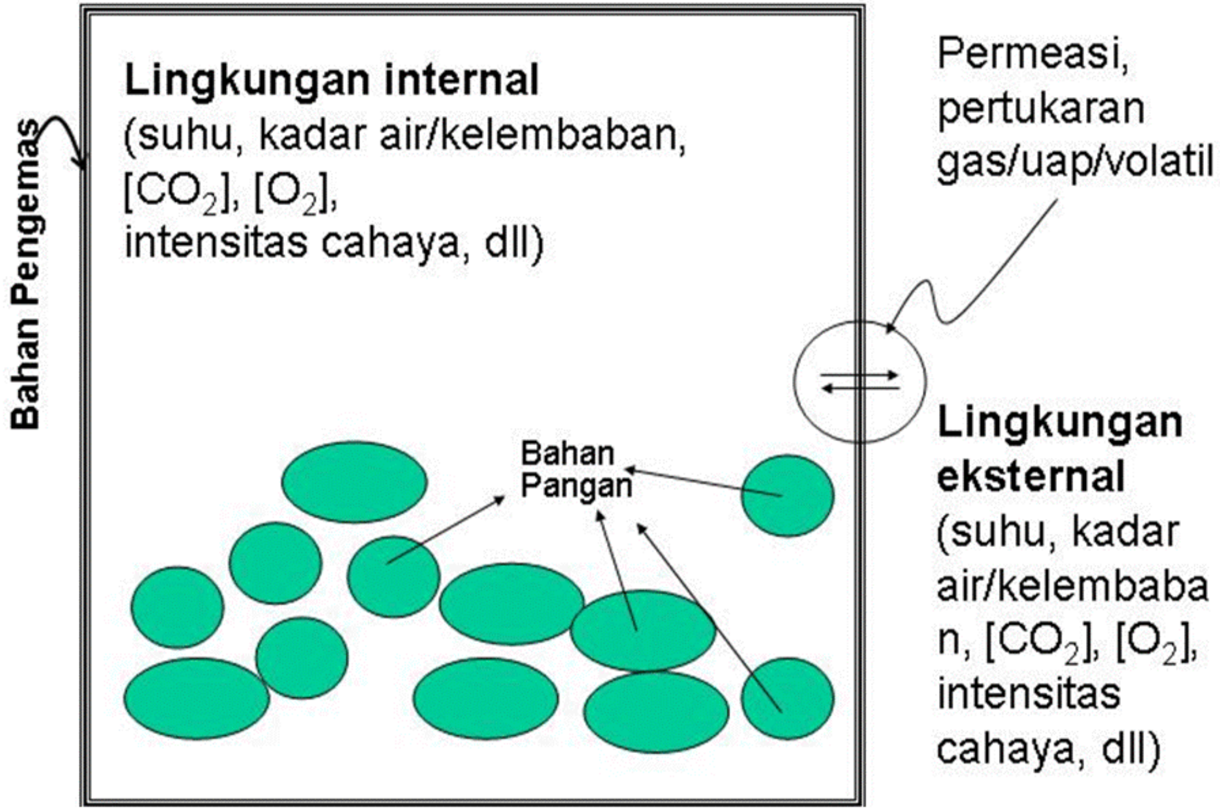


- Moisture migration can lead to:
  - texture changes
  - microbial growth
  - degradation reactions
  - organoleptic changes

- Examples of Multi-domain systems
  - cheese / cracker
  - cereal with fruit pieces
  - baked dough – filling
  - frozen pizza crust – sauce
  - ice cream in cone
  - gelatin capsules



Interaksi antara bahan pangan, pengemas dan lingkungannya selama penyimpanan



Prinsip Penentuan Umur Simpan Berdasarkan Model Kadar Air Kritis; Contoh

- Untuk produk pangan yang relatif mudah rusak akibat penyerapan kadar air dari lingkungan. Misal: Biskuit, chips
- Kerusakan produk didasarkan semata-mata pada kerusakan produk akibat menyerap air dari udara luar hingga mencapai batas yang tidak dapat diterima secara organoleptik.
- Kadar air pada kondisi dimana produk pangan mulai tidak dapat diterima secara organoleptik disebut **Kadar Air Kritis**. Batas penerimaan tersebut didasarkan pada standar mutu organoleptik yang spesifik untuk setiap jenis produk.
- Waktu yang diperlukan oleh produk untuk mencapai kadar air kritis menyatakan umur simpan produk.

Sensitivitas Produk Pangan Kering Terhadap Perubahan Kadar Air

Produk-produk "kering":

- sensitif terhadap perubahan kadar air
- mempunyai karakteristik k.a. kritis :
  k.a. produk (maksimum) dimana mutu produk masih diterima.

Contoh :

Biskuit (kadar air 2% pd RH 10%) pada kondisi RH penyimpanan tertentu :

RH 32%	k.a. 4,5%	Kadar air kritis
RH 44%	k.a. 6,5%	Ka > Ka kritis
RH 90%	k.a. 10%	lembek & berjamur

Sumber :
Feri Kusnandar, Departemen Ilmu dan Teknologi Pangan, Fateta IPB