DEN5406: Mass Transfer and Separations Processes I

Week 9: Adsorption, Stripping – continued Ion-Exchange, and Drying

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Separations and Syllabus Goals

Obtain Quantitative Understanding of the following processes:

✔ **Filtration - ✔ we started and continue!** **We'll also cover this week:**

Aggregation

✔ **Centrifugation**

Crystallization (controlled freezing) separation

Adsorption ✔

✔ **Leaching (extracting metals from ores, making coffee, dry cleaning)**

✔ **Osmosis**

- **Forward Osmosis**
- **Reverse Osmosis**

Ion-exchange membranes ✔

Drying ✔

✔ **Distillation (controlled evaporation and condensation)**
and the many kinds of distillation

Applications: Surviving in Space, on a desert island without fresh water

Recommended Reading

Available on Knovel – in the library:
De Haan & Bosch, Industrial Separation Processes, 2013, de Gruyter (Berlin)

Distillation Fundamentals and Principles, Gorak & Sorensen, eds., 2014, Elsevier

Reactive & Membrane-Assisted Separations, Lutze & Gorak, eds., 2016, de Gruyter

Also from
Seader, Henley, & Roper, Separations Process Principles, 2011, Wiley

Will assign pre-class reading -> will have a chance to discuss problems in class

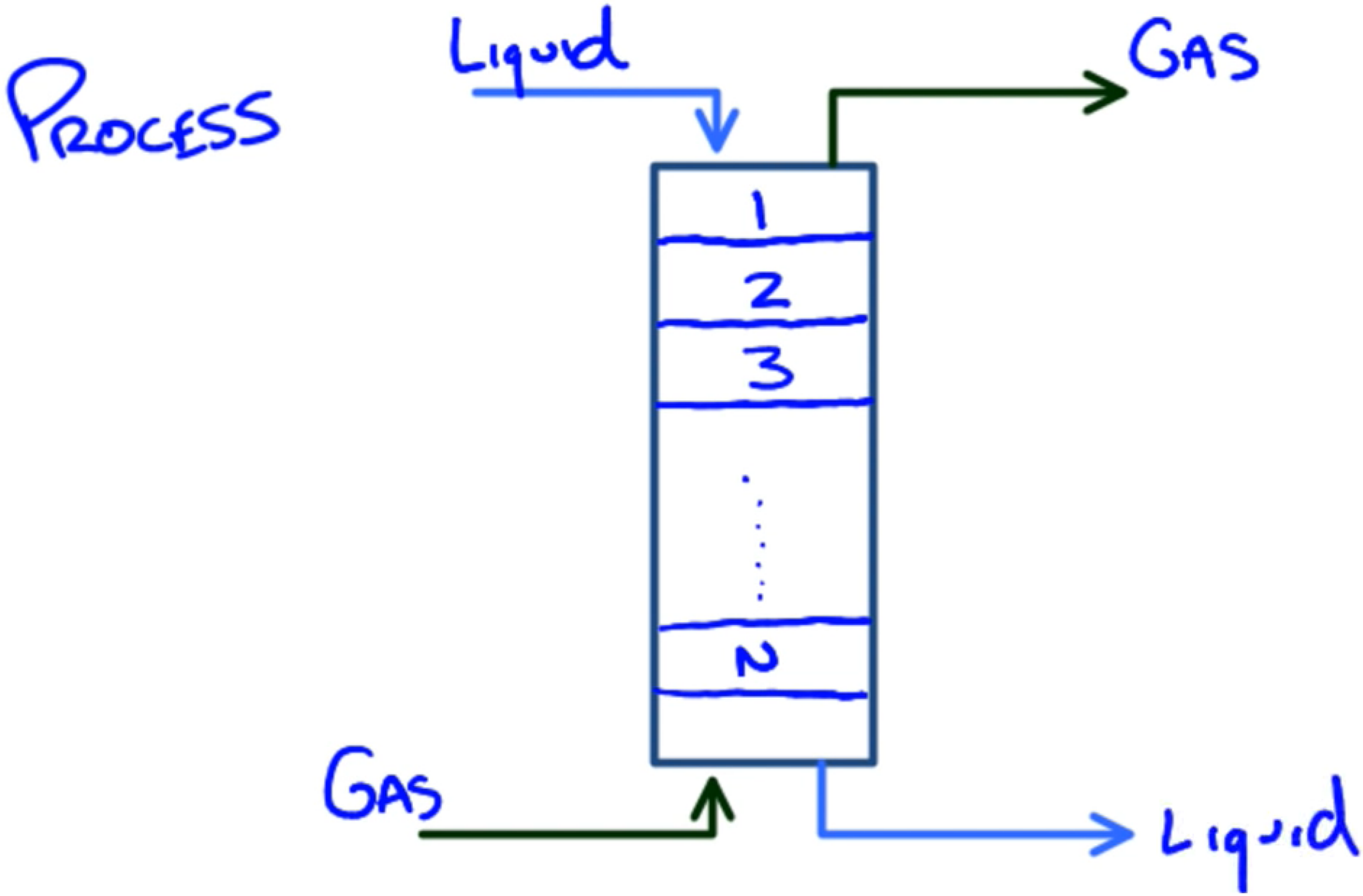
Absorption and stripping:
Ch. 3 in
De Haan & Bosch, Industrial Separation Processes, 2013, de Gruyter (Berlin)

Absorption and Stripping

Way to make Chem E impactful and sexy. And true!

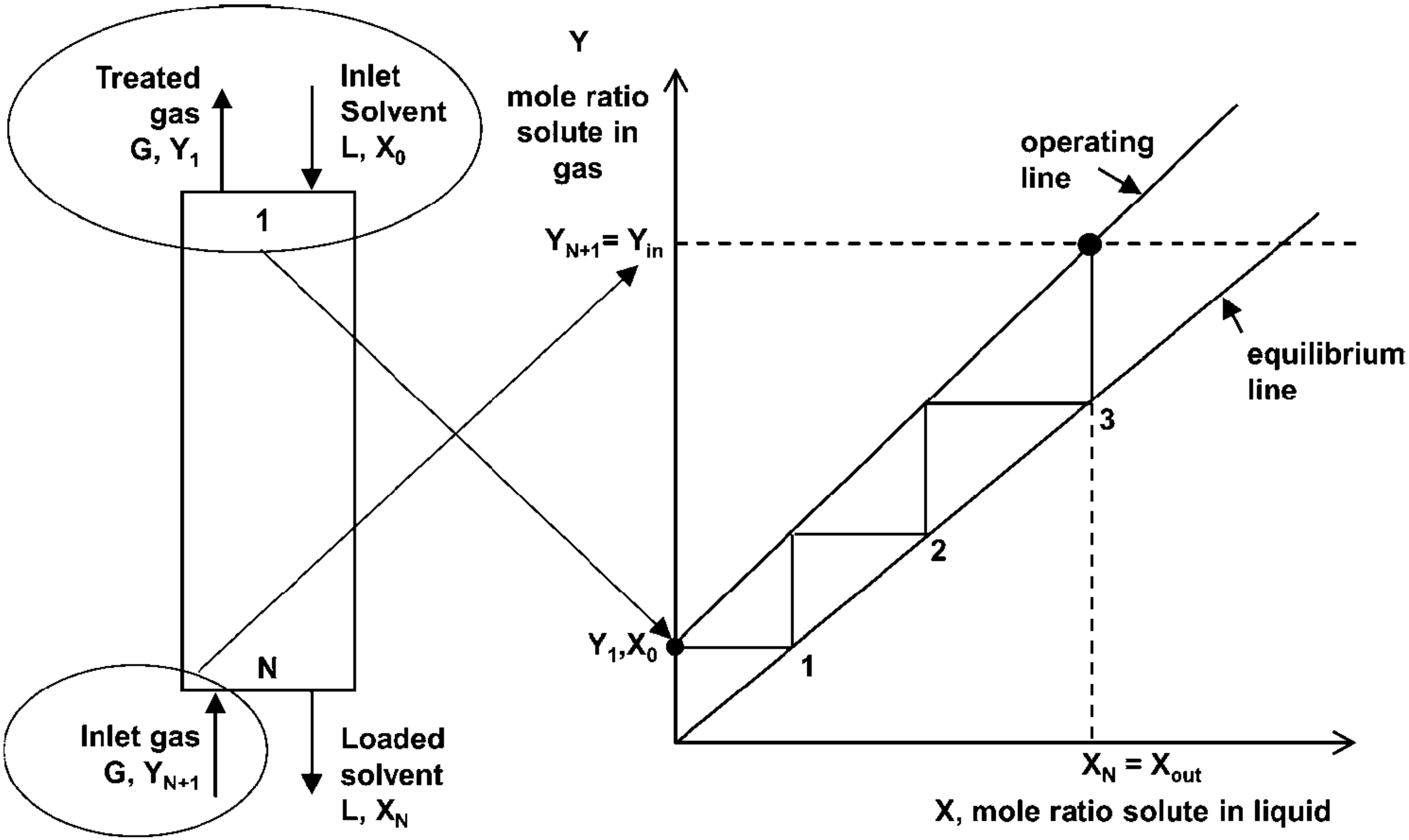
Would you survive?

Bubble Columns



Gas column absorber schematic – mixed gas in, pure gas out

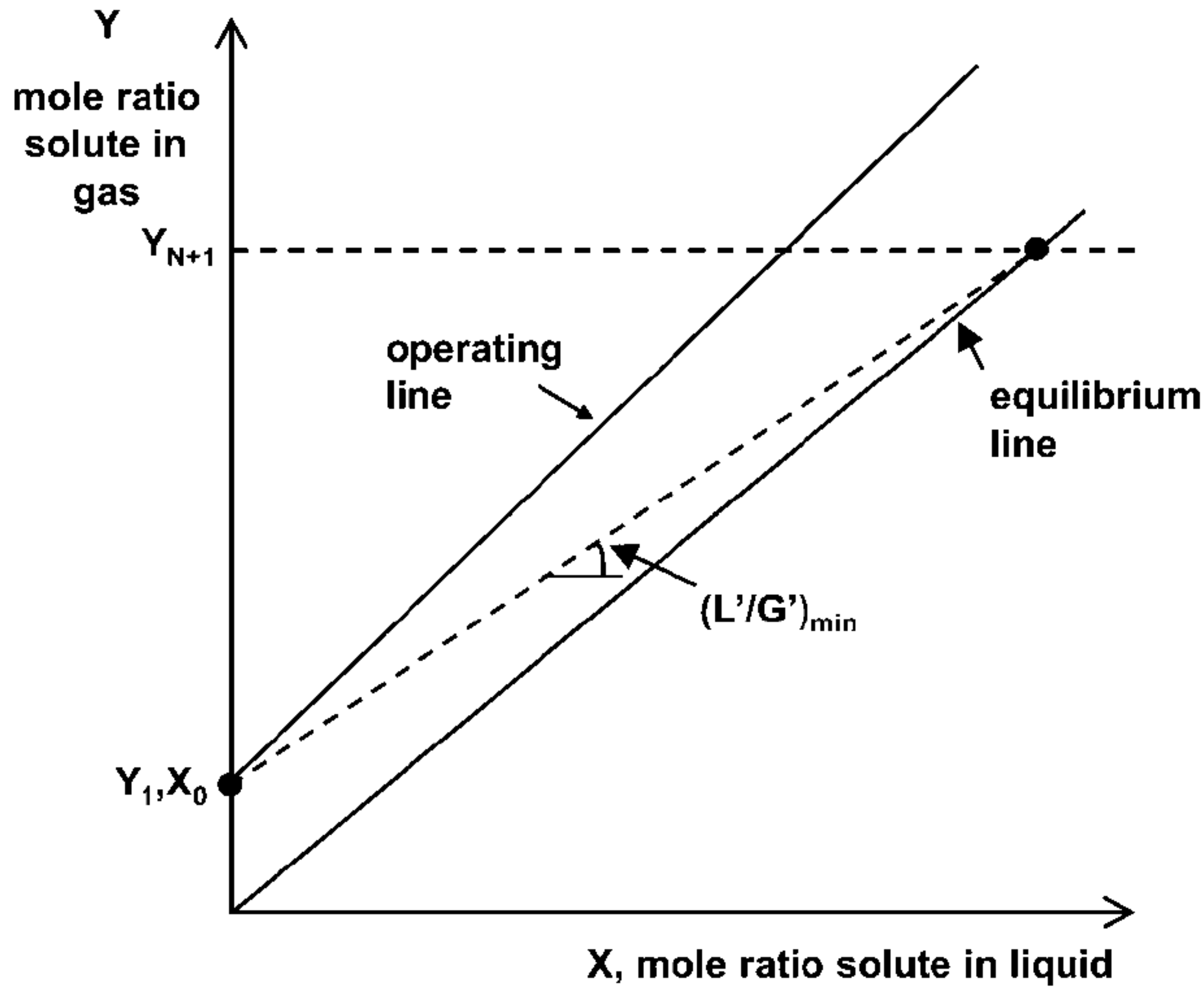
Operating Lines for Absorption



McCabe-Thiele diagram for absorption

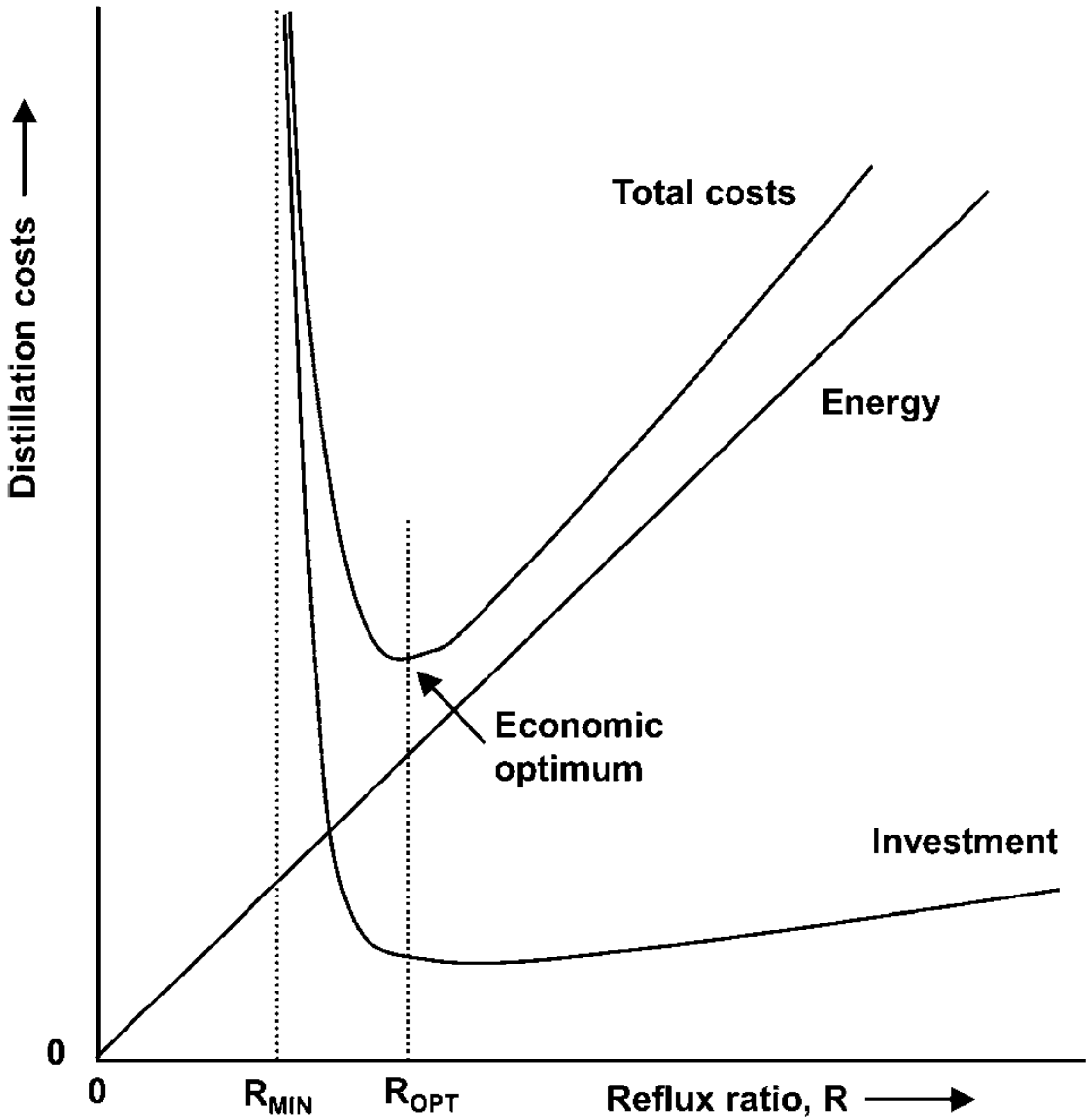
operating line in absorption is above the equilibrium line

Absorption and Stripping



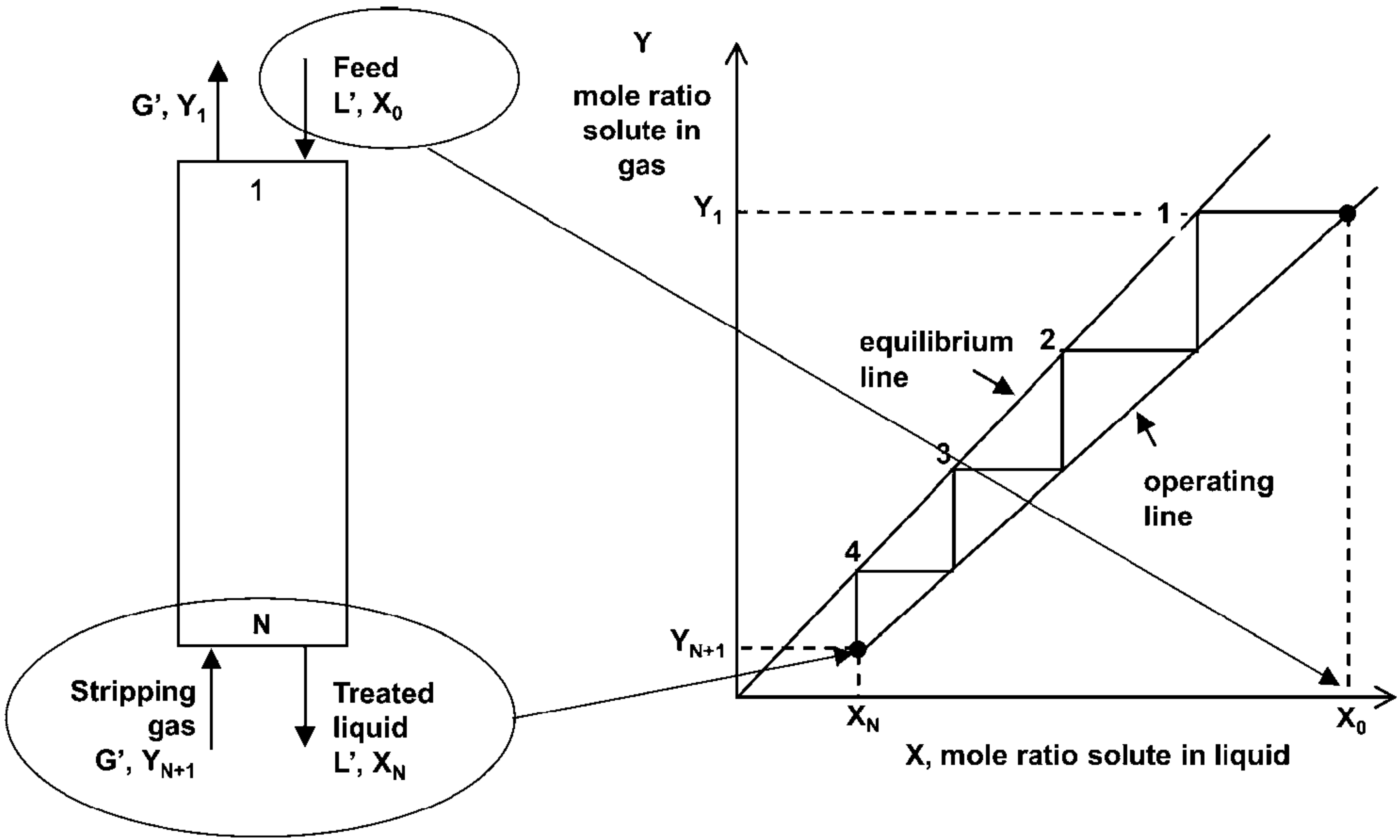
McCabe-Thiele diagram for minimum L/G ratio for absorption

McCabe-Thiele Analysis



Operational cost – lowest at L/V = 1.5*(L/V)min

Absorption and Stripping



McCabe-Thiele diagram for stripping operating line is below the equilibrium curve

Absorption and Stripping

$$G y_{in} + L x_{in} = G y_{out} + L x_{out}$$ Absorption Balances

G and L are the Gas and Liquid flow rates

$$L_{\min} = G \cdot \frac{y_{in} - y_{out}}{x_{\max} - x_{in}} = G \cdot \frac{y_{in} - y_{out}}{\frac{y_{in}}{K} - x_{in}}$$

Max gas solubility in liquid x_{out} determines minimum Liquid absorbent flow rate L_{min}

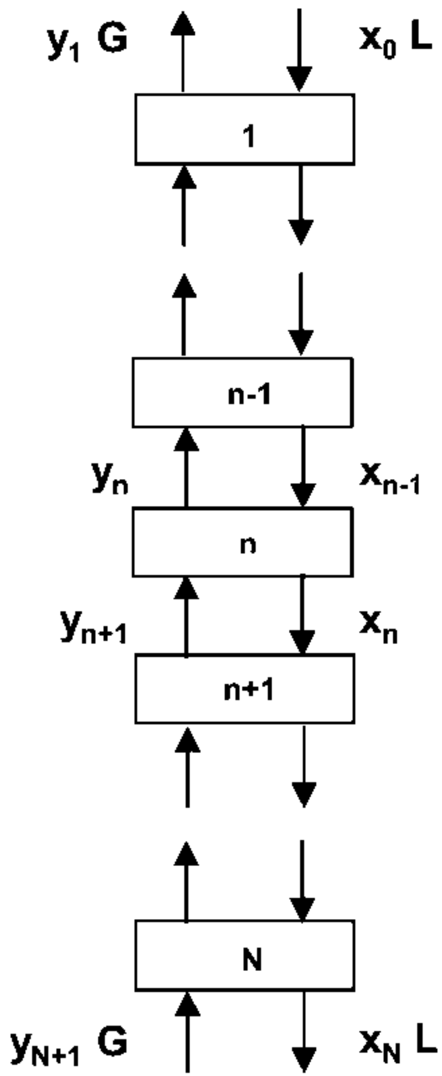
$$G y_{in} + L x_{in} = G y_{out} + L x_{out}$$ Stripping Balances

$$G_{\min} = L \cdot \frac{x_{in} - x_{out}}{y_{\max} - y_{in}} = L \cdot \frac{x_{in} - x_{out}}{K x_{in} - y_{in}}$$

Max y_{out} determines minimum stripping gas flow rate G_{min}

Single component mass balances

Absorption – Analytical Kremser Solution



$y_n = K\,x_n$

and

Introducing the Absorption factor A,

We can rewrite the equation:

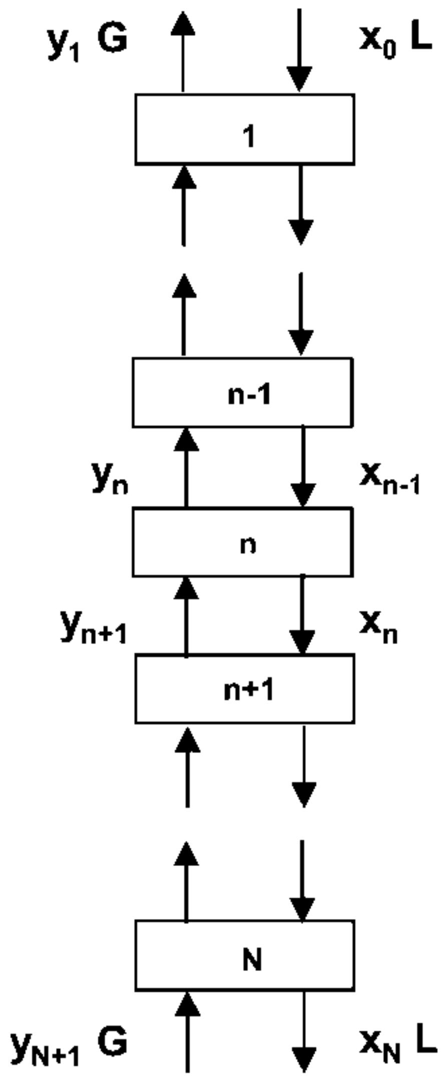
$$A \equiv \frac{L}{K\,G} = \frac{y_{n+1} - y_n}{K\,(x_n - x_{n-1})} = \frac{y_{n+1} - K\,x_n}{y_n - K\,x_{n-1}}$$

$$N_{ts} = \frac{\ln\left[\dfrac{y_{in} - K\,x_{in}}{y_{out} - K\,x_{in}}\left(1 - \dfrac{1}{A}\right) + \dfrac{1}{A}\right]}{\ln A}$$

Kremser Equation

It's a shortcut to the graphics

Absorption – Analytical Kremser Solution



$$x_{out} = x_{in} + \frac{G}{L} y_{in} - \frac{G}{L} y_{out}$$

resulting in:

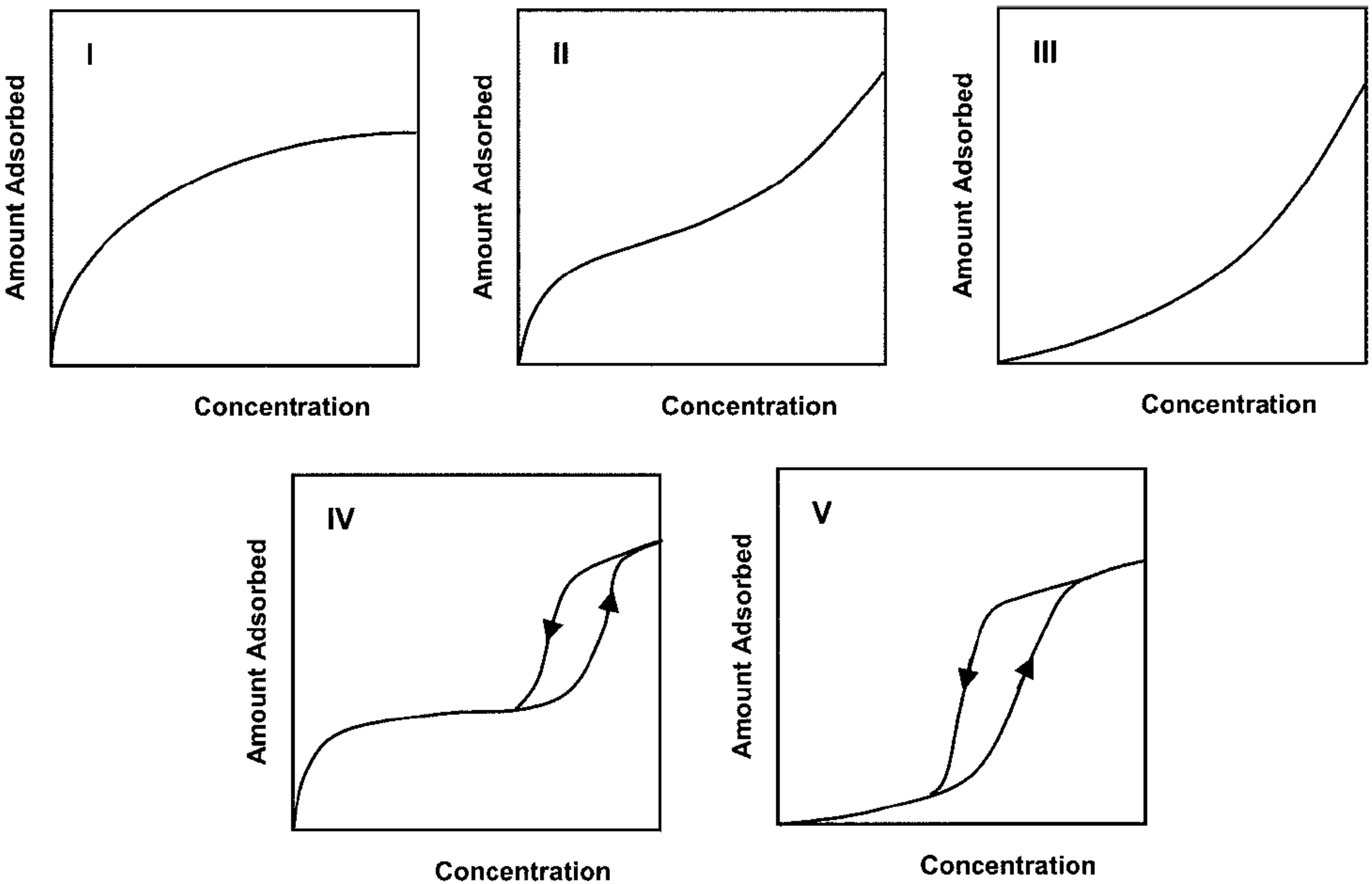
$$A^N = \left[\left(\frac{y_{in} - K x_{in}}{y_{out} - K x_{in}} \right) \left(1 - \frac{1}{A} \right) + \frac{1}{A} \right]$$

$$N_{ts} = \frac{\ln \left[\frac{y_{in} - K x_{in}}{y_{out} - K x_{in}} \left(1 - \frac{1}{A} \right) + \frac{1}{A} \right]}{\ln A}$$

Kremser Equation

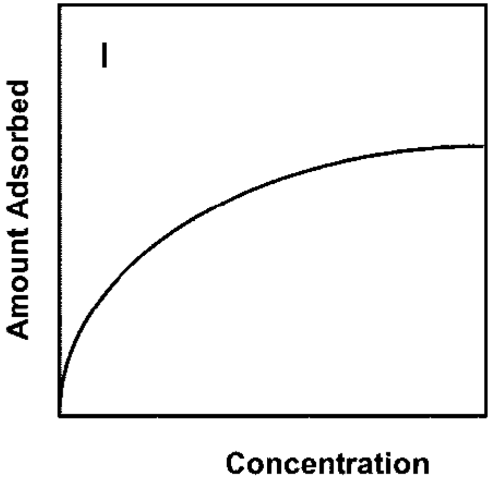
It's a shortcut to the graphics

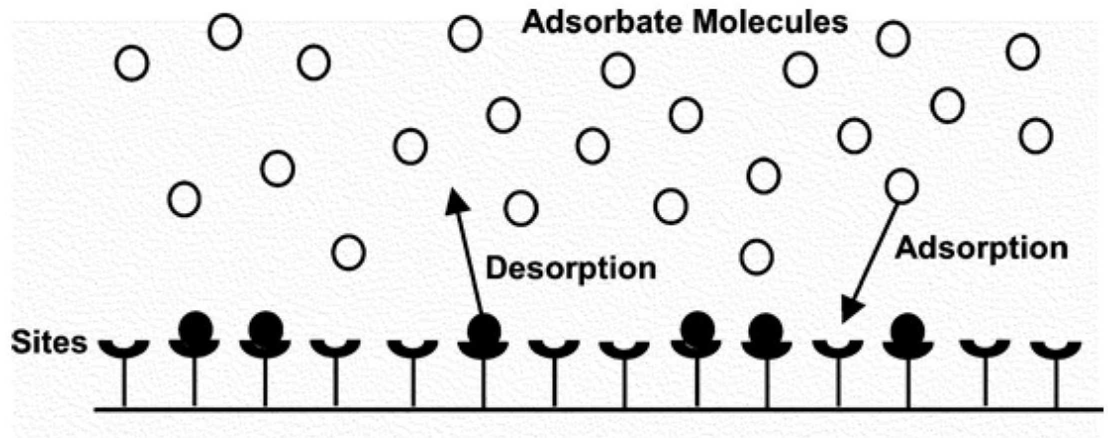
Adsorption



Brunauer classification Adsorption isotherms

Adsorption – on a monolayer





$$\theta_A = \frac{q_A}{q_{max,A}} = \frac{b_A\, p_A}{1 + b_A\, p_A} = \frac{b'_A\, c_A}{1 + b'_A\, c_A}$$

where

θ = fraction of sites occupied (see Fig. 6.8),

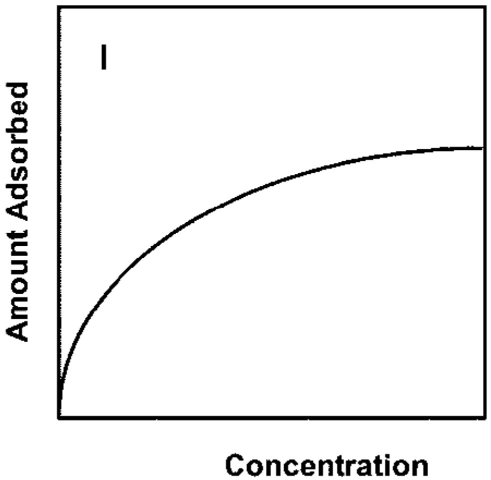
q = amount adsorbed per unit volume or unit weight adsorbent,

q_{max} = monolayer capacity, referring to maximum occupancy or $\theta = 1$, and

b = Langmuir adsorption constant in reciprocal pressure or concentration units.

Langmuir Adsorption Isotherm – Simplest, Most useful

Langmuir Equation



$$b_A = \frac{k_{ads}}{k_{des}}$$

$$q_A = q_{\max,A} \frac{b_A p_A}{1 + b_A p_A}$$

Langmuir Equation

$$b_A = b_A^0 e^{-\Delta E_{ads}/RT}$$

Temperature Dependence

Langmuir Adsorption Isotherm – Simplest, Most useful

Ion Exchange – Ch. 6

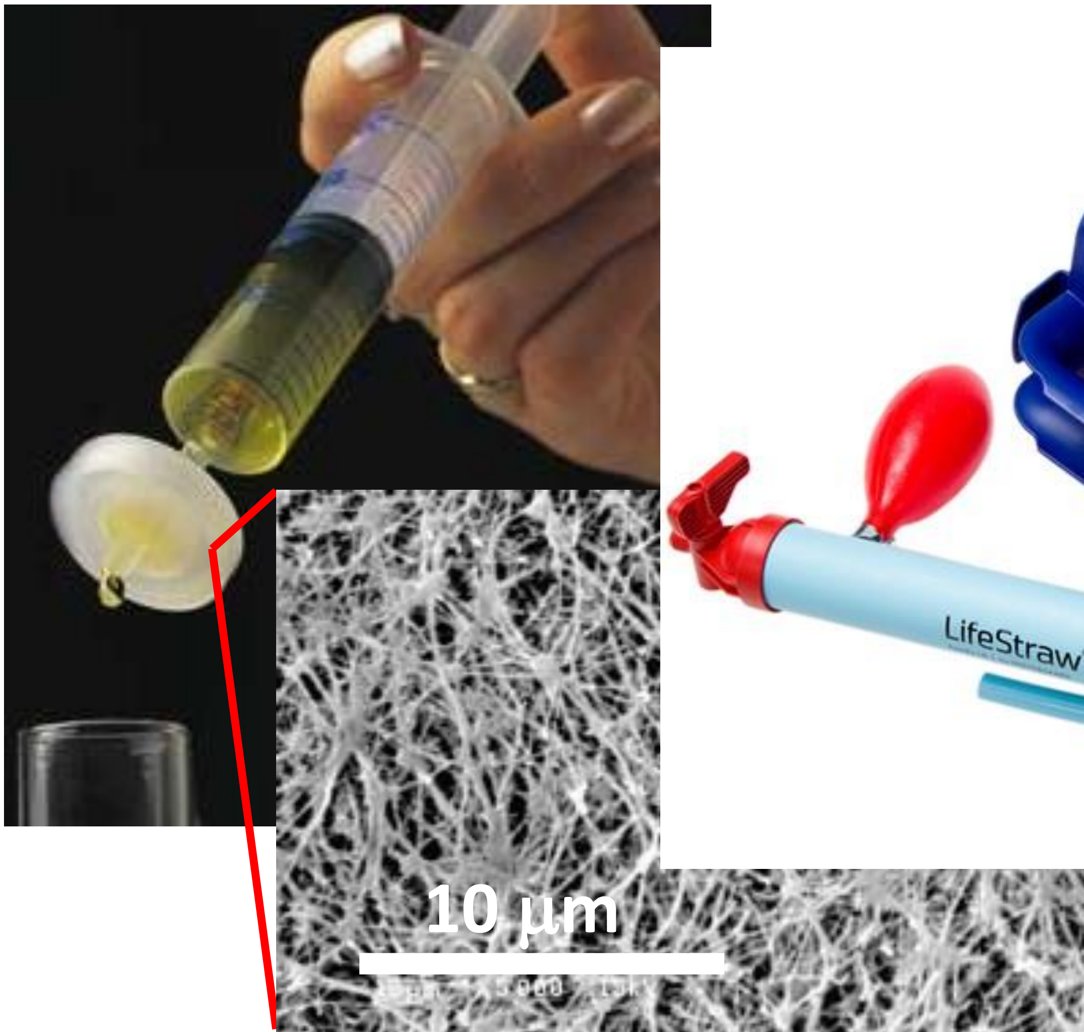
How to filter single ions – smaller than almost any pores?

And at small pressure drop?

Small Pore Filtration vs Ion Exchange

How to filter single ions – smaller than almost any pores?

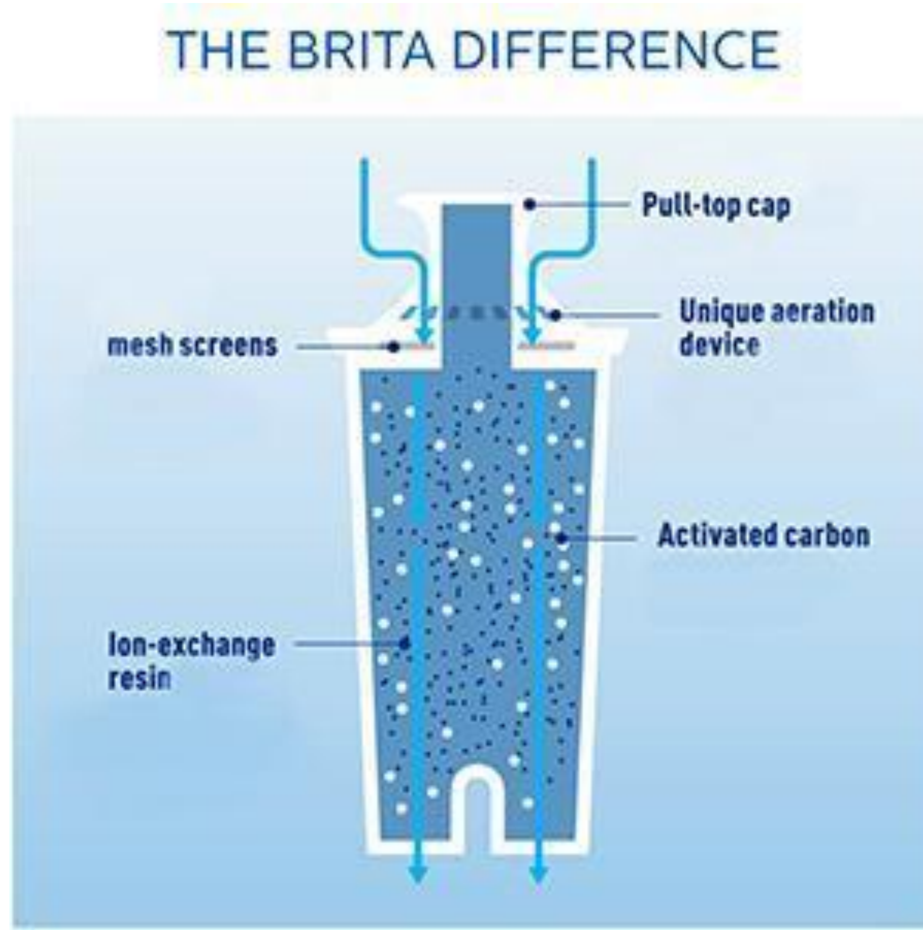
And at small pressure drop?



Ion Exchange – Ch. 6

How to filter single ions – smaller than almost any pores?

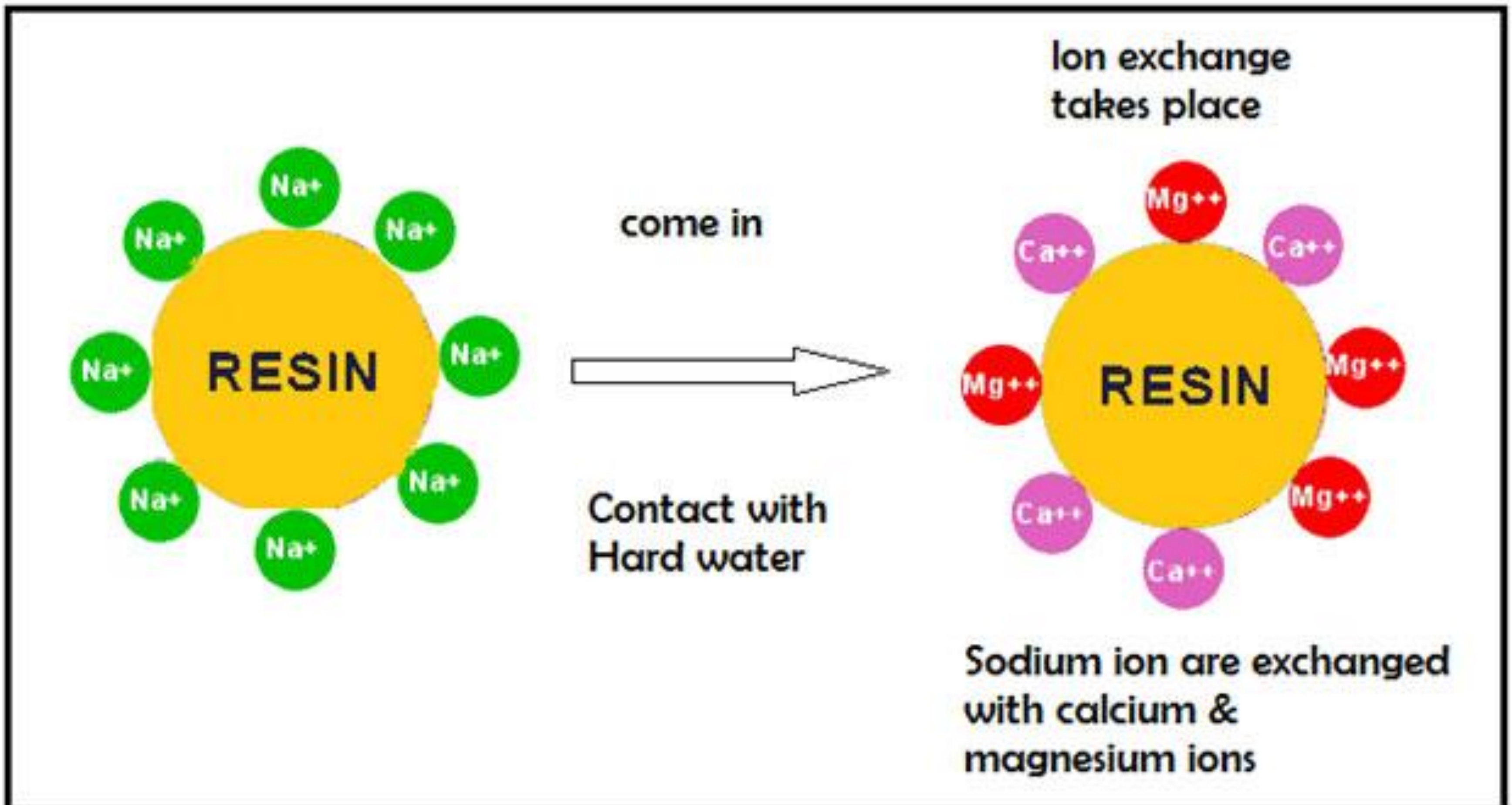
And at small pressure drop?



Ion Exchange – Ch. 6

How to filter single ions – smaller than almost any pores?

And at small pressure drop?



Ion Exchange – Terminology and Learning Goals

By the end of this lecture you'll be able to: **describe ion exchange.**

Say what are **Operating capacity, regeneration of adsorber, copolymer ionic resins, divalent vs. monovalent ions, .** Other vocabulary: **MCLG**= Maximum Contaminant Level Goal, **MCL**= Maximum Contaminant Level, **MRDL** = Maximum residual disinfectant level, **TSS**= Total Suspended Solids, **NTU**= Nephelometric Turbidity Units, **JTU** = Jackson Turbidity Units, **Secchi disk,**

We'll learn the principles of operation of ion-exchange, specifically a Brita Filter

We'll calculate – the capacity and longevity of a Brita cartridge and how long does it last, given the quality of our water.

Dissolved Compounds in Water

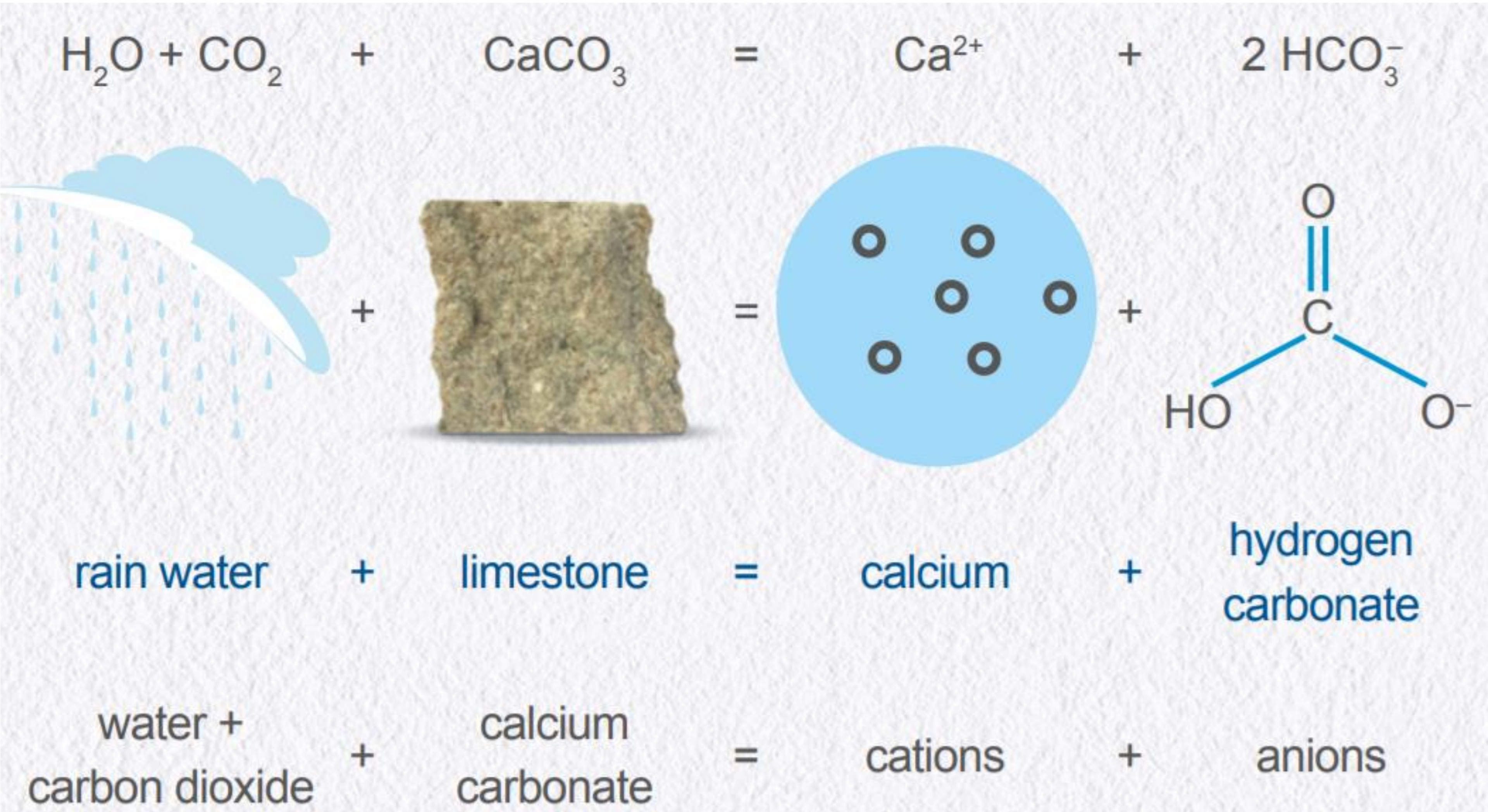
Some deliberately added to eliminate clouding (turbidity), (Fe, Al)

chlorine, chloramine essential, as they kill pathogens, but taste and smell bad.

and geosmin – can be smelled at parts-per-trillion (ppt) range! Removal= better odor.

But all of these are solids.
Can we get rid of them without distillation?

Carbonates and Scale

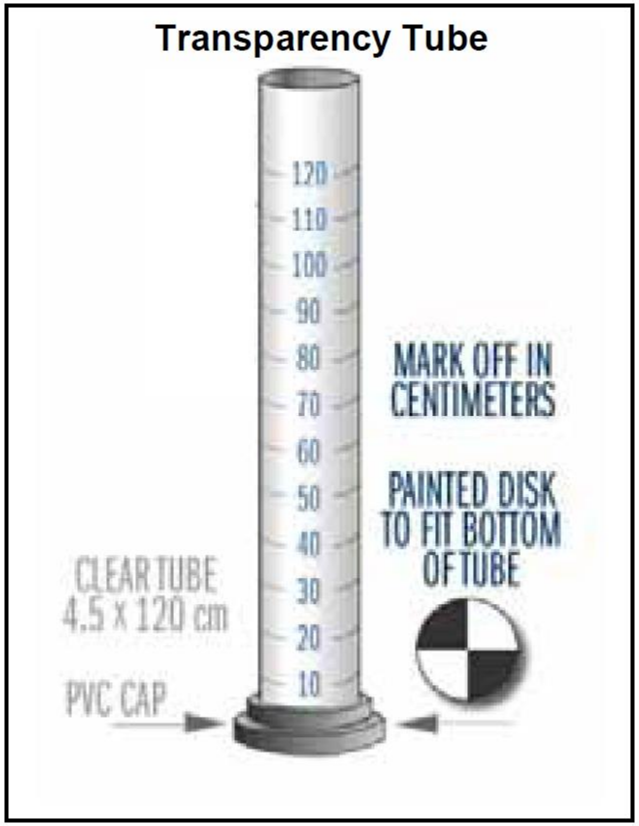


How we get hard water

Water Quality Terminology

5 NTU – Barely noticeable
<10 NTU Drinking Water

Flocculating agents are used to treat water turbidity . We'll cover their mechanisms and chemistry next year.



MCLG = Maximum Contaminant Level Goal

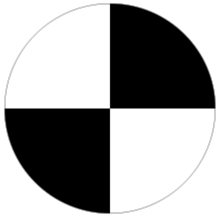
MCL = Maximum Contaminant Level (achievable with current technology)

MRDL = Maximum residual disinfectant level

TSS = Total Suspended Solids (ppm or mg/L)

NTU = Nephelometric Turbidity Units
90^o scattered light from white (400-680nm) light

JTU = Jackson (Candle) method Turbidity U
Inverse of tube distance which obscures light of a candle


= Secchi disk - record depth where the 20-30 cm disk cannot be seen

MRDL Cl_2: UK = 0.5 ppm, US = 4 ppm

http://dwi.defra.gov.uk/consumers/advice-leaflets/chlorine.pdf
https://www.cityofchicago.org/content/dam/city/depts/water/ConsumerConfidenceReports/2016_Water_Quality_Report_2.pdf

https://en.wikipedia.org/wiki/Turbidity
https://or.water.usgs.gov/grapher/fnu.html

Chlorination Reactions

Chlorine:

Cl_2– first disinfectant
stronger agent

Chloramine:

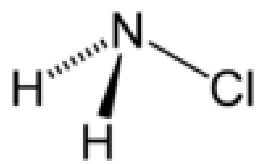
$Cl_2 + NH_3 \text{->} NH_2Cl$
weaker, stable over longer distances

NaDCC: Sodium dichloro isocyanurate - convenient for field-treatment of water
WHO TDI (tolerable daily Dose) = 2.2mg/kg body wt. (1100 mg/ 50kg weight)

Chlorine Equilibria: Reaction with water gives hypochlorous acid, which sets up an equilibrium with hypochlorite ion:

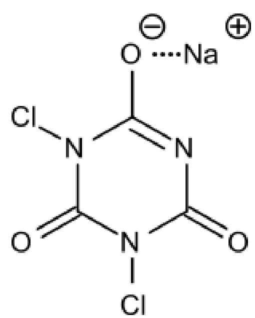
$$Cl_2 + H_20 \rightarrow HOCl + H^+ + Cl^–$$

$$HOCl \leftrightarrow H^+ + OCl^-$$



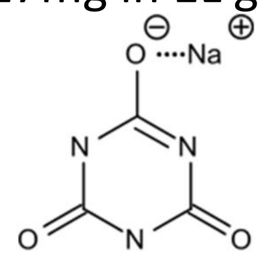
Chloramine: Reaction of residual Cl_2 with ammonia (about 4-6:1 ratio) – to give (at pH>7) mostly the mono chloro-amine:

$$NH_3\ (aq) + HOCl \text{->} NH_2Cl + H_2O$$



Hydrolysis: 17mg in 1L gives 10 ppm Cl

$+ 2H_2O \leftrightarrow$



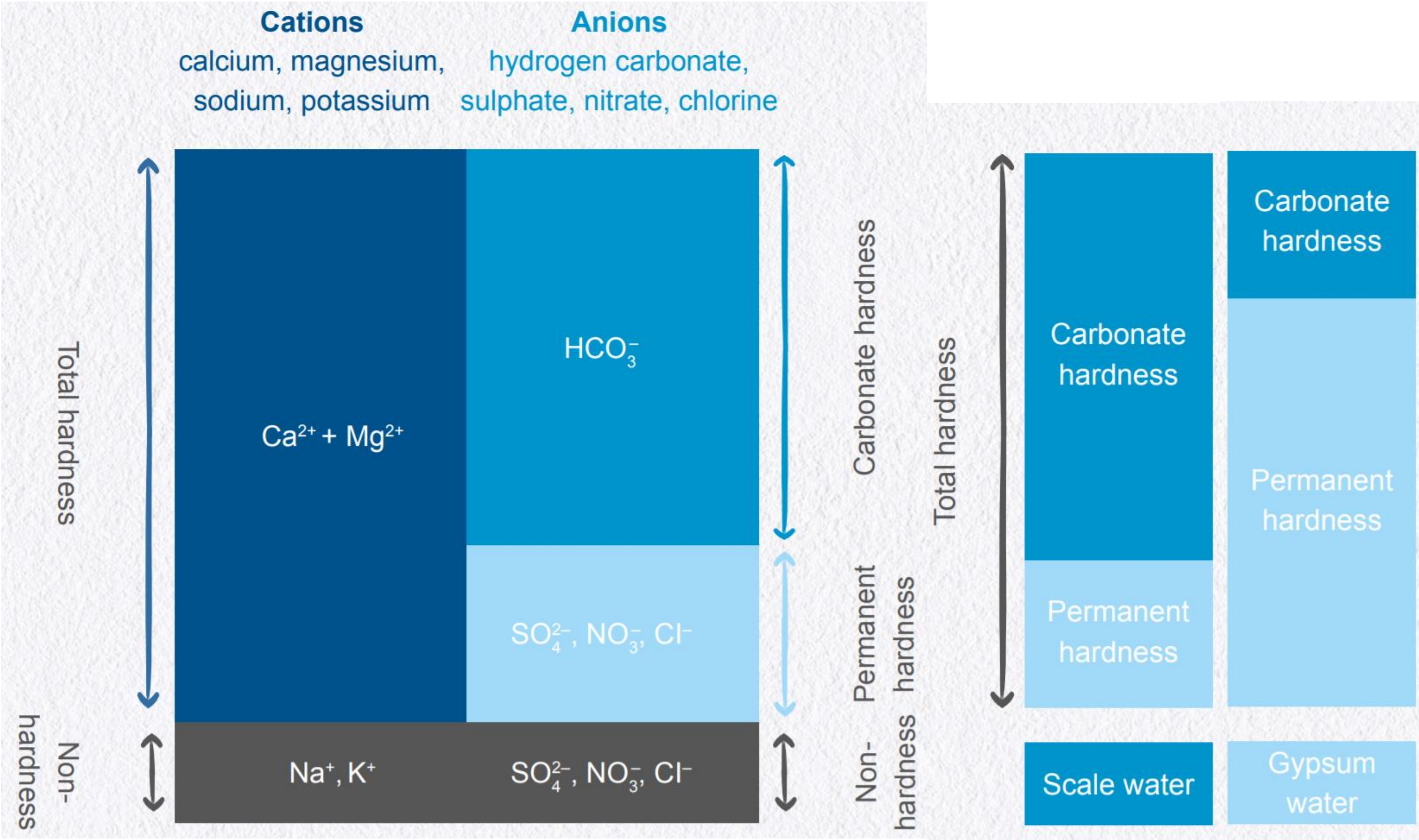
$+ 2HOCl$

Strip of 10x67mg costs US\$0.05 and treats 200 L

@3.5mg/L, **<u>30min contact time</u>**, kills all coliform bacteria (NTU<1), in raw river water (NTU>10), log1.8-2.8 reduction in viable bacteria

Clasen, ***Int. J. Hyg. Environ.-Health*** (2006) 173,DOI: 10.1016/j.ijheh.2005.11.004; Schlosser, 2001 ***J Travel Med*** 2001; 8:12.

Brita Filter



Ions present in hard water

$CaCO_3$ $CaSO_4 \cdot 2H_2O$

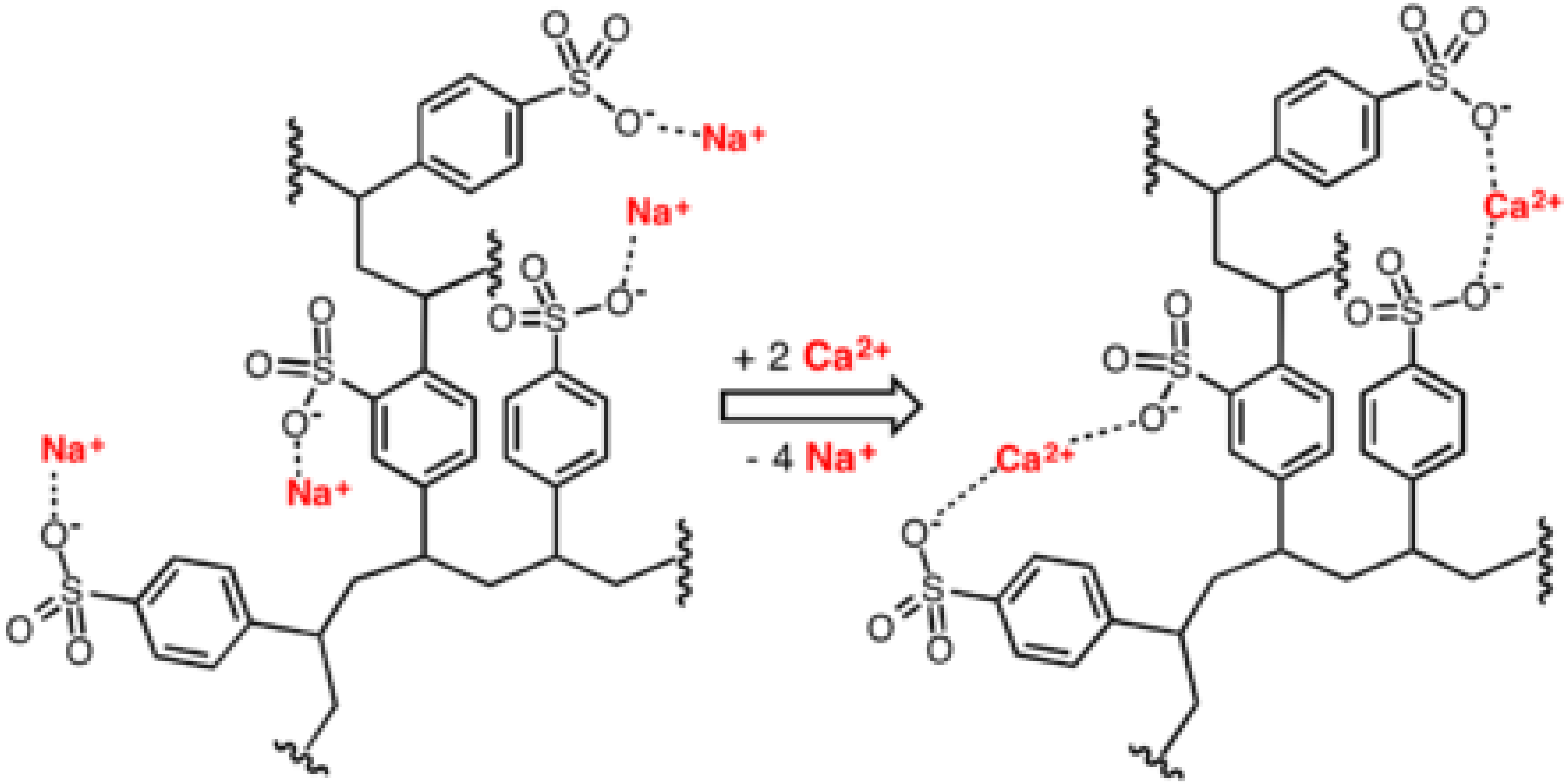
Hardness Unit Conversions

	Quasi-SI	American	German		English	French
	1 mmol/L	**1 ppm, mg/L**	**1 dGH, °dH**	**1 gpg**	**1 °e, °Clark**	**1 °fH**
mmol/L	1	0.009991	0.1783	0.171	0.1424	0.09991
ppm, mg/L	100.1	1	17.85	17.12	14.25	10
dGH, °dH	5.608	0.05603	1	0.9591	0.7986	0.5603
gpg	5.847	0.05842	1.043	1	0.8327	0.5842
°e, °Clark	7.022	0.07016	1.252	1.201	1	0.7016
°fH	10.01	0.1	1.785	1.712	1.425	1

A *mmol/L* is equivalent to 100.09 mg/L $CaCO_3$ or 40.08 mg/L Ca^{2+}.

Classification	hardness in mg-CaCO3/L	hardness in mmol/L	hardness in dGH/°dH
Soft	0–60	0–0.60	0-3.37
Moderately hard	61–120	0.61–1.20	3.38-6.74
Hard	121–180	1.21–1.80	6.75–10.11
Very hard	≥ 181	≥ 1.81	≥ 10.12

Cation Exchange Resin



Divalent ions bind strongly and release monovalent ions

How Long Does a Filter Last?

https://www.thameswater.co.uk/help-and-advice/water-quality/check-the-water-quality-in-your-area

Calculate life for a C150 filter with 267 ppm water?

Hardness

The water supplied in the MILE END zone is HARD water.

Calcium carbonate(CaCO3): 267 ppm

PURITY C Finest	C150	C500
Technology		softening
Capacity[1] with a total hardness of 10 °dH and 0 % bypass[2]	1.100 l	3.414 l
Max. operating pressure		8,6 bar
Water intake temperature		4 – 30 °C
Flow at 1 bar pressure loss	145 l/h	140 l/h
Nominal flow	60 l/h	100 l/h
Pressure loss at nominal flow	0.25 bar	0.5 bar
Dimensions (W/D/H) Filter head with filter cartridge	117/104/419 mm	144/144/557 mm
Weight (dry/wet)	1.8/2.8 kg	4.6/6.9 kg

10 dH = 178 ppm, so Capacity = 1100 L *178 mg/L = 196g $CaCO_3$

so x = 196 g / 267 mg/L = 734 L And it costs £74

So £74 / 734 L = £0.10 / L – for good tasting and no-scale water

<u>If it cleans molecular ions, does it also filter bacteria and viruses?</u>

How Long Does a Filter Last?

https://www.thameswater.co.uk/help-and-advice/water-quality/check-the-water-quality-in-your-area

Life of a (consumer) Maxtra filter – when do you change?
As well as cost per L water =?

Hardness

The water supplied in the MILE END zone is HARD water.

Calcium carbonate($CaCO3$): 267 ppm

The MAXTRA+ Universal cartridge filters up to 100 litres in an area with hard water (primarily based on carbonate hardness of 12° to 14,5° German hardness).

Added to your basket!

BRITA MAXTRA+ 3 pack

Love great tasting water? Enjoy it for up to twelve weeks with MAXTRA+ 3 pack.

Item no.: 1025349

Price per unit: £17.25

Total price: £17.25
(incl. VAT)

13.5 dH = _____ ppm, so Capacity = 100 L *_____ mg/L = _____g $CaCO_3$

so x = _____ g / 267 mg/L = _____ L. So 3 cartridges = ______L

So £17.25 / _____L = £0._____ / L – for good tasting and no-scale water

<u>This is just cleaning the taste. Cl_2 is what kills the microorganisms!</u>

How do we remove the Chlorine?

How much chlorine can a Maxtra filter remove?

UK = 0.5 ppm, US = 4 ppm (g/L Cl_2)

http://dwi.defra.gov.uk/consumers/advice-leaflets/chlorine.pdf
https://www.cityofchicago.org/content/dam/city/depts/water/ConsumerConfidenceReports/2016_Water_Quality_Report_2.pdf

Reactions with Activated Carbon

Also for Next Year's Advanced Separations!

Turbidity Treatment, Chemical Removal

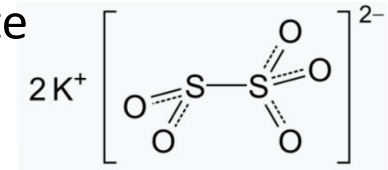
Flocculation – to be covered next year in **Advanced Mass Transfer & Separations**
Chemical reagents for treating turbidity include aluminium sulfate or alum ($Al_2(SO_4)_3 \cdot nH2O$), ferric chloride ($FeCl_3$), gypsum ($CaSO_4 \cdot 2H2O$), poly-aluminium chloride, long chain acrylamide-based polymers and proprietary reagents.
Important not only for aesthetics, but for effective chlorination, UV disinfection.

Dechlorination involves a chemical reaction of the chlorine oxidizing the activated carbon's surface. Reactions of hypochlorous acid and hypochlorite (shown below):

Carbon + HOCl → C*O + H^+ + Cl^-

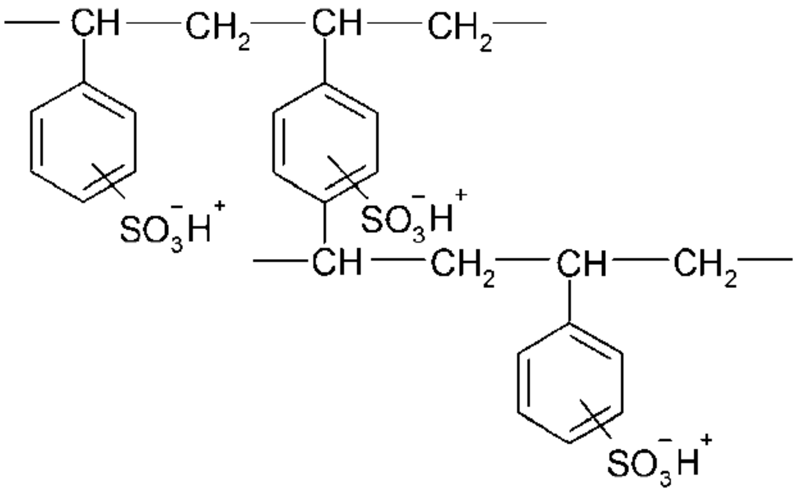
Carbon + OCl– → C*O + Cl^- and for chloramine the rxn is: $C^* + NH_2Cl + H_2O \rightarrow CO^* + H^+ + Cl^- + NH_3$

Dechloamination in commercial brewing by Potassium metabisulfite $K_2S_2O_5(s) \rightarrow K_2SO_3(s) + SO_2(g)$ also reacts with chloramine to give:

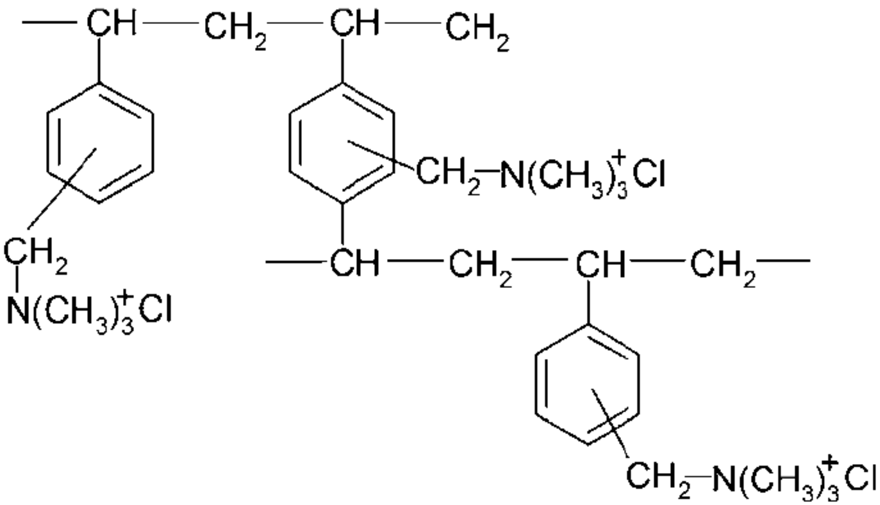


$$S_2O_5^{-2} + 2H_2NCl + 3H_2O \rightarrow 2SO_4^{-2} + 2H^+ + 2Cl^- + 2NH_4^+$$

Types of Exchange Resins



Sulfonated side groups for Cation exchange



Aminated side groups for Anion exchange (Cl^- or OH^- form)

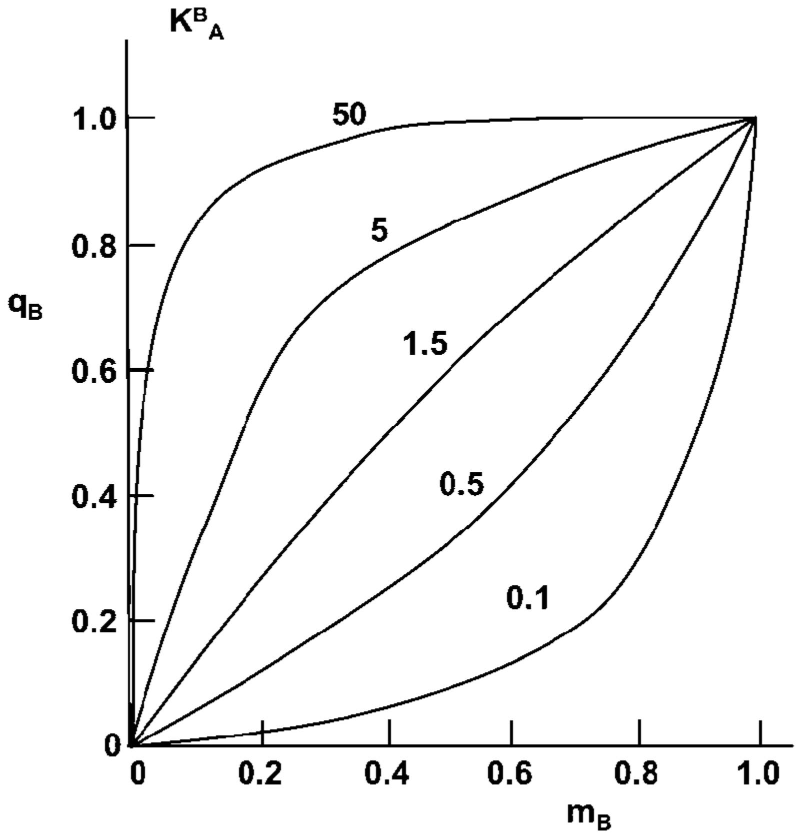
De-ionization of water makes use of both types of resins.
Cationic resins are placed first to avoid precipitaiton of metal hydroxides
Mixed bed systems give better results than sequential columns.

Styrene-divinyl benzene based exchange resins

Ion-Exchange Capacity and Rate

For Cations B+ from solution in exchange for A+ on the resin:

resin-$SO_3^-A^+$ + B^+ ⇔ resin-$SO_3^-B^+$ + A^+



Univalent ion-exchange plot

$$K_A^B = \frac{q_{B,resin}\, m_{A,liquid}}{q_{A,resin}\, m_{B,liquid}}$$

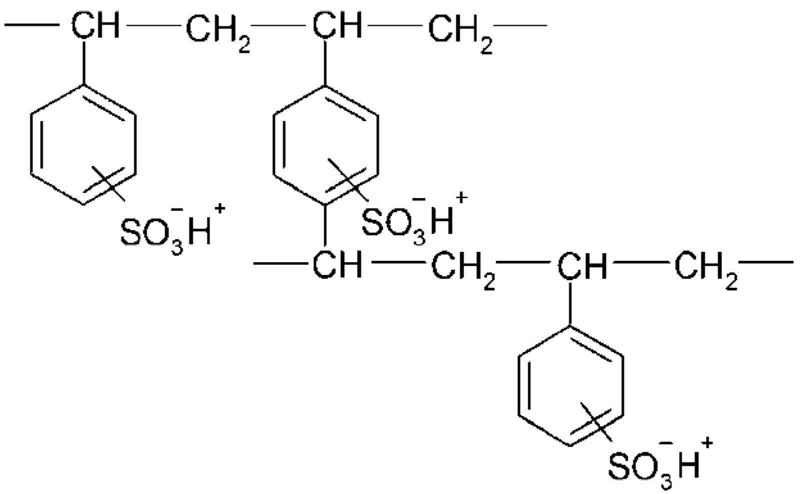
Equilibrium constant determining selectivity of a resin for B over A

q = capacity (conc.) ions in resin [mol/kg]

m = concentrations of the ions in the solution [mol/L] or [mol/kg]

B is preferred if $K_A{}^B > 1$

Problem Solving



Sulfonated side groups for Cation exchange

Problem 7. A commercial ion-exchange resin is made of 88 wt% styrene (MW = 0.104 kg/mol) and 12 wt% divinyl benzene (MW = 0.1302 kg/mol). Estimate the maximum ion-exchange capacity in equivalents/kg resin when an sulfonic acid group (MW = 0.0811 kg/mol) has been attached to each benzene ring.

How do we go about solving this?

Hints: What is ion-exchange capacity?
What are the units of capacity?

Drying of Solids
Please read – Ch. 7from De Haan & Bosch, Industrial Separation Processes, 2013, de Gruyter (Berlin) (on Knovel)

You’ll learn about drying fruit, and bread, and vapor in pores