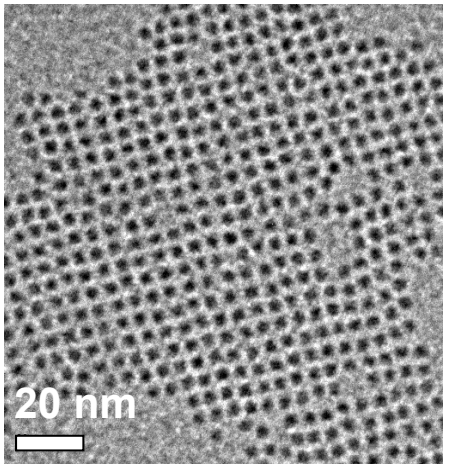
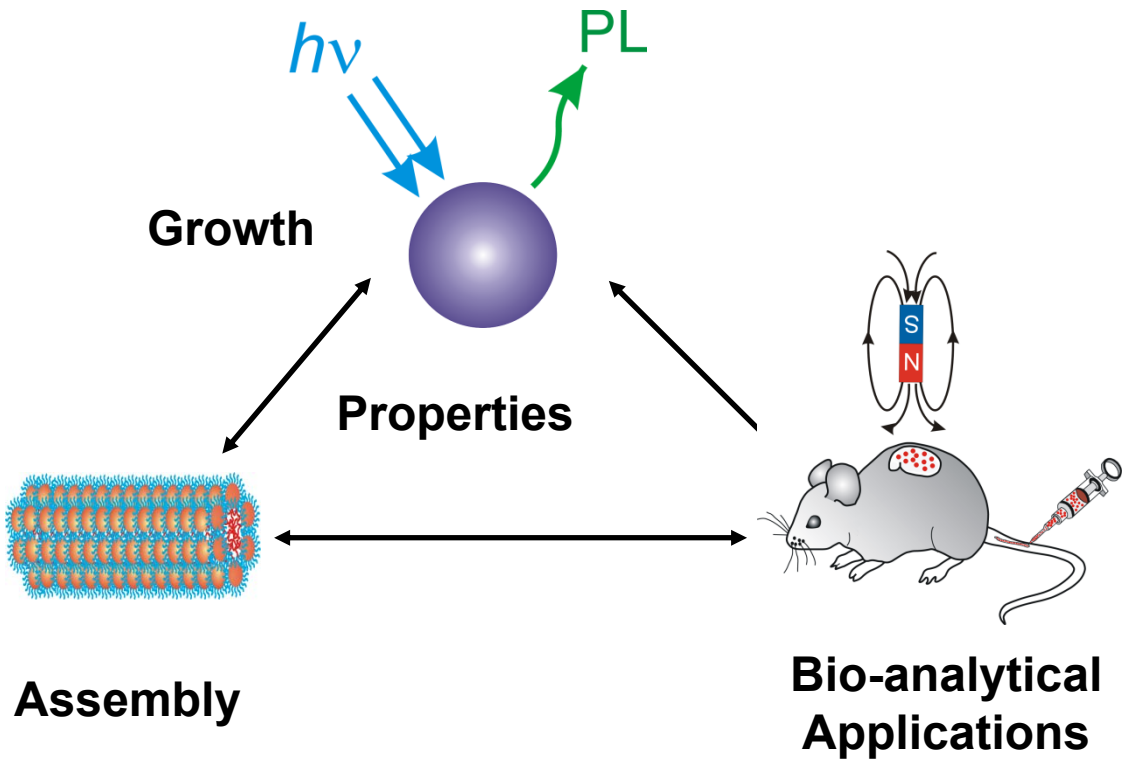
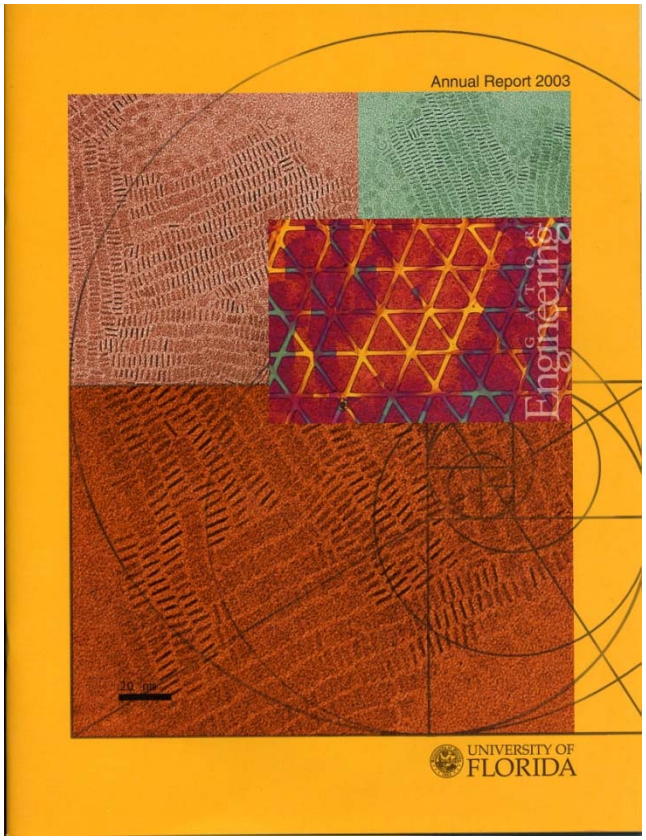
Charles Cao

(cao@chem.ufl.edu), 226 Leigh hall.







CHM 6154 (Spring, 2015)

Chemical Separations

Instructor: Charles Cao (cao@chem.ufl.edu), 226 Leigh Hall.

Lectures: M, W, F, 6th Period (12:50 pm to 1:40 pm), 328 Weil Hall

Office hours: M, W, F, - 7th Period (1:55 pm to 2:45 pm), or by appointment

Website: http://www.chem.ufl.edu/~cao/CHM6154/index.html

Requirement: Strong background in calculus and thermodynamics

Textbook: Unified Separation Science by J. Calvin Giddings
(John Wiley & Sons, INC)

Reference: *The Essence of Chromatography* by Colin Poole (Elsevier)

Themes:
1. Introduction: Fundamentals of Distribution Equilibrium
2. Gas Chromatography
3. Liquid Chromatography
4. Other Analytical Separations

Homework: Problems will be assigned throughout the semester as an aid in comprehending the course material. They will not be graded. Answers to the assigned problems will be discussed in the class.

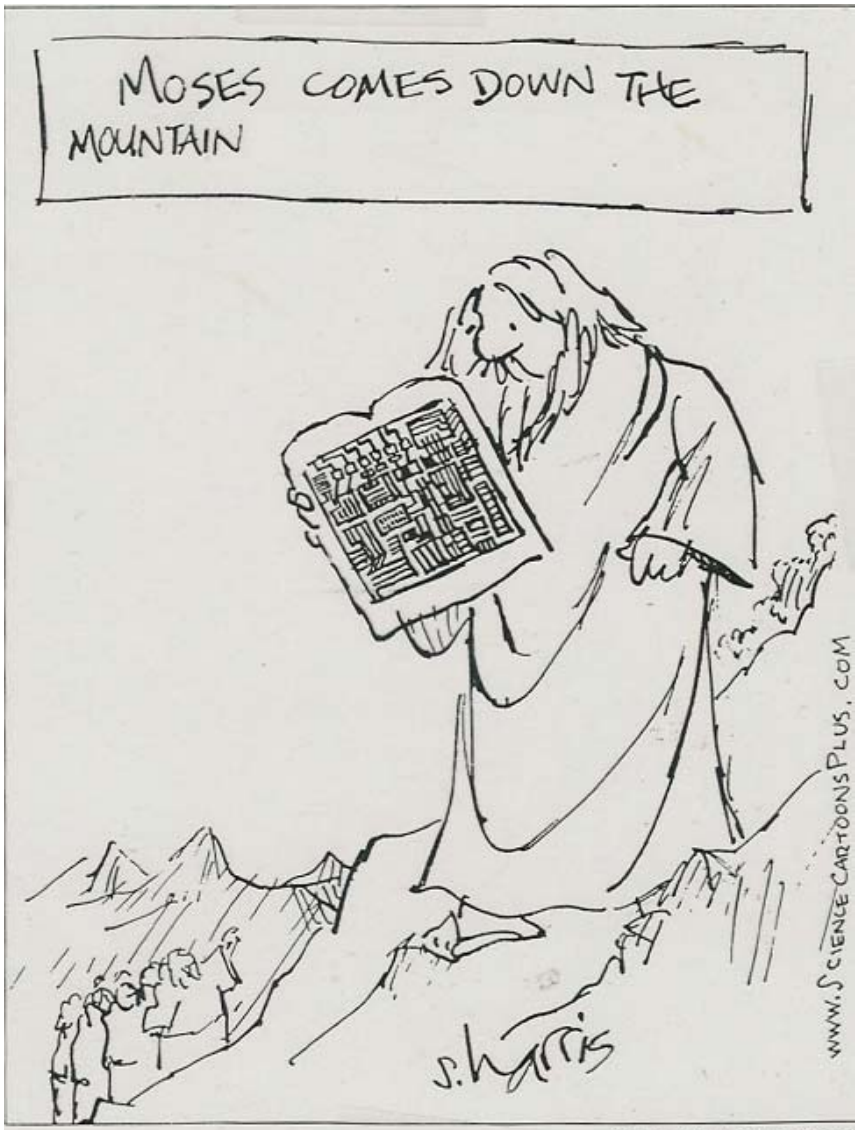
Quiz and Exams: Fourth quizzes will be given throughout the semester as an aid to review the course material periodically. Two exams will be included in the course. The midterm exam covers the first and second part of the themes, and it will be a 2-h exam during March. The final one is a comprehensive exam, but it will emphasize the last two parts of the themes. Note that students are invited to submit one or more suggested questions for the midterm and final exam.

Group study: Reach-oriented study on a specific topic related to separation. The topic will be given by the instructor. One group is composed of two students. The group study includes (1) a thorough review of the current state of art on the research work related to the chosen topic and (2) a new and novel solution from the student group. The results from the group study will be shown as group presentation: 20-min talk. Presentation data: April 18

Research Proposal: The topic of the proposal is on a separation technique. This topic can be related to the work from group study, but each student must submit a unique proposal. The proposal should present a novel idea that can be evaluated experimentally. The length of the proposal is about 1800 words. The final dual date: April 27, and no score will be given for a late submission.

Grading:

Homework:……..0 points
4 Quizzes……....20 points (5 points for each)
Midterm Exam:……...80 points
Final Exam:…….100 points
Research Proposal:……..……60 points
Group Study:……...40 points



Cartoon by Sidney Harris

Teaching

Discussion

1. Fundamental knowledge
2. Power of creativity in use of the knowledge that you have learnt.

Chemical Separations

Goals

1. I know the reasons why I need to learn chemical separations
2. I know the fundamentals of chemical separations
3. I know the basic techniques in chemical separation
4. I know how to use these techniques
5. I know how to use the fundamental knowledge to improve these separation techniques

How do we achieve the goals?

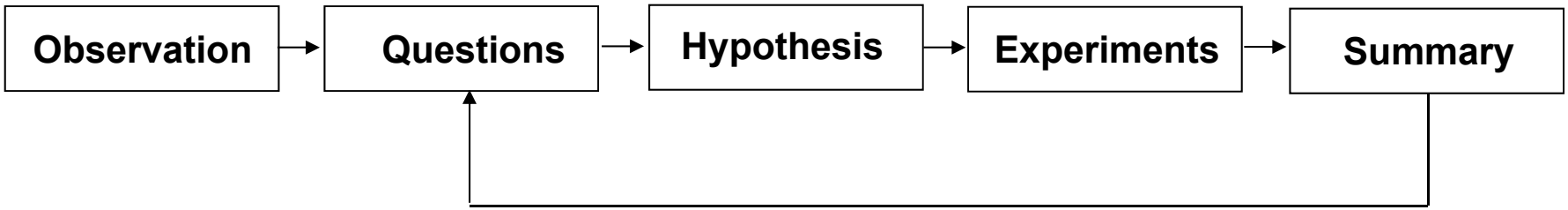
1. Homework and class discussion
2. Four Quizzes (5 points each): during classes.
3. Exams (Midterm: 80 points, and final: 100 points)

A makeup exam for midterm exam is available (The highest point will be picked up).

5. Research-oriented study: 40 points
4. Research proposal: 60 points

Problem Solving and Research

A scientific research activity:



Problem solving:

1. Understanding concepts and formulas
2. Logical Analysis

Formal logic laws: (a) A event is determined by many parameters; (b) all the parameters have some sort of connection between each other.

Scheme 1. A four-step method for problem solving

1. Understand the question.
2. Lay out all the parameters regarding the question.
3. Use concepts and formulas to build connections between these parameters.
4. Solve the question.

How Can You Read?

Nature: A research paper cannot exist alone in an isolated manner; it must exist in a literature network in a "3-D" manner (the three dimensions are time, research field, and research group).

Levels of Understanding a research paper

Level 1: Fully understand the general language: including all terminologies.

Level 2: Fully understand the technical details: including the details of experimental and/or theoretical methods, and the details on how these technical methods were used in the generation of experimental and/or theoretical results.

Level 3: Fully understand the structure of this paper: including the main scientific points, and the way that the main points are supported by the newly generated experimental or theoretical results. Do the arguments follow the general rules of scientific logic?

Level 4: Advanced understanding of paper structure: Can you write a better paper if you have all the data from the paper?

Level 5: Understanding of scientific value of the paper: Why was the paper published in a specific journal?

Level 6: Understanding of authors: Which type of researcher are they in person? What did they really think during the paper writing?

Content of part one

Part 1. Introduction; Fundamentals of Distribution Equilibrium

1. Chemical Separations: The Big Picture
   Classification and comparison of methods

2. Fundamentals of Distribution Separations

3. Separation Methods Based on Distributions in Discrete Stages
   Such as solvent extraction and distillation

4. Introduction to Distribution Separations in chromatographic methods

   The plate theory, the rate theory; van Deemter's equation

Chemical Separations: The Big Picture (1/09/15)

Chemical Separation is a central part of analytical chemistry

Analytical chemistry: What? and How many?

The concepts we need to remember

1. The essential feature of separations:

2. Driving force for separative transport

3. Limitations for separation

4. Analytical and Preparative Separations

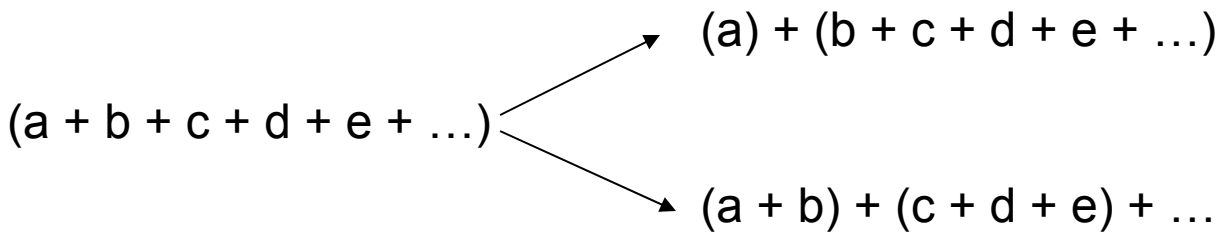
5. Names for Chromatography techniques

What is Chemical Separation? (I)

1. A complete separation of a mixture of chemical species:

$$(a + b + c + d + e + \ldots) \longrightarrow (a) + (b) + (c) + (d) + (e) + \ldots$$

2. A partial separation of a mixture of chemical species:



3. The essential feature of separations:

Components must be transported and redistributed in space in order to realize the goals of the separative operation.

What is Chemical Separation? (II)

4. The transport basics do not stand alone:

(a) Equilibrium (driving force),

(b) The macroscopic, microscopic, and molecular structure of the system

(c) The details of flow

(d) Mechanics of sample handling

5. Limitations:

(a) Physical limitations: parameter controlling (e.g., T, P)

(b) Chemical limitations:
(i) equilibrium,

$$A_1 \underset{}{\overset{k}{\rightleftharpoons}} A_2$$

What is Chemical Separation? (III)

(ii) thermodynamic limitations: the second law of thermodynamics

Spontaneous direction of change: Entropy: $\Delta S > 0$ for an isolated system

$$(a) + (b) + (c) + (d) \underset{\text{Separation}}{\overset{\text{Mixing } (\Delta V=0)}{\rightleftharpoons}} (a + b + c + d)$$

Spontaneous direction of change: Gibbs free energy: $\Delta G < 0$

$$\Delta G = \Delta H - T\,\Delta S$$

Enthalpy: $H = U + PV$

The first law of thermodynamics ⟶ Internal energy: $\Delta U = q + w$

(a) external work, (b) heat or (c) dilution

$$(a) \xrightarrow{\text{dilution}} (\quad a \quad)$$

Dilution: $\Delta S = n\,R \ln \dfrac{V_{(final)}}{V_{(initial)}}$

Question:

Calculate the entropy change that accompanies the separation of four oligonucleotides from one another in an aqueous containing 0.1 μmole of each. When separated, each component occupies one-quarter of original volume. Deduce from your results whether or not the separation is thermodynamically spontaneous.

four oligonucleotides: (1) AAA-TCA-GA; (2) AGA-TAC-GAT-ATA; (2) ATA-CAC-TGT-AGA-TTT-CTA; (4) AAC-CTC-GTT-AGA-TCC-CTA-TCA

$$(a) \xrightarrow{\text{dilution}} (\quad a \quad)$$

$$\text{Dilution: } \Delta S = n R \ln \frac{V_{(final)}}{V_{(initial)}}$$

What is Chemical Separation? (IV)

6. No absolute separations

(1) Separation limitations
(2) Detection limitations

7. General methods

(1) Named after underlying forces or phenomena:
extraction, adsorption, crystallization, precipitation, ion exchange, diffusion, sedimentation, centrifugation.

(2) Named after the forms of operation:

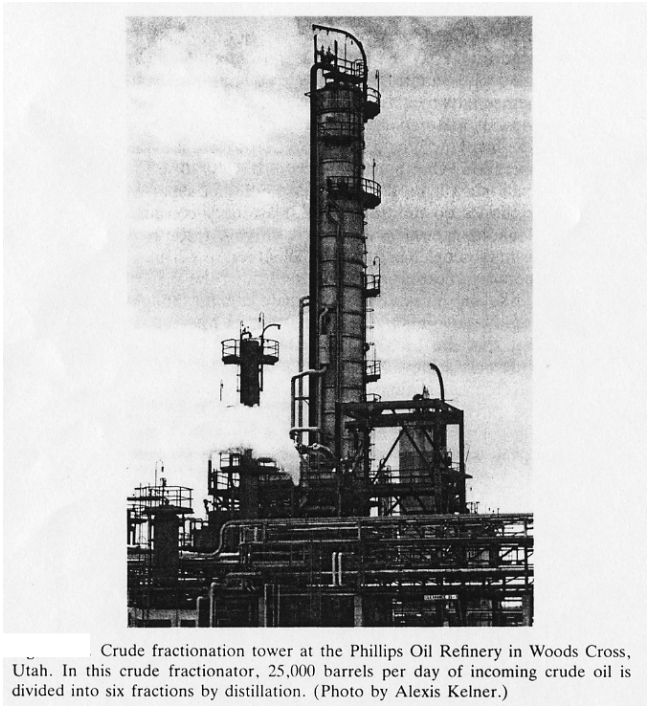
Chromatography, distillation, zone melting, filtration, dialysis, elutriation, field-flow fractionation, electrostatic precipitation.

(3) Both
Adsorption chromatography, ion exchange chromatography, extraction chromatography

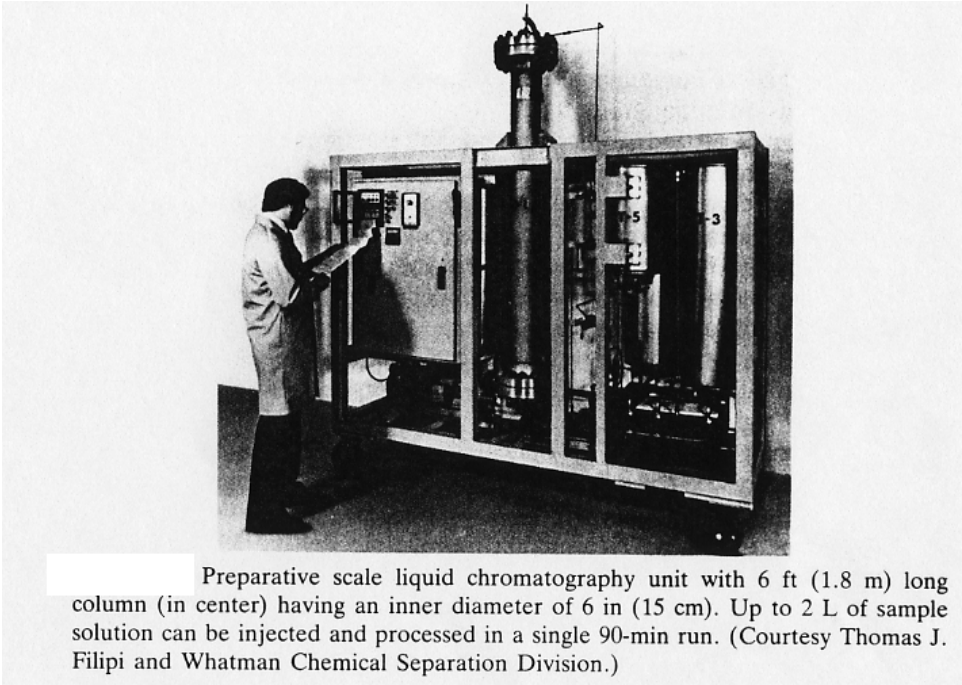
Analytical and Preparative Separations (I)

1. General goals of separation: preparative and analytical

2. Preparative separation: for drugs, fuels, metals, chemical feedstock for synthesis….
   Characteristics: (i) continuous in operation and (ii) large in scale
   distillation, extraction, smelting, (many tons per day)
   preparative liquid chromatography (biotechnology industry).



Crude fractionation tower at the Phillips Oil Refinery in Woods Cross, Utah. In this crude fractionator, 25,000 barrels per day of incoming crude oil is divided into six fractions by distillation. (Photo by Alexis Kelner.)



Preparative scale liquid chromatography unit with 6 ft (1.8 m) long column (in center) having an inner diameter of 6 in (15 cm). Up to 2 L of sample solution can be injected and processed in a single 90-min run. (Courtesy Thomas J. Filipi and Whatman Chemical Separation Division.)

Analytical and Preparative Separations (II)

2. Analytical separations:

Goal: understanding of mechanisms of separation, sample analysis, and for subsequent detection.

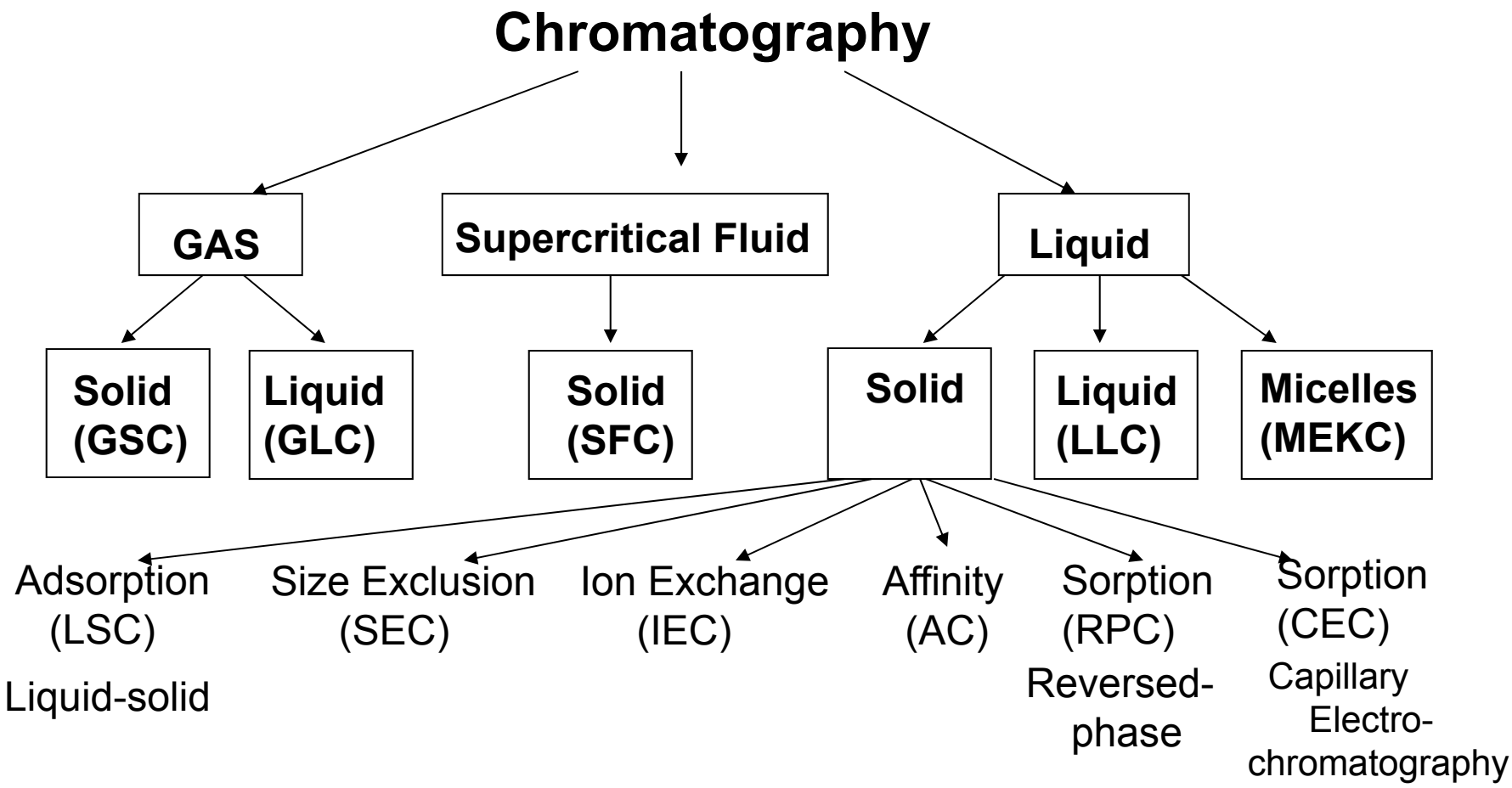
Characteristics: (i) High purity and (ii) small scale

☺**Chromatography techniques**

(i) A physical separation technique

(ii) Components partition between two phases:
Stationary phase: does not move
Mobile phase: does move

(iii) Solutes separated in the two phases due to differences in how they interact with the phases.



Micellar electrokinetic chromatography (MEKC)

A little history

Tswett - 1903

First observed separation of plant pigments as bands on chalk columns

Little additional work for next 28 years.

Kuhn & Lederer - 1931

LC separation of carotenoids

Development of Chromatography

1903	Tswett first outlines principles
1931	Lederer & Kuhn - LC application
1936	First book on chromatography
1938	Use of TLC and ion exchange
1939	First synthetic exchange resins
1941	First LLC paper
1944	First PC paper (paper chromatography)
1950	Reverse phase LC described
1959	Gel permeation
1965	Instrumental HPLC

The concepts we need to remember

1. The essential feature of separations:

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