SEPARATION PROCESSES

CHAPTER ONE:

TYPICAL CHEMICAL PROCESS

- LARGE SCALE
- ECONOMICAL

EXAMPLES:
1) DISTILLATION
2) ABSORPTION
3) LIQ-LIQ EXTRACTION
4) ADSORPTION
5) MEMBRANES
6) CRYSTALLIZATION

OPERATION: CONTINUOUS, SEMI-CONTINUOUS, BATCH
Processes with only reaction

- complete reaction
- stoichiometric feed
- no side reactions
- no catalyst

Processes with only separation

- clean stream
- low purity products ok (enriched air)
- phase separation

Not very common ⇒ usually have both,

Mixtures:

⇒ In general very stable

Why?

More disorder ⇒ entropy increases

Why are separations difficult (and expensive)?
SEPARATION $\Rightarrow$ ENTROPY $\downarrow$

(THERMODYNAMICALLY UNFAVORABLE)

$\Rightarrow$ ADD ENERGY $\Rightarrow$ $$$

MECHANISMS FOR SEPARATION OF MIXTURES:

1. PHASES

$\Rightarrow$ CREATE MORE THAN ONE PHASE

$\Rightarrow$ COMPOSITION IN EACH PHASE DIFFERENT

i.e., $X_i \neq Y_i$

(GOVERNED BY THERMODYNAMIC EQUILIBRIUM)

$\Rightarrow$ SEPARATE PHASES

$\Rightarrow$ GENERATE 2 STREAMS, EACH WITH COMPOSITION DIFFERENT FROM FEED.

EXAMPLES: 1) DISTILLATION $\{$(VLE)$\}$

2) ABSORPTION

3) CRYSTALLIZATION $\{$(SLE)$\}$
2. MASS SEPARATING AGENT

- ADD 3rd COMPONENT (USUALLY NEW PHASE)
- MASS TRANSFER TO NEW PHASE

Eg.: LIQ PHASE $\rightarrow$ LIQ PHASE (EXTRACTION)

LIQ/GAS PHASE $\rightarrow$ SOLID PHASE (ADSORPTION)

- IN ALL CASES WANT GOOD CONTACT BETWEEN PHASES
  $\Rightarrow$ MIXING IN LLE

$\Rightarrow$ LARGE SURFACE AREA FOR SOLIDS
3. **Barrier (Membranes)**

![Diagram of selective transport across a membrane]

4. **Solid Agent (~ Packed Beds)**
   - Activated Carbon (Organics in H₂O)
   - Ion Exchange (Ions)

5. **Force Field or Gradient**
   - Imposed Electric Field (Liq)
   - Velocity Gradient (Liq)
   - Pressure (Centrifuge) (Vapor)
   - Electrophoresis (Liq)
EVALUATING THE SEPARATION
(HOW WELL ARE YOU DOING?)

① RATE OF SEPARATION (MASS TRANSFER)
   → GOOD CONTACT
   → T, P, COMPOSITION
   → PHASE (GAS, LIQ, SOLID)

② EXTENT OF SEPARATION (THERMODYNAMICS)
   → DIFFERENCES BETWEEN MOLECULES
   → INTERACTIONS

TO GET A SEPARATION, LOOK FOR ASPECTS THAT
YOU CAN EXPLOIT (PROPERTY DIFFERENCES)

① MOLECULAR PROPERTIES
   MOLECULAR WEIGHT, POLARIZABILITY, DIELECTRIC
   CONSTANT, ELECTRIC CHARGE, MOLECULAR SHAPE,
   RADIUS OF GYRATION, DIPOLE MOMENT

② THERMODYNAMIC PROPERTIES
   VAPOR PRESSURE, ADSORPTIVITY, SOLUBILITY,
   DIFFUSIVITY
More on Mechanisms of Separation

1. Phase Addition / Creation

   a. Energy Separation Agent (ESA)
      → Heat Transfer (Vaporization)
      → Shaft Work (Compression)
      → Lower Pressure (Condensation)

   b. Mass Separation Agent (MSA)
      → Liquid (Clean Solvent)
      → Vapor (Clean Air)
      → Solid (Ion Exchange Resin, Molecular Sieves)

Exercise:
Separations that utilize this mechanism (ESA or MSA, how is phase added/created?)

a. Simple (One Stage)
   Partial Vaporization or Flash Distillation

b. Better Purity (Multiple Stages)
   Distillation ← Most popular in Industry
(c) Not easy to condense (dilute comp. in air) absorption

(d) Dilute component in liquid (+ volatile) stripping

(e) Azeotrope or temperature sensitive
Azeotropic distillation and extraction

(f) Very pure solid product
Crystallization

2. Barriers - Membrane
- Reverse osmosis (ions), pervaporation
  (organics, dehydration), ultrafiltration, gas

3. Solid Agents - Generally batch or semi-continuous
  (finite capacity)
- Adsorption
  \[\text{Low concentration of component to be removed}\]
- **CHROMATOGRAPHY**
  - PACKED COLUMN
  - COLLECT AS FRACTIONS
  - RATE THROUGH COLUMN DIFFERS

- **ION EXCHANGE**
  - CHARGED SPECIES

4. **EXTERNAL FIELD OR GRADIENT**
   - CENTRIFUGE
     - MOLECULAR WEIGHT DIFFERENCE
   - ELECTRODIALYSIS
     - APPLIED ELECTRIC FIELD & MEMBRANE
   - ELECTROPHORESIS
     - APPLIED ELECTRIC FIELD
   - FIELD FLOW FRACTIONATION
     - PARTICLE SEPARATION
ACCOUNTING IN SEPARATIONS

⇒ CONSERVATION OF MASS

HOWEVER, SINCE NO REACTION, MOLES CONSERVED,

NOTE: WE WILL USE MATERIAL BALANCES EXTENSIVELY IN THIS COURSE (CHE 254).

⇒ MOLE FRACTIONS USED COMMONLY
⇒ BEST TO WORK WITH THESE UNLESS OTHERWISE STATED.

SELECTING YOUR SEPARATION PROCESS:

⇒ IN GENERAL GOVERNED BY ECONOMICS

ALSO: A) FEED CONDITIONS

COMPOSITION, FLOW RATE, T, P, PHASE

B) PRODUCT CONDITIONS

PURITY, T, P, PHASE

C) PROPERTY DIFFERENCES THAT CAN BE EXPLOITED: MOLECULAR, THERMO, TRANSPORT

D) CHARACTERISTICS OF SEPARATION OPERATION E.G.: SCALE-UP, STABILITY, T, P, PHASE, SIZE LIMITATIONS, ENERGY REQUIREMENTS.
MOST COMMON:

T, P, PHASE

WHY? CAN BE ALTERED EASILY

A) FEED CONDITIONS

1) COMPOSITION

a) LOW CONCENTRATION SPECIES OF INTEREST
   ⇒ ADSORPTION
   ⇒ MEMBRANES

b) QUALITY OF FEED
   ⇒ EXAMPLE: H$_2$SO$_4$ PRODUCTION

C) TEMPERATURE SENSITIVE
   ⇒ SOLVENT EXTRACTION
   ⇒ E.G.: AROMATICS + SULFUR FROM KEROSENE
   OIL FROM SEEDS (+ FLAVORINGS)
   ⇒ SOLID-LIQ EXTRACTION
2) Flow Rate
   a) Large Flow Rates
      ⇒ Distillation
      ⇒ Absorption

      (Packed bed would be bad. Why? Large ΔP)
   b) Small Flow Rates
      ⇒ Membranes
      ⇒ Adsorption
      ⇒ Batch Separations

3) Temperature
   a) Heat of Vaporization ($¥$)
      ⇒ Distillation
      ⇒ Membranes (Some)
   b) Cooling ($¥$)
      ⇒ Crystallization

4) Pressure
   ⇒ Distillation (~ Atmospheric Pressure)
   ⇒ Membrane (Sea Water Desalination)
   ⇒ Extraction
5) PHASE STATE
   a) GAS
      → ADSORPTION
      → ABSORPTION
   b) LIQUID
      → EXTRACTION
      → DISTILLATION
   c) SOLID
      → EXTRACTION

B) PRODUCT CONDITIONS
   → HOW GOOD DO YOU HAVE TO DO?
   → WHAT CONDITIONS?

1) PURITY
   a) HIGH
      → EXTRACTION
      → ADSORPTION
   b) LOW
      → MEMBRANES

2) TEMPERATURE
   AVoid HEATING/COOLING UNNECESSARILy
3) PRESSURE
   -> AVOID PACKED BEDS
   -> MEMBRANES -> KEEP SPECIES OF INTEREST ON FEED (HIGH PRESSURE) SIDE

   E.g.: FUEL CELL + H₂/CO₂
   SELECTIVELY TRANSPORT CO₂ ACROSS MEMBRANE TO AVOID NEED FOR REPRESSURIZATION OF H₂

4) PHASE
   -> PRODUCT IN CORRECT PHASE

C) PROPERTY DIFFERENCES TO BE EXPLOITED
1) RELATIVE VOLATILITY
   ⇒ DISTILLATION

2) SOLUBILITY
   ⇒ CRYSTALLIZATION, ABSORPTION, EXTRACTION

3) SPECIFIC INTERACTIONS
   ⇒ ADSORPTION, CHROMATOGRAPHY

4) SIZE / MASS
   ⇒ MEMBRANES, CENTRIFUGATION

5) DENSITY
   ⇒ FLOTATION
D) CHARACTERISTICS OF SEPARATION OPERATION

1) EASE OF SCALE-UP

   a) EASIEST: DISTILLATION, ABSORPTION
   b) NEXT EASIEST: EXTRACTION, MEMBRANES
   c) HARDEST: ADSORPTION, CRYSTALLIZATION

   ECONOMY OF SCALE \( \Rightarrow \) \( \text{SIZE} \uparrow \)
   \[ \frac{\text{\$$/VOLUME}}{\downarrow} \]
   (TRUE FOR DISTILLATION, ABSORPTION)

   NOT TRUE FOR MEMBRANES \( \Rightarrow \) \( \text{SIZE} \uparrow \)
   \[ \frac{\text{\$$/VOLUME}}{\text{CONSTANT}} \]

   WHY? PARALLEL UNITS VS. ONE LARGER UNIT
   (MEMBRANES) (DISTILLATION)

2) EASE OF STAGING

   COLUMN VS. MODULE
   NEED FOR REPRESSURIZATION

3) T, P, COMPOSITION (LIKE BEFORE)

4) SIZE

   E.G.: NAVY SHIP \( \Rightarrow \) LIMITED SPACE
   EXISTING PLANT \( \Rightarrow \) LIMITED SPACE
5) ENERGY

⇒ PHASE CHANGE
⇒ UTILITIES (LOCATION)

OTHER FACTORS:

1) DILUTE PRODUCT ⇒ HIGHER SELLING PRICE
TO BE SEPARATED

⇒ CAN USE EXOTIC SEPARATION (PHARMACEUTICALS)

2) HIGH PURITY ⇒ LARGE # OF STAGES

3) SCALABILITY

SMALL OR BATCH ⇒ MORE EXOTIC
LARGE ⇒ TRADITIONAL

4) MATURITY (+ COMFORT LEVEL)

MOST MATURE

DISTILLATION
ABSORPTION
EXTRACTION

MOST USED

ADSORPTION
ION EXCHANGE
CRYSTALLIZATION

MEMBRANES
CHROMATOGRAPHY

LEAST MATURE

AFFINITY SEPARATIONS

LEAST USED