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Estimation of water equilibrium properties in food processing

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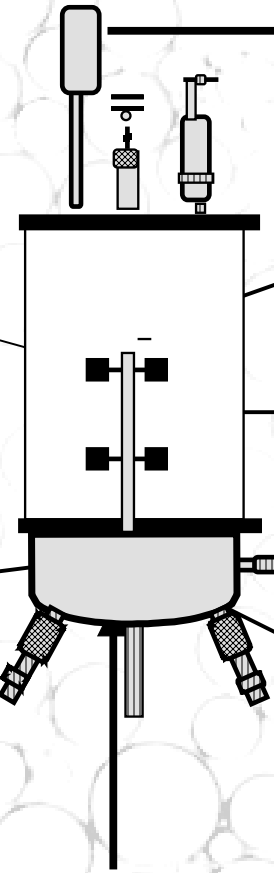
Equilibrium properties: for what ?

- Analysis and design of processes
  - material balances
  - operating conditions- scale up
  - yields determination- losses
  - modeling and simulation
- Food control
- Food formulation (recipe)
  - What if ?

A typical aerobic culture process



Gases (O_2, CO_2, N_2, ethanol, ..

Macromolecules

Proteins
Polysaccharides

Weak electrolytes

Amino acids (glutamic acid...)
Carboxylic acids (lactic acid...)
Weak inorganic acids (H_3PO_4)

Water

Non electrolytes

Sucrose, glucose,
Ethanol

Strong electrolytes

Salts (NaCl)
Bases (NaOH)
Acids (HCl)

Gases (O_2, N_2...)

Which thermodynamic properties ?

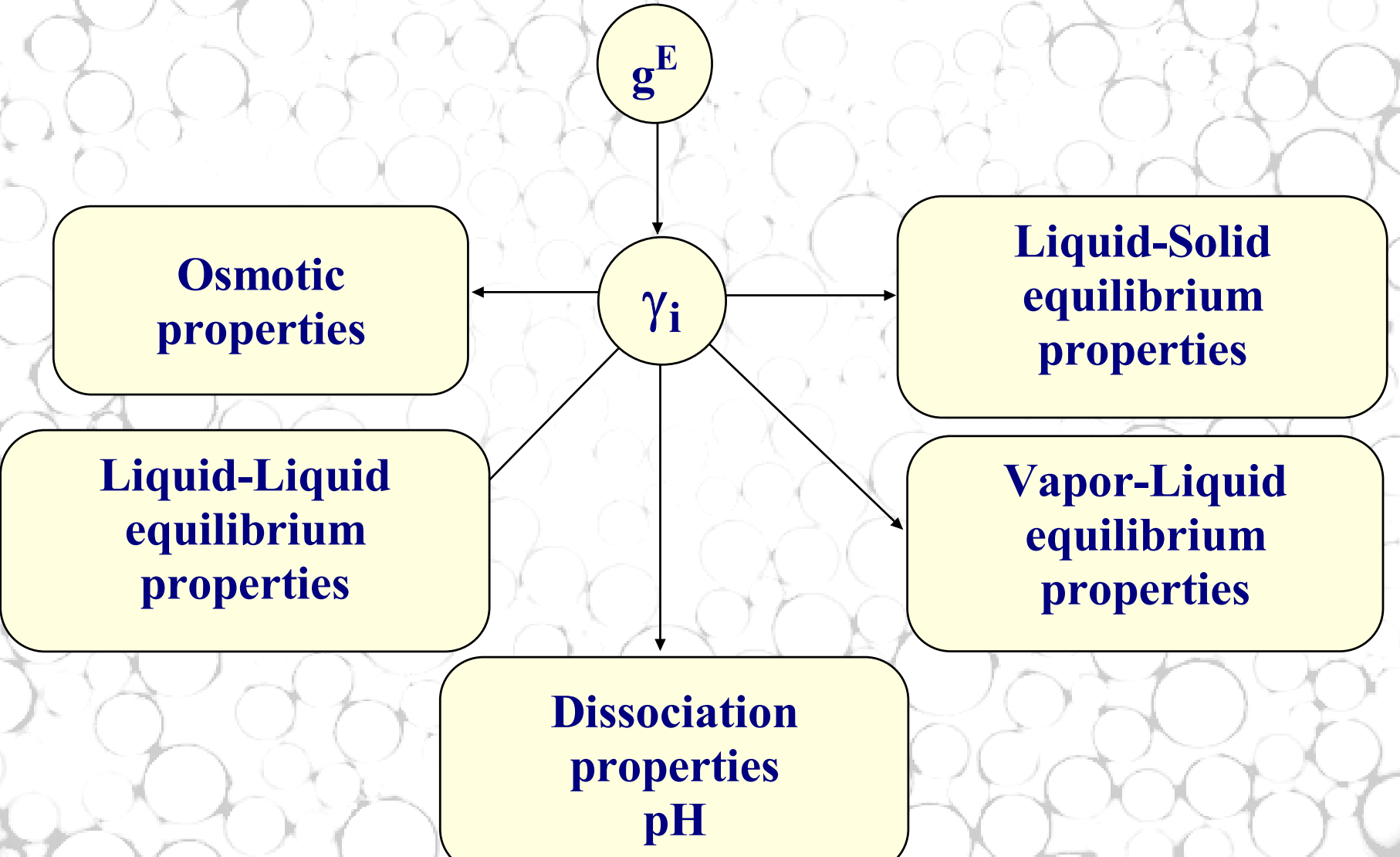
- Solubility of gases
- Partition coefficients
- Solubility of dissolved compounds in water

→ Representation of physical equilibrium

- Activity of dissolved species
- Water activity
- Osmotic pressure
- pH

→ Representation of chemical equilibrium

Thermodynamic properties derived from excess Gibbs energy



Selected model : γ_i

U L P D H S

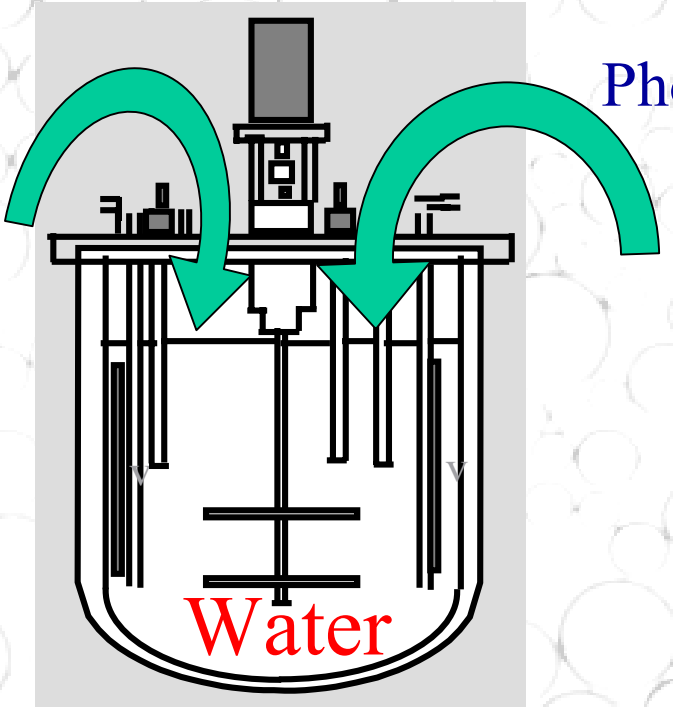
Unifac Larsen Pitzer Debye Hückel Solvation

- A predictive model UNIFAC (1975)
  Group contribution method
- Larsen modification (1987) for short range interactions
- Long range interactions : Pitzer term (Debye-Hückel)
- Solvation of ions by water molecules

No salt dependent coefficients
Only ions or group dependent coefficients

Example : elementary bioconversion medium

Glucose



Phosphate buffer

$K_2 H PO_4$

$K H_2 PO_4$

Groups

5 OH

4 CH + H_2O

1 CH_2

1 CHO

Ions and molecules

H^+, OH^-, K^+

H_3PO_4

$H_2PO_4^-$

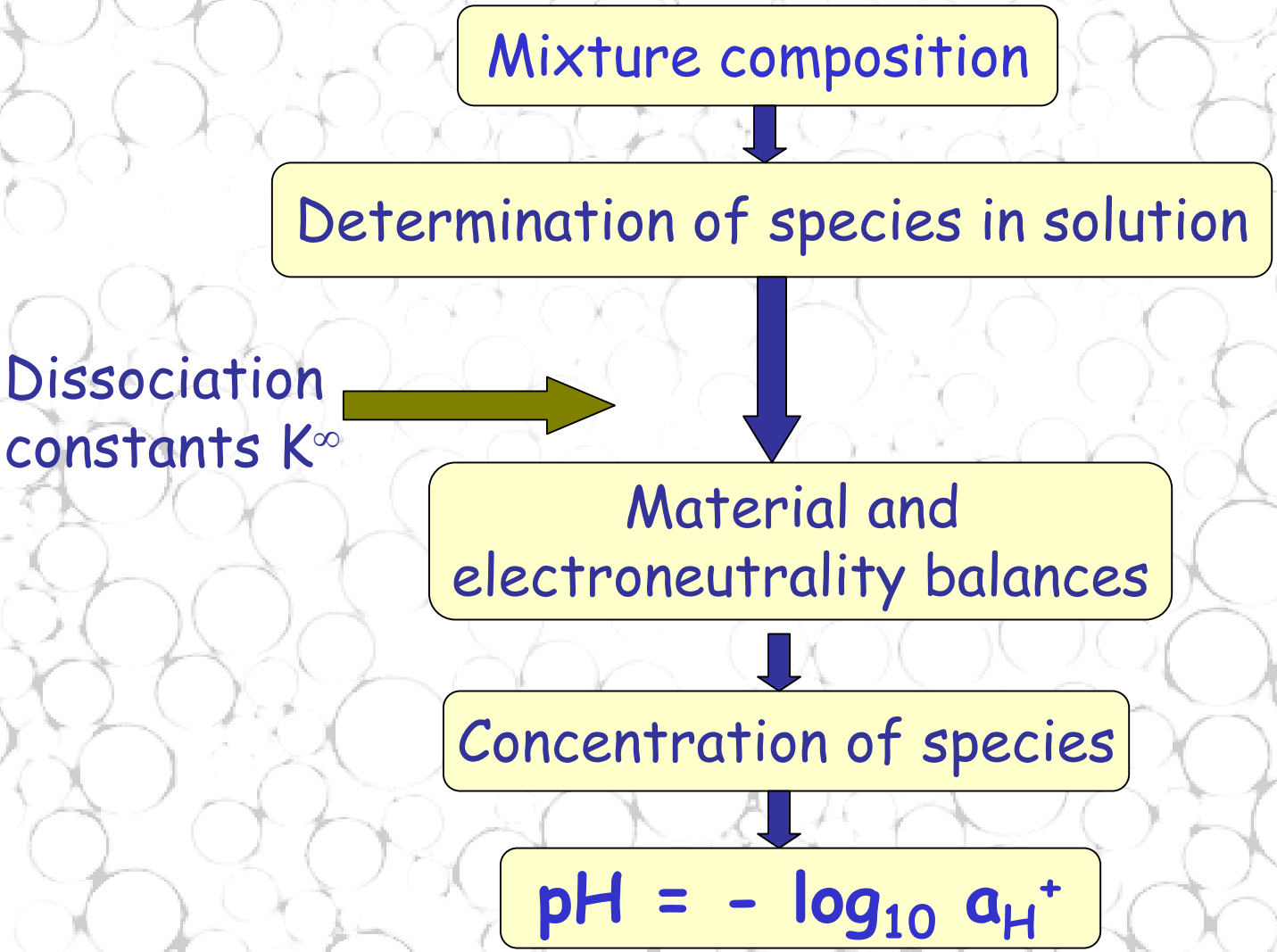
$H PO_4^{--}$

PO_4^{3-}

Coefficients of the model

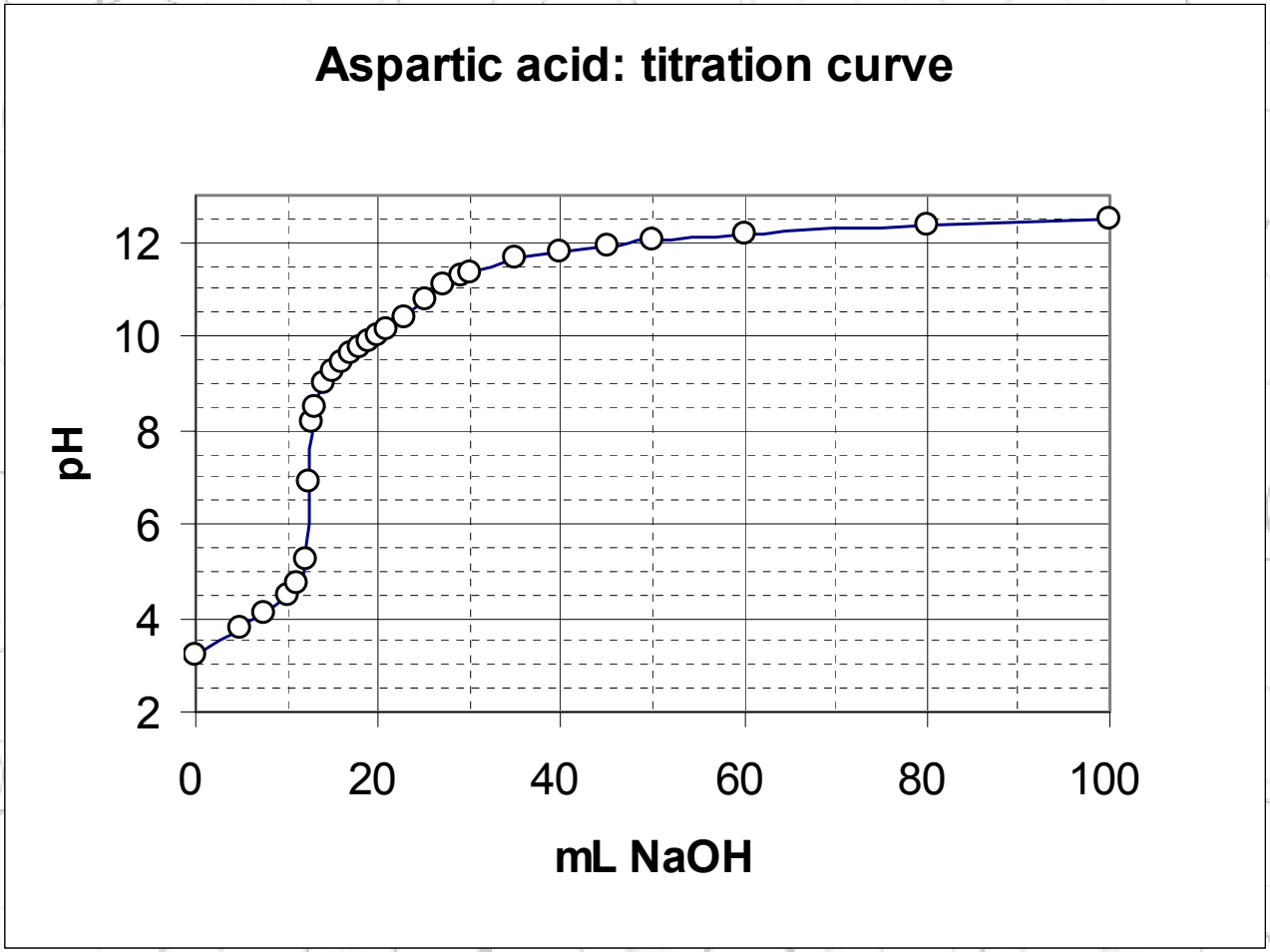
- Interactions energies between
  - ions and water
  - ions and groups...
- Hydration number of each ion

pH estimation

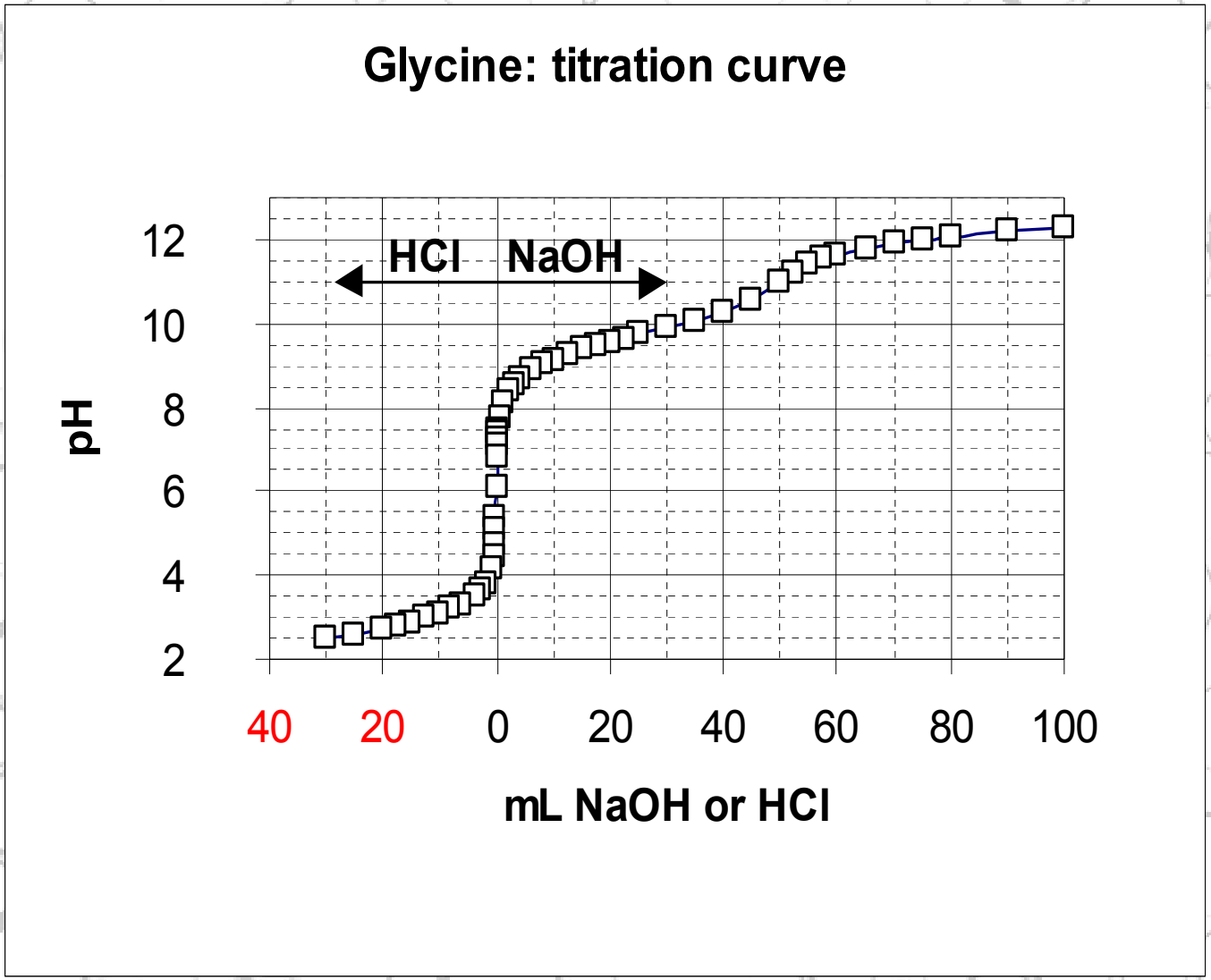


Achard et al., AIChE J. 1994, 40, 1210-1221

Performance

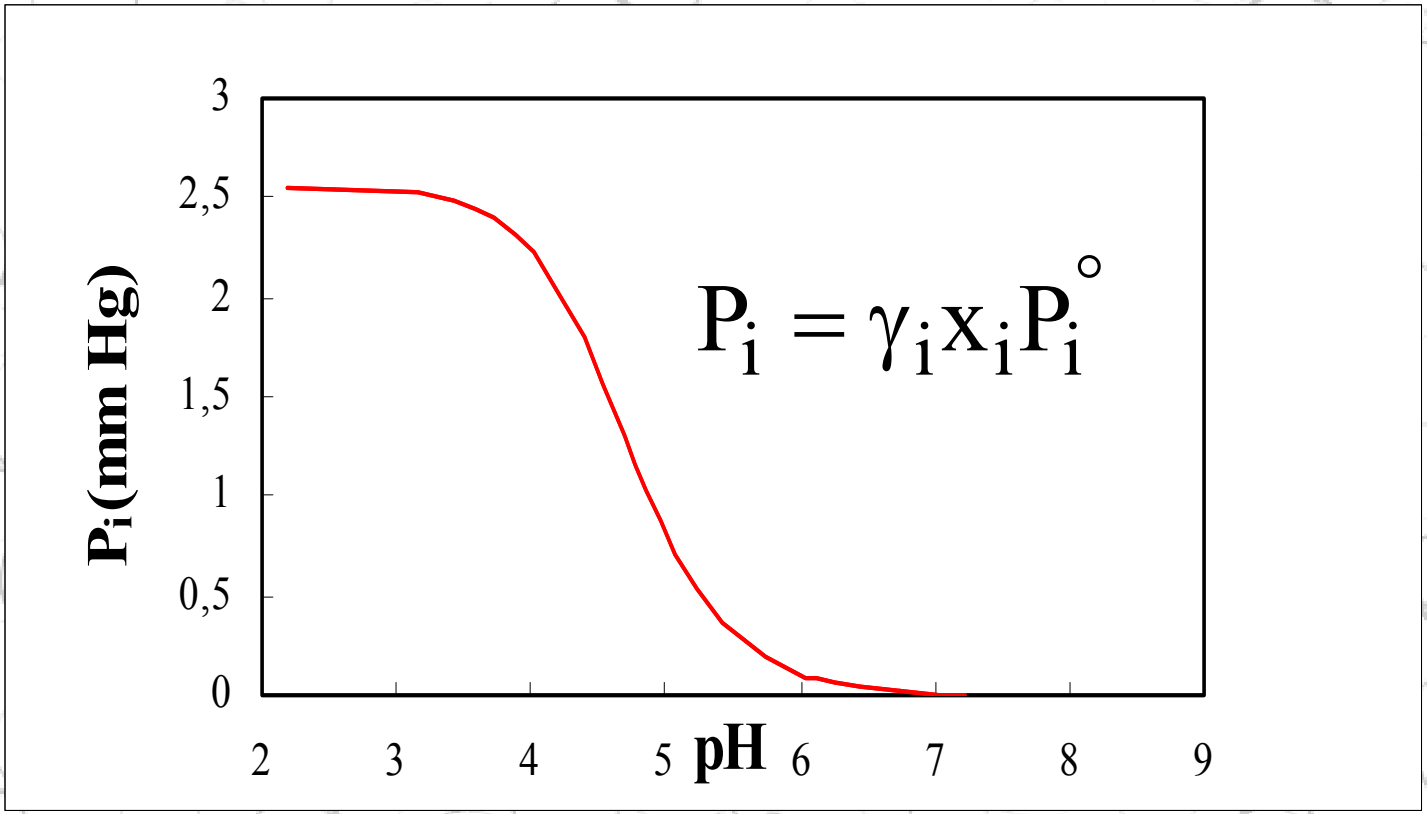


Performance



Vinegar production process

Partial pressure of acetic acid



NaOH-acetic acid 2M-water solution at 25°C.

Ould-Moulaye et al., R. Prog. G.P., 1999, 13, 35-42

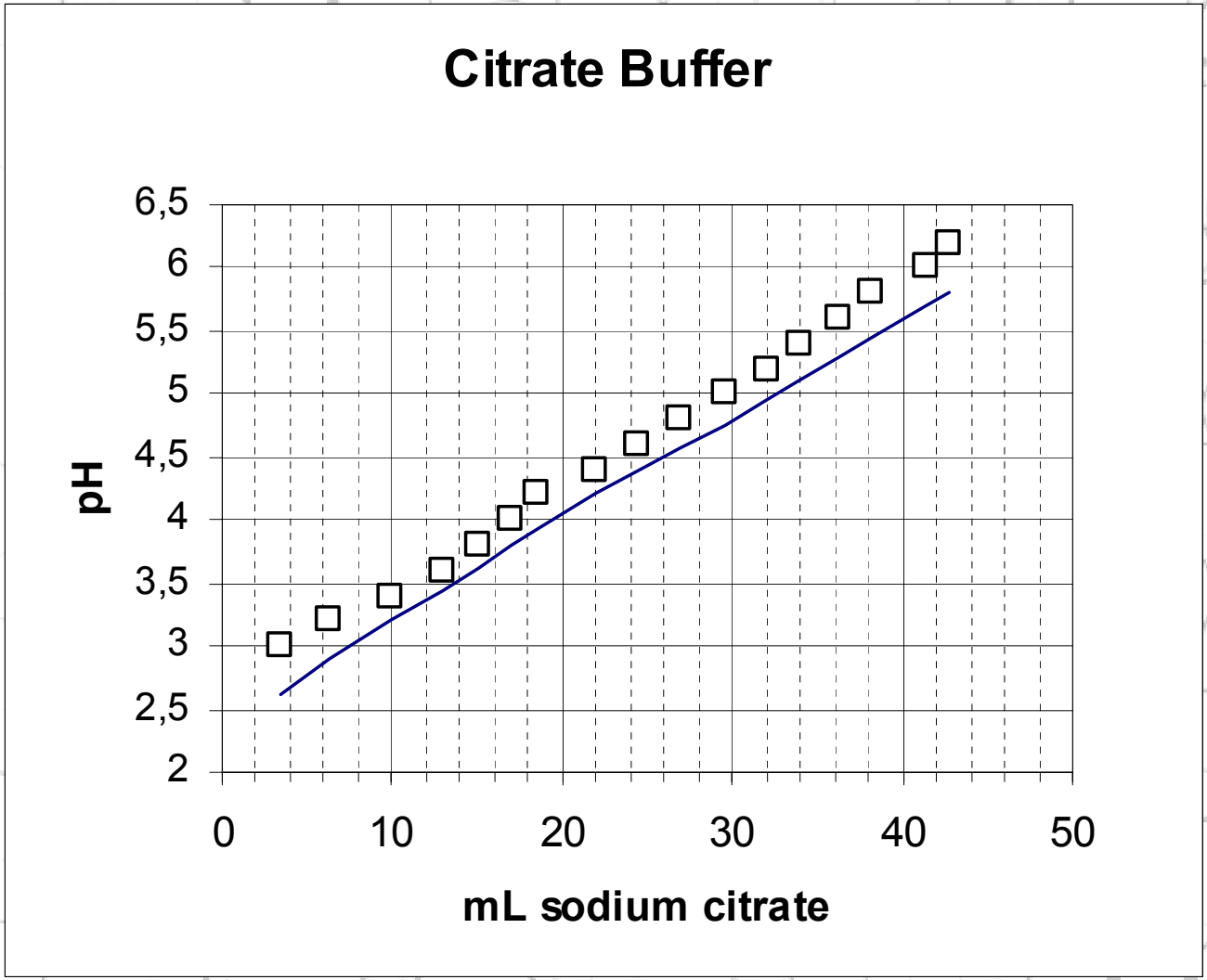
Vinegar production: VOCs pollutants

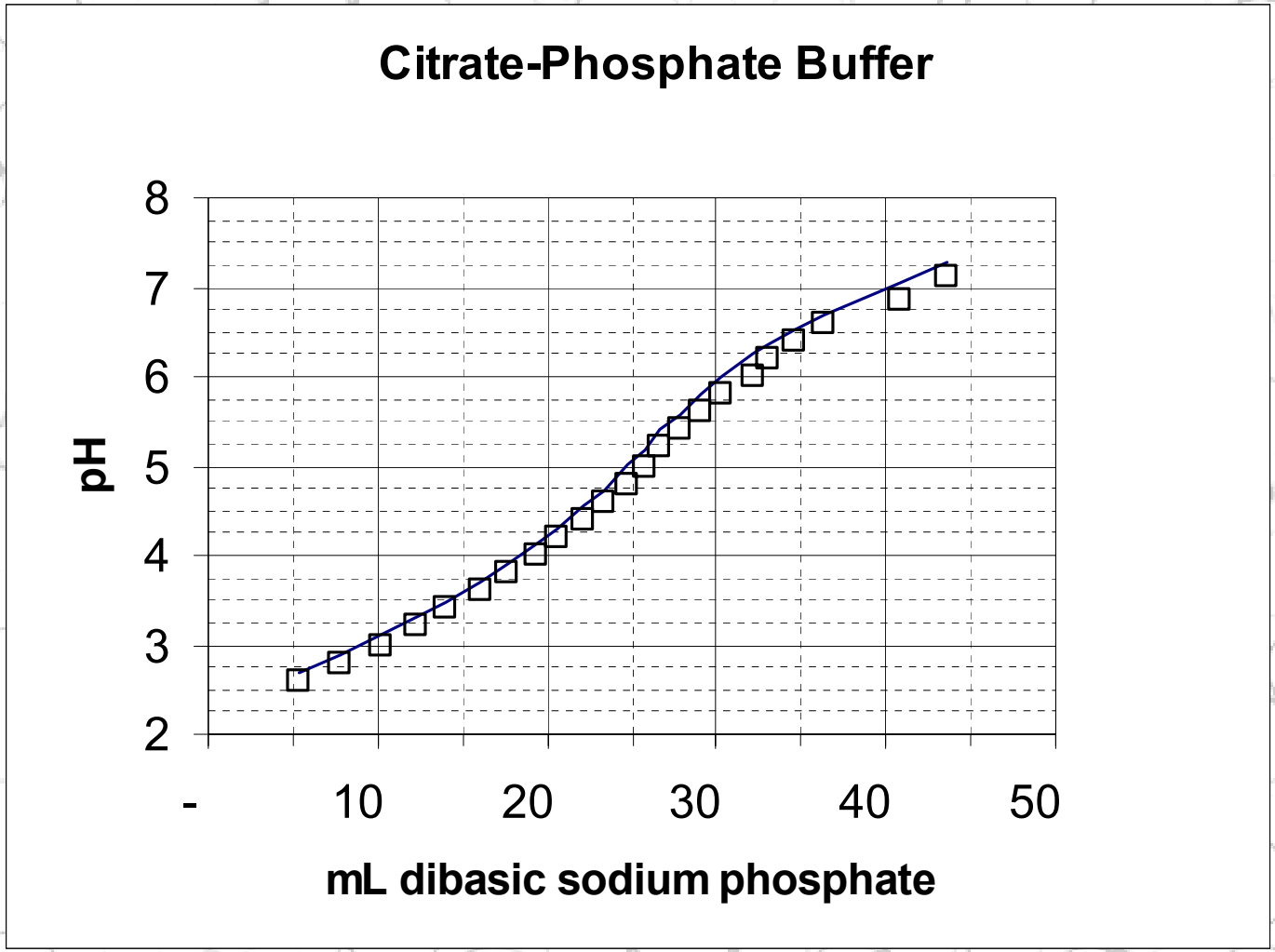
Component	Concentration ($g.L^{-1}$)	$K_i^{LV} = \gamma_i \frac{P_i^o}{P}$
Water	to 1.000 L	
Ethanol	16.0	0.38
Acetic acid	120.0	0.075
Frings salts	1.7	
glucose	1.0	0.
Ethyl acetate	0.05 - 0.3	10.3
Acetaldehyde	0 - 0.2	3.28

pH = 2.15

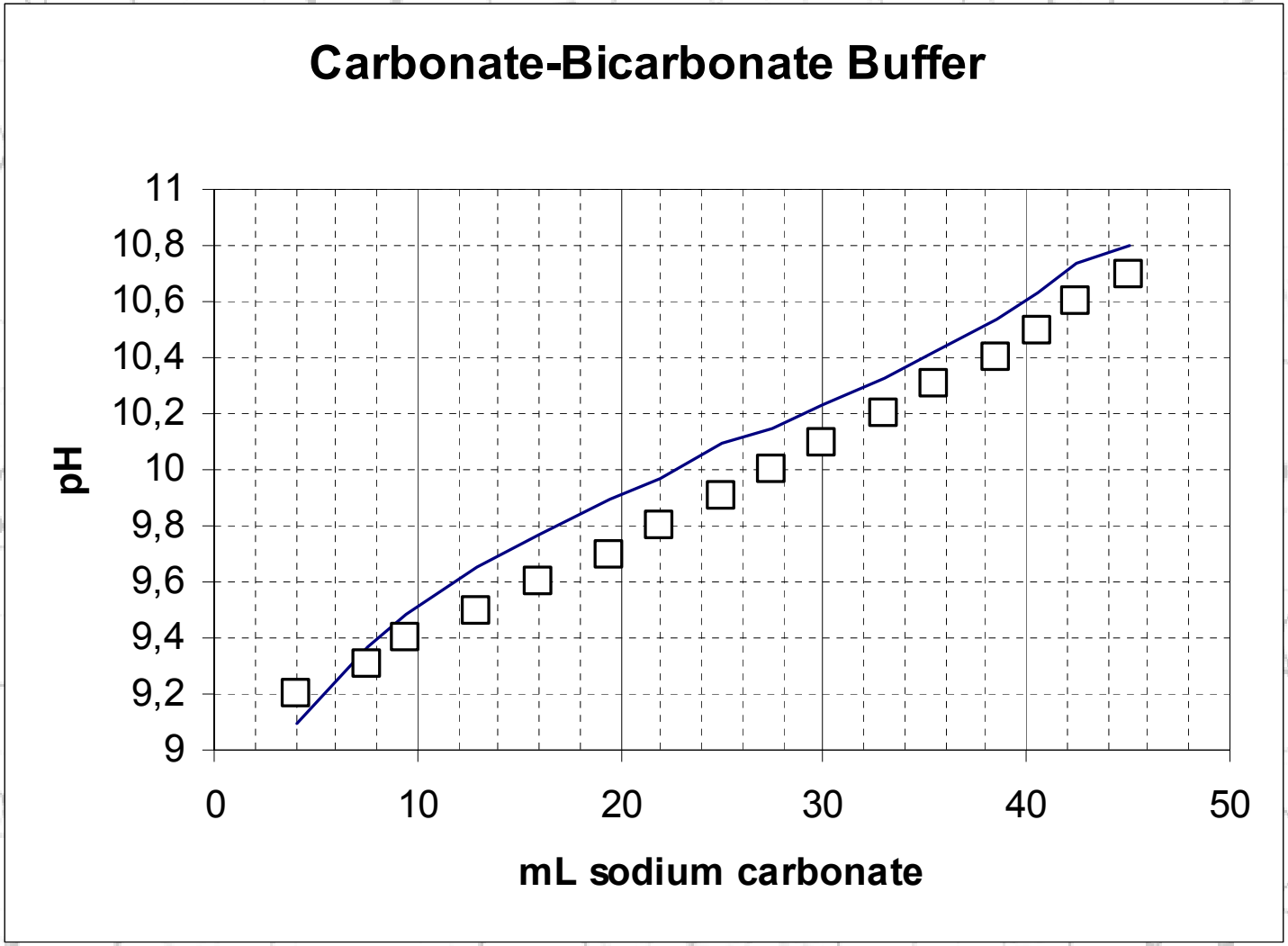
$$y_i = K_i^{LV} x_i$$

Additives: acidulant




Citrate-Phosphate Buffer
pH
8
7
6
5
4
3
2
-
10
20
30
40
50
mL dibasic sodium phosphate

Carbonation of drinks



High-energy drink

Components	Concentration ($mmol.L^{-1}$)	
Total sugars (glucose, sucrose, fructose)	232	$pH_{cale} = 8.2$
NaCl	12	$pH_{exp} = 8.3$
Magnesium lactate	0.62	
Calcium bicarbonate	2.00	$a_w = 0.995$
Potassium gluconate	0.85	

Composition of bovine milk

Component	Concentration ($g.L^{-1}$)	
Water	902	
Lactose	49	
Proteins	32	
Caseins		26
Whey proteins		6
Lipids	38	
Saturated fatty acids		
• soluble in water		1.9-3.4
• non soluble in water		19
Unsaturated fatty acids		
• monounsaturated		10.2
• polyunsaturated		0.9
Salts	9	
Calcium		1.23
Sodium		0.5
Potassium		1.51
Magnesium		0.13
Chloride		1.11
Citrate		1.70
Phosphate		1.93
Bicarbonate		0.15

How to tackle

micelles of caseins ?

globules of fat ?

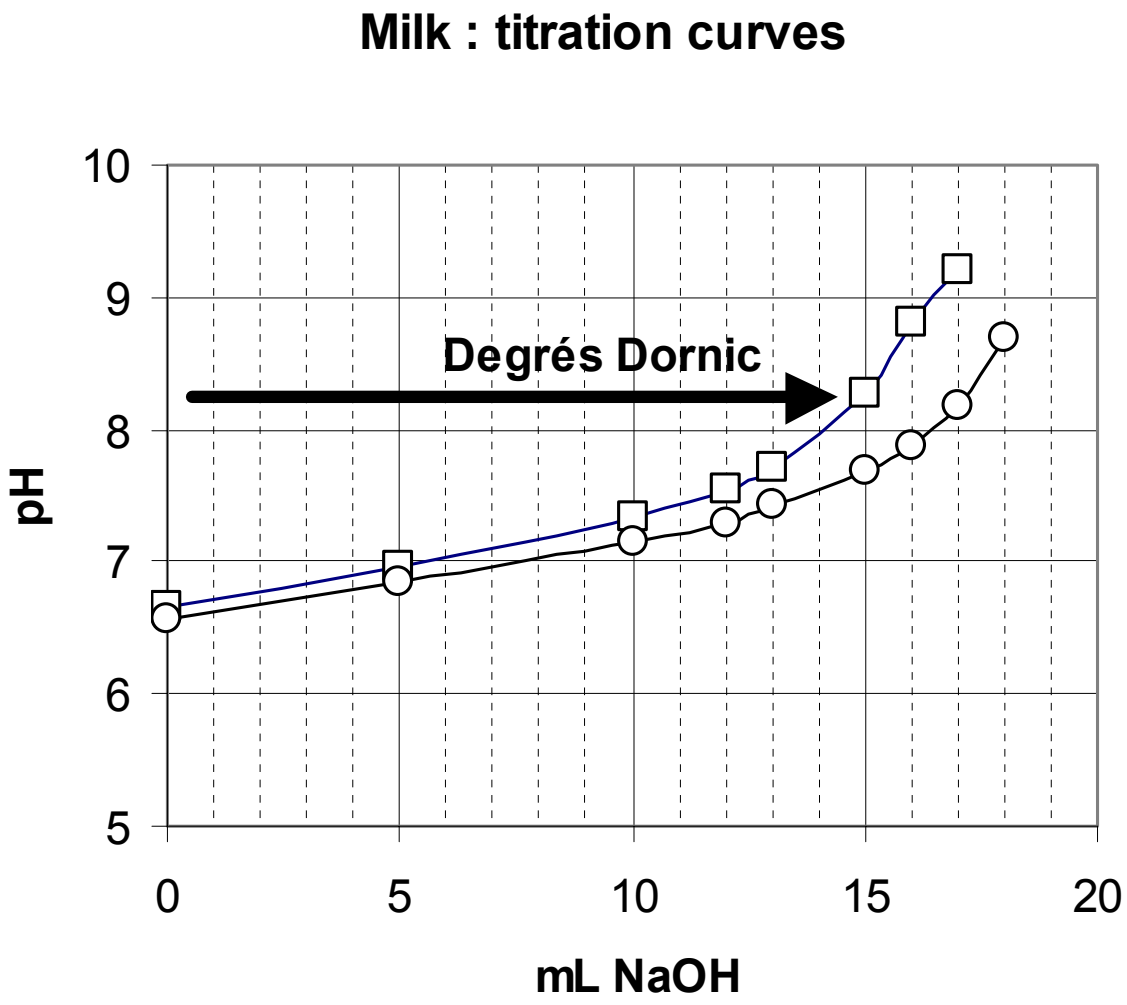
Assumptions

- properties of the plasma phase of milk (skim milk)
- only lipids soluble in water are considered
- ions (Ca,Mg..) interact with amino acids lateral chains of caseins.

Model milk: properties

	Normal cow milk	Model milk 1	Model milk 2
pH	6.6-6.8	6.67	6.57
Osmotic pressure (kPa)	700	750	750
Freezing point depression (K)	0.53-0.57 (mean 0.54)	0.61	0.61
Ionic strengh (molar)	0.08		
Water activity	0.993	0.994	0.994
Acidity (°Dornic)	16-18	15	17

Model milks


Milk : titration curves
10
9
8
7
6
5
pH
Degrés Dornic
0
5
10
15
20
mL NaOH

Conclusion

- Models are presently available and we must use them to estimate physico-chemical properties in biological processes.
- Progress is still necessary to estimate the influence of macromolecules
  - Polysaccharides
  - Proteins

  but we are on the way.