

INTERDISCIPLINARY (ID)

**CHEMISTRY OF FOOD AND
BEVERAGES**

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❖ WATER ACTIVITY

- Water Activity is the measure of the availability of **water** molecule to enter into **microbial, enzymatic or chemical reactions**
- It can be represented by the symbol a_w
- The availability determines the **shelf life** of food
- Regarding the forms of water, **bound** water is inversely related to water activity
- As the % of **bound** water in a food **increases** the a_w **decreases**



Water activity and sorption isotherm

- The water activity (a_w) of a food is the ratio between the vapor pressure of the food itself, when in a completely undisturbed balance with the surrounding air media, and the vapor pressure of distilled water under identical conditions.
- A water activity of 0.80 means the vapor pressure is 80 percent of that of pure water. The water activity increases with temperature. The moisture condition of a product can be measured as the equilibrium relative humidity (ERH) expressed in percentage or as the water activity expressed as a decimal.

Sorption Isotherm

- The food sorption isotherm describes the thermodynamic relationship between water activity and the equilibrium of the moisture content of a food product at constant temperature and pressure.
- Weaker water molecule interactions generate a greater water activity, thus, the product becomes more unstable. Water activity depends on the composition, temperature and physical state of the compounds

- Knowledge of sorption behavior of food is useful in concentration and dehydration processes for two reasons:
- It is of importance in design of the processes themselves; because it has an important impact on the ease or difficulty of water removal, which depends on the partial pressure of water over the food and on the energy of binding of the water in the food.
- Water activity affects food stability and therefore it must be brought to a suitable level at the conclusion of drying and maintained within an acceptable range of activity values during storage.

- Sorption isotherms can be generated from an adsorption process or a desorption process; the difference between these curves is defined as hysteresis, as it is shown in [figure 1](#).

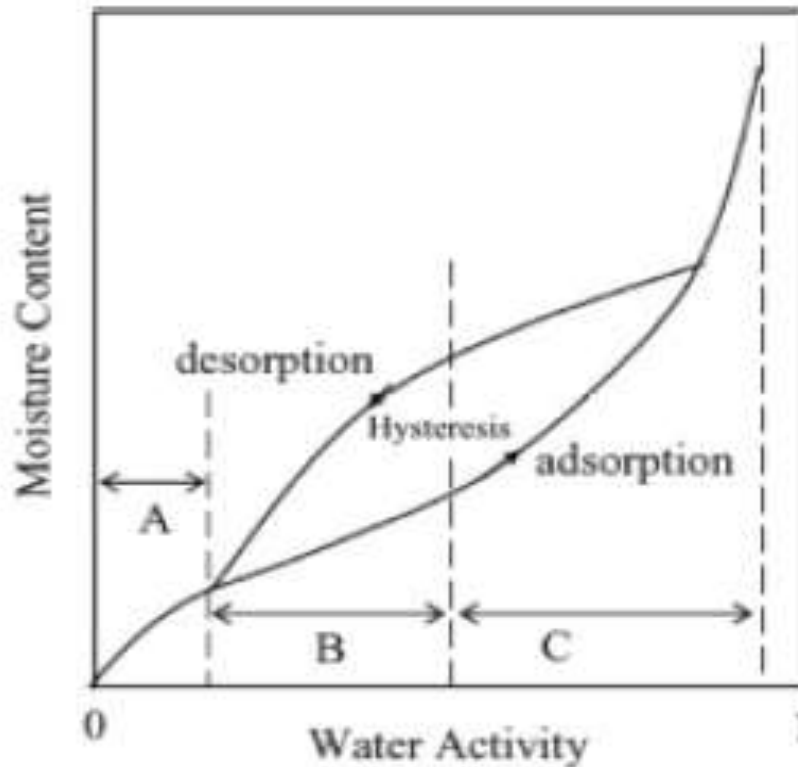


Figure 1. Sorption isotherm for a typical food product, showing the hysteresis.

- An isotherm can be typically divided into three regions;
- The water in region A represents strongly bound water, and the enthalpy of vaporization is considerably higher than the one of pure water. The bound water includes structural water (H-bonded water) and monolayer water, which is sorbed by the hydrophilic and polar groups of food components (polysaccharides, proteins, etc.). Bound water is unfreezable and it is not available for chemical reactions or as a plasticizer.

- In region B, water molecules bind less firmly than in the first zone, they usually present in small capillaries. The vaporization enthalpy is slightly higher than the one of pure water. This class of constituent water can be looked upon as the continuous transition from bound to free water.
- The properties of water in region C are similar to those of the free water that is held in voids, large capillaries, crevices; and the water in this region loosely binds to food materials.

- ❖ a_w is calculated as ratio of the **water vapour pressure** of the **substance divided** by the **vapour pressure** of **pure water** at **same** temperature
- ❖ Vapour pressure can be measured by using a **manometer**

$$a_w = \frac{p}{p_o}$$

where

a_w = water activity

p = vapor pressure of water in a food

p_o = vapor pressure of water at the same temperature

- In simpler terms a_w is a measure of **relative humidity (RH)**
- By multiplying a_w by **100**, the relative humidity (RH) of the atmosphere in equilibrium with the food (RH % or ERH) is obtained
- The **ERH** of a product is defined as the relative humidity of the air surrounding the food at which the product neither gains nor loses its natural moisture & is in equilibrium with the environment

$$\text{RH (\%)} = 100 \times a_w$$

$$a_w = \frac{\text{ERH}}{100}$$



❖ WATER ACTIVITY OF SOME FOODS

FOOD	a_w
Pure water	1
Fresh meat	0.985
Milk	0.97
Bread	0.96
Potato chips	0.80
Flour	0.72
Raisins	0.60
Macaroni	0.45

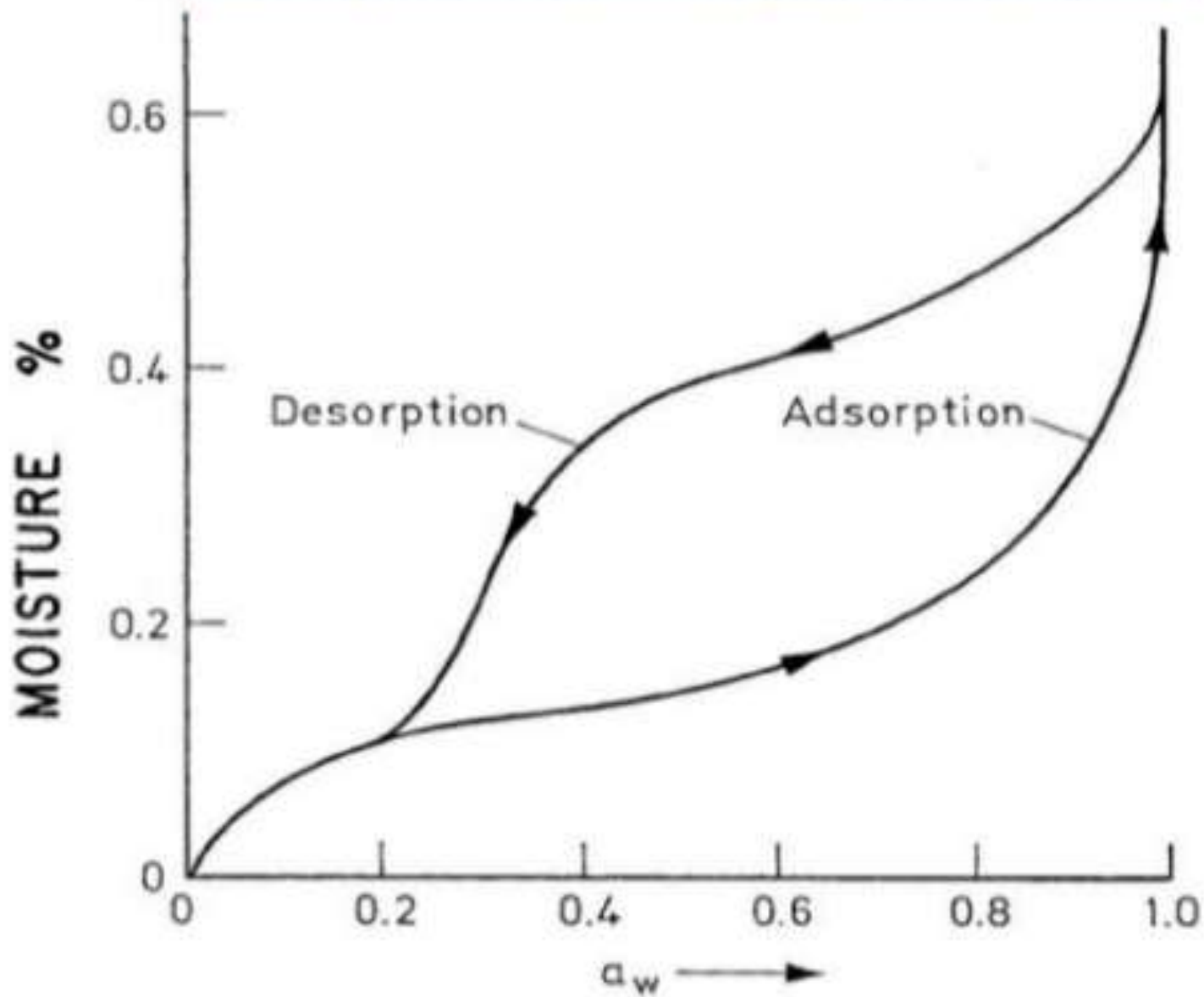
❖ Some foods are stable at **low** moisture content where as others are stable at relatively **high** moisture content

✓ E.g.: **Peanut oil** deteriorates at moisture content **above 0.6%** where as **potato starch** is stable at **20%** moisture

- **Water activity** is related to moisture content in a **non-linear** relationship known as **moisture sorption isotherm curve**
- The relationship between **water content & a_w** is indicated by the **sorption isotherm** of a food
- The plotting of the **uptake** termed **adsorption** or the **loss** of water termed **desorption** provides a record of **a_w** of a particular **food** at a particular **temperature** over **varying** levels of **humidity** in the environment
- The plot of **adsorption** is **not identical** with the plot of **desorption**



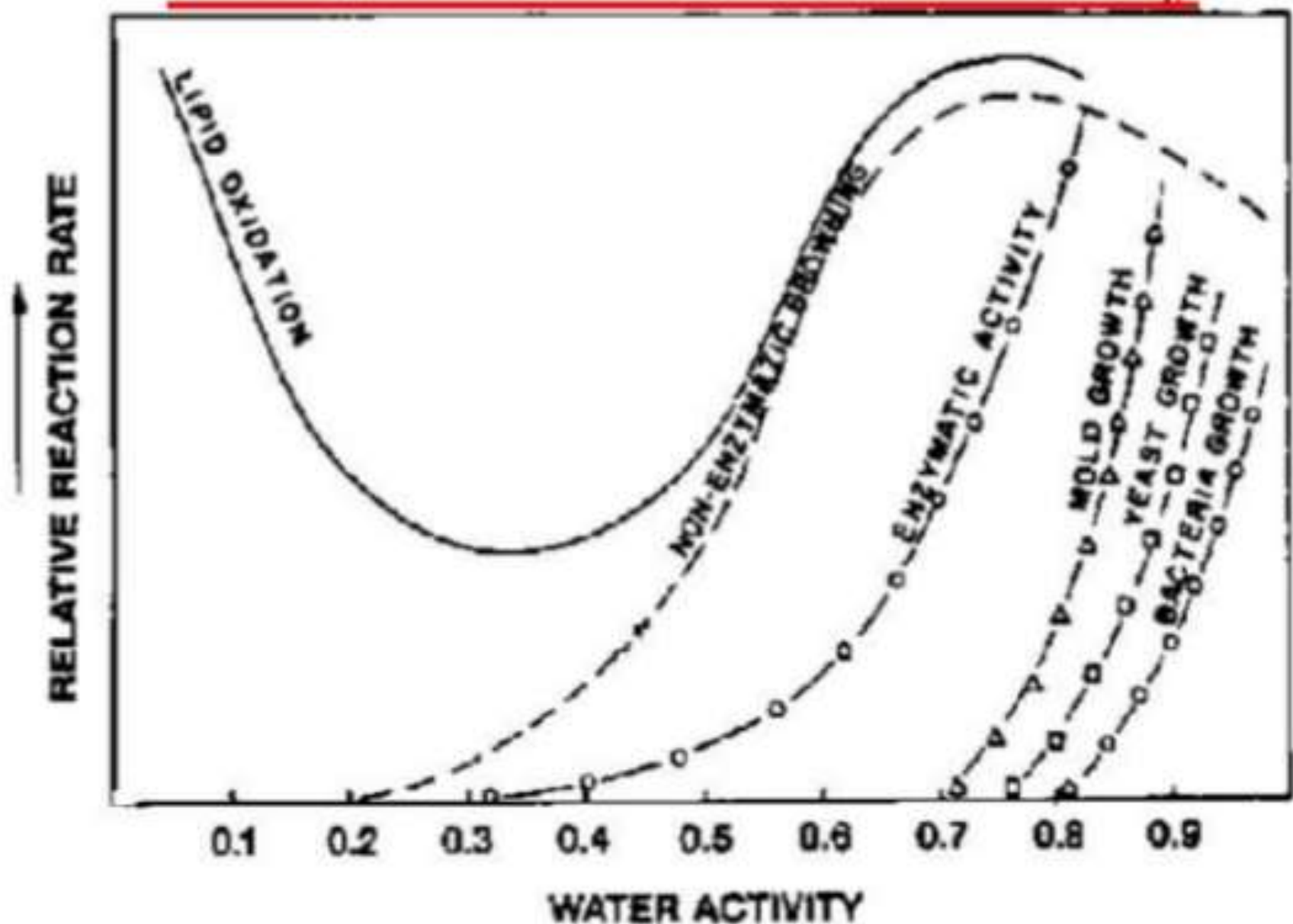
❖ Adsorption & Desorption Isotherms



- ❖ Water activity has an important role in **food preservation**
- Each microorganism has a **critical a_w** below which the growth **cannot** occur
- ✓ For e.g.: **Pathogenic** microorganisms cannot grow at a_w below **0.86**, **Yeast & molds** are tolerant & usually no growth occurs at or below **0.62**
- So a_w is important in foods and it is a major factor in food spoilage & safety
- **Decreased a_w** retards the growth of microorganisms, slows enzyme catalyzed reactions & retards non enzymatic browning
- **Lipid oxidation** rates are **high** in a_w values from a minimum at **0.3 – 0.4** to a maximum at a_w **0.8**



❖ Relationship of Food Deterioration Rate as a Function of Water Activity



- With a_w at **0.3**, the product is most stable with respect to lipid oxidation, non enzymatic browning, enzymatic activity & the various microbial parameters
- As a_w **increases** towards the **right** the probability of the food product **deterioration increases**
- For decreasing a_w & thus improving the **shelf life** of food is by the use **additives** with high water binding capacity (**humectants**)
- In addition to common salt, glycerol, & sucrose have the potential as humectants

Molecular mobility

- The **molecular mobility**, Mm (also known as the **glass transition** or **polymer science**) approach is a recent development (1980s) in food science designed to explain how freezing and drying change the storage stability of foods and is an alternative and complementary method to the older water activity (a_w)-moisture sorption ideas.

- The key concept is that most food materials do not form crystalline structures. To join in a crystal, the molecule in solution must slot into an existing lattice, rather like a jigsaw piece, it can only fit in at one orientation.
- Molecules rotate and flex in solution but they must be able to do so fast enough to form crystals before all the water leaves and movement stops.
- In relatively slow drying operations of small molecules crystals may have a chance to form: table sugar and salt are largely crystalline. However, large slow moving molecules or fast drying operations do not provide time for the crystals to grow and practically, in most cases crystals do not form.

- Instead, the solution becomes very viscous and eventually behaves like a **rubber**.
- The molecular mobility of a material is inversely related to its viscosity (if the molecules don't move much the liquid is thicker) and viscosity affects the rate of diffusion limited reactions.
- For a reaction between two molecules to occur, the molecules must first collide and then have enough thermal energy to overcome the activation energy barrier to reaction.

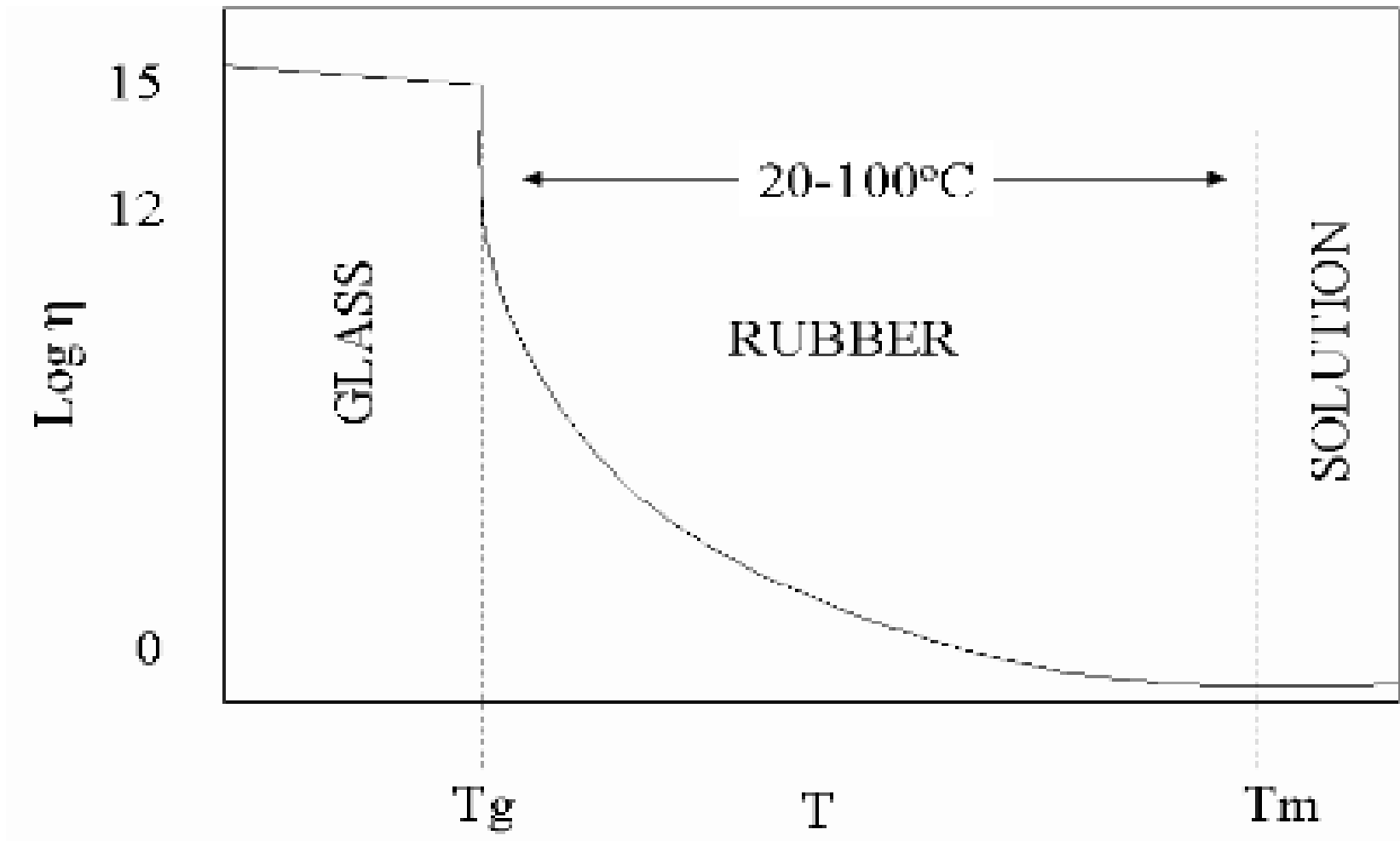
- Either factor may limit the kinetics of the process but in this case we are only concerned with diffusion limited reactions.
- **Smolowkowski kinetics** gives the rate of a diffusion limited reaction as follows, here stated for the reaction between two identical molecules:

$$k_{diff} = \frac{2 \pi N_A D^2 r}{1000}$$

- The diffusion coefficient is a parameter describing the capacity of a solute to diffuse in a solvent and can be calculated using the **Stokes-Einstein** equation:

$$D = \frac{kT}{6 \pi \eta r}$$

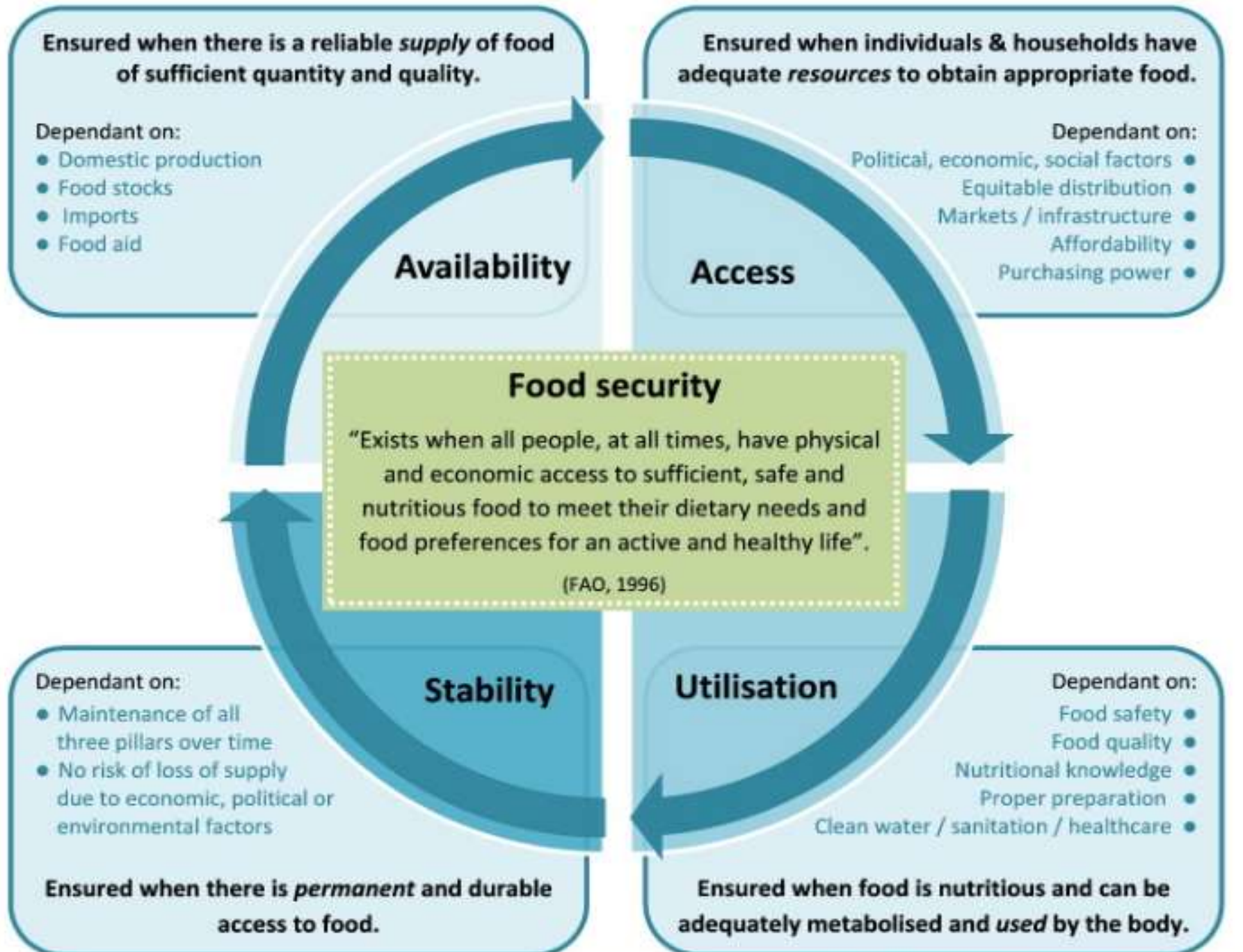
- A way to get a more quantitative understanding of this is to consider how the viscosity of a food sample changes as it is cooled



Food Stability

- Foods are physicochemical systems in which a number of phases and chemical compounds can coexist in a metastable condition (that is, far from true thermodynamic equilibrium), and in the presence of microbes, whose metabolism may cause significant modifications of the chemical composition and physical properties of the hosting product.
- For this reason, food science not only deals with protection from external chemical, physical, and microbial injuries

- (for example, through the use of suitable additives or packaging), but also investigates the intrinsic causes of food instability,
- such as phase separations of dispersed systems, phase transitions (which mainly concern food polymers, such as starch, gluten and other proteins, and fats), enzymatic reactions (often related to the “endogenous” microbial agents), and
- preparation procedures (such as cooking, extruding, and freezing), all of which can profoundly modify the nutritional and sensory properties of the product.



- **Food stability** refers to the ability to obtain food over time.
- Food insecurity can be transitory, seasonal, or chronic.
- In transitory food insecurity, food may be unavailable during certain periods of time.
- At the food production level, natural disasters and drought result in crop failure and decreased food availability.
- Civil conflicts can also decrease access to food.
- Instability in markets resulting in food-price spikes can cause transitory food insecurity.

- Other factors that can temporarily cause food insecurity are loss of employment or productivity, which can be caused by illness.
- Seasonal food insecurity can result from the regular pattern of growing seasons in food production.
- Chronic (or permanent) food insecurity is defined as the long-term, persistent lack of adequate food.

- In this case, households are constantly at risk of being unable to acquire food to meet the needs of all members.
- Chronic and transitory food insecurity are linked, since the reoccurrence of transitory food security can make households more vulnerable to chronic food insecurity.