Table 1.1 Continuous separation operations based on interphase mass transfer
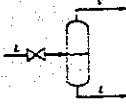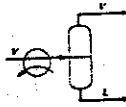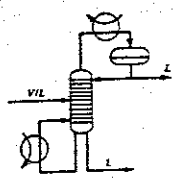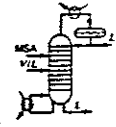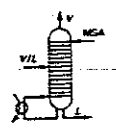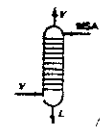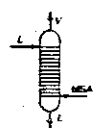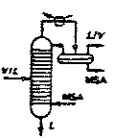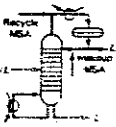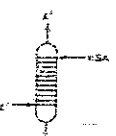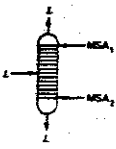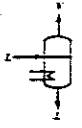
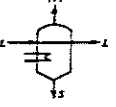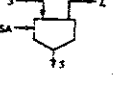| Unit Operation	Symbol[b]	Initial or Feed Phase	Developed or Added Phase	Separating Agent(s)	Industrial Example[c]
Flash vaporization[a] (1)		Liquid	Vapor	Pressure reduction	Recovery of water from seawater (Vol. 22, p. 24)
Partial condensation[a] (2)		Vapor	Liquid	Heat transfer (ESA)	Recovery of H_2 and N_2 from ammonia by partial condensation and high-pressure phase separation (Vol. 2, pp. 282–283)
Distillation[a] (3)		Vapor and/or liquid	Vapor and liquid	Heat transfer (ESA) and sometimes work transfer	Stabilization of natural gasoline by distillation to remove isobutane and lower molecular weight hydrocarbons (Vol. 15, p. 24)
Extractive Distillation[a] (4)		Vapor and/or liquid	Vapor and liquid	Liquid Solvent (MSA) and Heat transfer (ESA)	Separation of toluene from close-boiling nonaromatic compounds by using phenol as a solvent to improve the separability. (Vol. 20, p. 541)
Reboiled absorption[a] (5)		Vapor and/or liquid	Vapor and liquid	Liquid absorbent (MSA) and heat transfer (ESA)	Removal of ethane and lower molecular weight hydrocarbons from the main fractionator overhead of a catalytic cracking plant (Vol. 15, pp. 25–26)
Absorption[a] (6)		Vapor	Liquid	Liquid absorbent (MSA)	Separation of carbon dioxide from combustion products by absorption with aqueous solutions of an ethanolamine (Vol. 4, p. 358, 362)
Stripping[a] (7)		Liquid	Vapor	Stripping vapor (MSA)	Stream stripping of naphtha, kerosene, and gas oil side cuts from a crude distillation unit to remove light ends (Vol. 15, pp. 17–18)
Refluxed stripping (steam distillation)[a] (8)		Vapor and/or liquid	Vapor and liquid	Stripping vapor (MSA) and heat transfer (ESA)	Distillation of reduced crude oil under vacuum using steam as a stripping agent (Vol. 15, p. 55)
Reboiled stripping[a] (9)		Liquid	Vapor	Heat transfer (ESA)	Removal of light ends from a naphtha cut (Vol. 15, p. 19)
Azeotropic distillation (10)		Vapor and/or liquid	Vapor and liquid	Liquid entrainer (MSA); heat transfer (ESA)	Separation of acetic acid from water using n-butyl acetate as an entrainer to form an azeotrope with water (Vol. 2, p. 851)
Liquid-liquid extraction[a] (11)		Liquid	Liquid	Liquid solvent (MSA)	Use of propane as a solvent to deasphalt a reduced crude oil (Vol. 2, p. 770)

Table 1.1 (Cont.)

Unit Operation	Symbol[b]	Initial or Feed Phase	Developed or Added Phase	Separating Agent(s)	Industrial Example[c]
Liquid-liquid extraction (two-solvent) (12)		Liquid	Liquid	Two liquid solvents (MSA₁ and MSA₂)	Use of propane and cresylic acid as solvents to separate paraffins from aromatics and naphthenes (Vol. 15, pp. 57–58)
Drying (13)		Liquid and often solid	Vapor	Gas (MSA) and/or heat transfer (ESA)	Removal of water from polyvinyl-chloride with hot air in a rotary dryer (Vol. 21, pp. 375–376)
Evaporation (14)		Liquid	Vapor	Heat transfer (ESA)	Evaporation of water from a solution of urea and water (Vol. 21, p. 51)
Crystallization (15)		Liquid	Solid (and vapor)	Heat transfer (ESA)	Crystallization of p-xylene from a mixture with m-xylene (Vol. 22, pp. 487–492)
Desublimation (16)		Vapor	Solid	Heat Transfer (ESA)	Recovery of phthalic anhydride from gas containing N_2, O_2, CO_2, CO, H_2O, and other organic compounds by condensation to the solid state (Vol. 15, p. 451)
Leaching (17)		Solid	Liquid	Liquid solvent (MSA)	Aqueous leaching of slime to recover copper sulfate (Vol. 6, p. 167)
Adsorption (18)		Vapor or liquid	Solid	Solid adsorbent (MSA)	Removal of water from air by adsorption on activated alumina (Vol. 1, p. 460)

[a] Design procedures are fairly well standardized.
[b] Trays are shown for columns, but alternatively packing can be used. Multiple feeds and side streams are often used and may be added to the symbol (see example in Fig. 1.7).
[c] Citations refer to volume and page(s) of *Kirk-Othmer Encyclopedia of Chemical Technology* 2nd ed., John Wiley and Sons, New York, 1963–1969.

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Table 1.4   Separation operations based on intraphase mass transfer

Unit Operation	Phase State	Method of Separation	Separating Agent	Industrial Example[a]
Pressure diffusion (1)	Gas	Pressure gradient induced by centrifugal force	Centrifugal force	Separation of isotopic mixtures, Vol. 7, p. 149
Gaseous diffusion (2)	Gas	Forced flow through porous barriers	Porous barrier	Separation of isotopes of uranium, Vol. 7, p. 110
Reverse osmosis (3)	Liquid	Pressure gradient to overcome osmotic pressure	Membrane	Desalination of water, Vol. 14, p. 347
Permeation (4)	Gas or liquid	Forced flow through semipermeable membrane	Membrane	Dehydration of Isopropanol, Vol. 9, p. 284
Dialysis (5)	Liquid	Difference in diffusion rate across membrane	Membrane	Recovery of purified caustic soda from rayon process liquid, Vol. 7, p. 14
Foam fractionation (6)	Liquid	Selective concentration of species at interface	Foam interface	Enzyme and dye separations, Vol. 9, p. 896
Chromatographic separations (7)	Gas or liquid	Selective concentration in and on solids	Solids	Mixed vapor solvent recovery, Vol. 5, p. 413
Zone melting (8)	Solid	Liquid zone travels through metal ingot	Temperature gradient	Germanium purification, Vol. 22, p. 680
Thermal diffusion (9)	Gas or liquid	Temperature-induced concentration gradient	Temperature gradient	Separation of gaseous isotopic mixtures, Vol. 7, p. 138
Electrolysis (10)	Liquid	Electric field plus membranes	Electric field and membranes	Separation of hydrogen and deuterium, Vol.6, p. 895
Electrodialysis (11)	Liquid	Electric field plus charged membranes	Membrane and electric field	Desalination of water, Vol. 7, p. 857

[a] Citations refer to H. F. Mark, J. J. McKetta, and D. F. Othmer, Eds., *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., John Wiley & Sons, New York, 1969.

PRELIM - PROCESS

Separation Factor $\alpha_{ij} = \dfrac{x_{i1}/x_{j1}}{x_{i2}/x_{j2}}$

best for reduction of separation agent and purity   counter > cross > cocurrent

staging

Reflux - convert a portion of a product stream into the other counterflowing phase or add a mass separating agent.

Macabe-Thiele Diagram
Constant Molal Overflow

equilibrium

rectifying $y_A = \dfrac{D\, x_{A,D}}{V} + \dfrac{L}{V} x_A$

intersection line $m = -L_F/V_F$

stripping $y_A = \dfrac{-x_{A,b}}{V'} + \dfrac{L'}{V'} x_A$

$L' = L + L_F \quad V' = V - V_F$
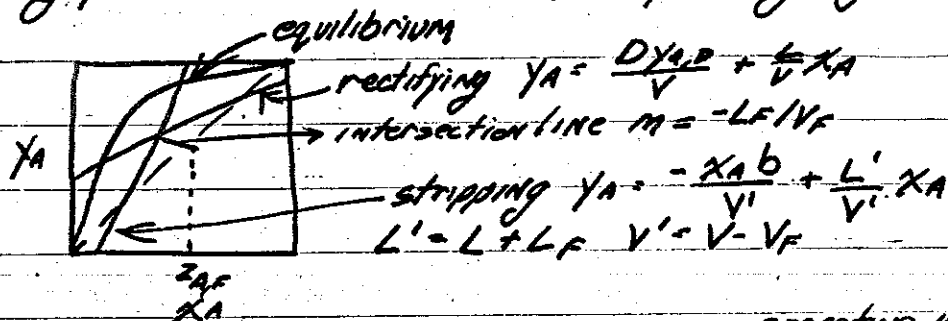
Limiting Conditions   MINIMUM REFLUX (∞ stages) operating intersect with equilibrium

minimum stages (∞ reflux) operating $y = x$

Multistage Batch Distillation $\quad -\ln\dfrac{b'}{F'} = \displaystyle\int_{x_{A,F}}^{x_{A,b}} \dfrac{d x_{A,b}}{x_{A,d} - x_{A,b}}$

constant reflux ratio ($x_{A,d}$ varies)

constant $x_{A,d}$ (reflux varies

Effect of Pressure - high $\rightarrow$ high vapor density, lower volumetric flow rate

column diameter lower

Steam Distillation - lower the partial pressures, thus lowering the temp.

Curved Operating Lines - enthalpy balance - chord = local $\dfrac{L}{V}$

Liquid-Liquid Extraction
   $R - S = F - E$

tie lines w/ equilibrium
use difference point for operating
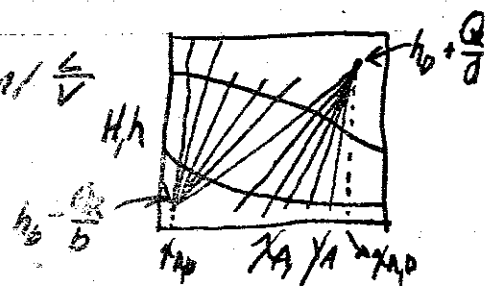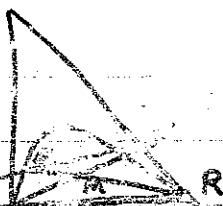
PRELIM - PROCESS

Patterns of cha___
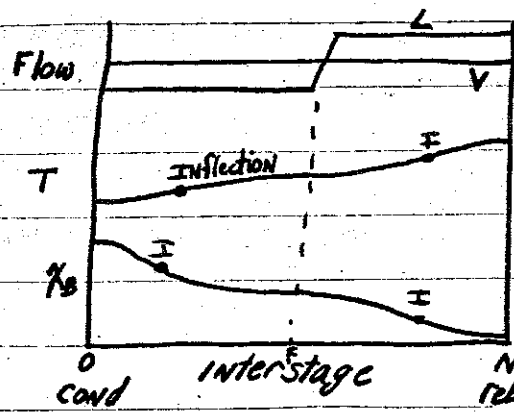
saturated liquid feed

T profiles in dist. columns reflect compos__ while interstage flow reflects enthalpy balance (In Absorbers + strippe__ opposite)

Absorber

GAS → LIQUID/SOLID
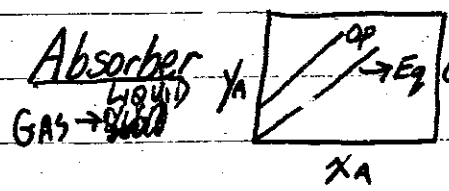
(Henry's Law) dilute heat effects

Minimum solvent by Assuming, absorbers - heat up (saturation strippers - cool down

Extractive Distillation

- adding a solvent serves to volatize one component over another, useful when close b.p. (low volatility

Azeotropic Distillation

- similar but solvent forms azeotrope which is volatile.

Minimum Stage Requirement

$$N_{MIN} = \frac{\log \left[(x_a/x_b)_d / (x_a/x_b)_b \right]}{\log \alpha_{AB}}$$

Stages versus reflux correlation Gilliland

Stage Efficiency

- Murphree - change equilibrium curve

Extraction

- selectivity, recoverability, Distribution coefficient, Capacity, solvent solubility, density, interfacial tension

Prelim - Process

Mass Transfer - molecular diffusion, convection, turbulent mixing

$$N_A = -cD_{AB}\nabla x_A + x_A(N_A + N_B)$$

Chilton-Colburn: $\quad j_D = j_H = \dfrac{f}{2}$

$$N_A = K_G(p_{AG} - p_{AE}) = K_L(C_{AE} - C_{AL})$$
$$= k_g(p_{AG} - p_{Ai}) = k_L(C_{Ai} - C_{AL})$$
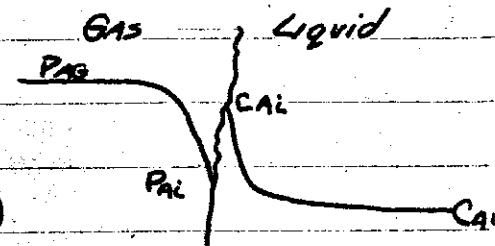
$$p_A = HC_A$$
$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{H}{k_L}$$
$$\frac{1}{K_L} = \frac{1}{Hk_G}$$

Counter Current Contactors

$$\frac{V}{A}\frac{dy_A}{dh} = \frac{L}{A}\frac{dx_A}{dh} = K_G P a (y_{AE} - y_A)$$

$$h = \frac{V}{A}\int_{y_{A in}}^{y_{A out}} \frac{dy_A}{K_G P a (y_{AE} - y_A)}$$

Gas Phase Control

$$(NTU)_{OG} = \int_{y_{A in}}^{y_{A out}} \frac{dy_A}{y_{AE} - y_A} = \frac{hAK_G P a}{V}$$

$$(NTU)_{OL} = \int_{x_{A in}}^{x_{A out}} \frac{dx_A}{x_{AE} - x_A} = \frac{h K_L \rho_{ma} a A}{L}$$

Liquid Phase Control

$$(HTU)_{OG} = \frac{V}{K_G P A A}$$

$$(HTU)_{OL} = \frac{L}{K_L \rho_{ma} a A}$$

$$h = (HTU)_{OG}(NTU)_{OG}$$

$$h = (HTU)_{OL}(NTU)_{OL}$$
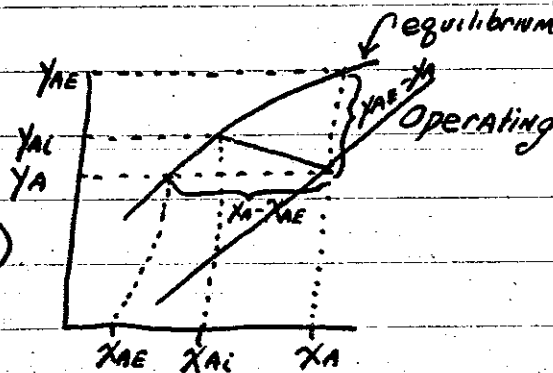
PRELIM PROCESS

SEPARATE Similar MP+BP L-L Extraction, Azeotropic, Entrainment Distillation
Cool Water at 150°F Cooling Tower (Wet Bulb Temp) (Adiabatic Saturation
Remove H_2O (200 ppm) to 1 ppB in Ar $T_{crit} = -185.7°C$ (Cryogenic, Stripper Absorber)
Remove 1% phenol from H_2O - IsoAmyl acetate L-L extraction
Ethanol + H_2O

DISTILLATION Column CONTROL
monitor X_B, X_D change reflux
ratio $r = \frac{V}{D}$, thus changing D/B.
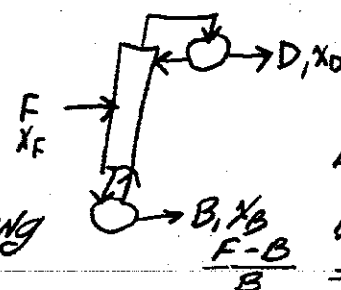
$$F = D + B$$
$$F X_F = D X_D + B X_B$$
$$D X_F + B X_F = D X_D + B X_B$$
$$D(X_F - X_D) = B(X_B - X_F)$$
$$\frac{F-B}{B} = \frac{D}{B} = \frac{X_B - X_F}{X_F - X_D}$$

COST ESTIMATION

Scaling $\qquad a = b * \left[\frac{CAP(a)}{CAP(b)} \right]^{0.6}$

Material $\downarrow$

Pipe + fitting → Nom id
Pump → gal/min
Tank → gal
Agit → hp
Filter → area
Crusher → ton/h
Dry Dust Coll → ft^3/min
heat exchanger → ft^2 tube diam.
Furnace → Btu/hr
Shells → weight
Trays → diameter
Reactor → gal

I. Evaporation:

 - Vapor from a boiling liquid soln is removed and a more concentrate
 soln remains. Usually removal of H_2O from aq. soln.

 - typical Examples:

  aqueous solns of: sugar, $NaCl$, $NaOH$, glycerol, glue, milk, & OJ.

 - Also for Seawater → Drinking H_2O.

A. Processing Factors:

 1. Concentration of liquid
  - usually low, viscosity ~ H_2O, high heat transfer coef.

 2. As evaporation proceeds - soln becomes viscous & h.t. coef ↓
  ∴ Circulation necessary

 3. Solubility may limit maximum concentration in soln
  - Also Solubility of salt ↓ w/ Temp; when condensing crystal
  may occur.

 4. Temp. Sensitive mat'l (ie. biological)

 5. Foaming or frothing (ie. skim milk) - foam accompanies vapor
  & entrainment losses occur.

 6. Pressure & Temp (Remember: P↑ $T_{B.P.}$ of soln ↑ and
  as soln conc. increases $T_{B.P.}$ may rise)
  - Sometimes operate under 1 atm or vacuum.

 7. Keep in mind - Scale deposition & mat'l construction.

B. Types of Evaporators:

 1. Open Kettle

 2. Horizontal-tube, nat'l circulation evaporator.
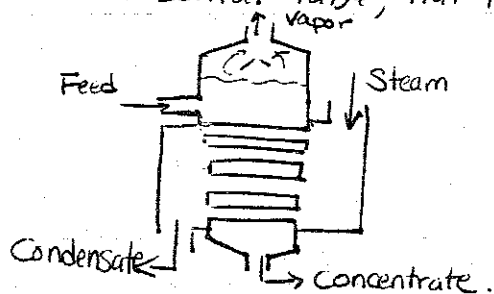
 - Cheap
 - nonviscous liq. w/ high heat trans. coef
 - no deposit scale
 - Continuous operation.

3.) Verticle type nat'l circulation evaporator.
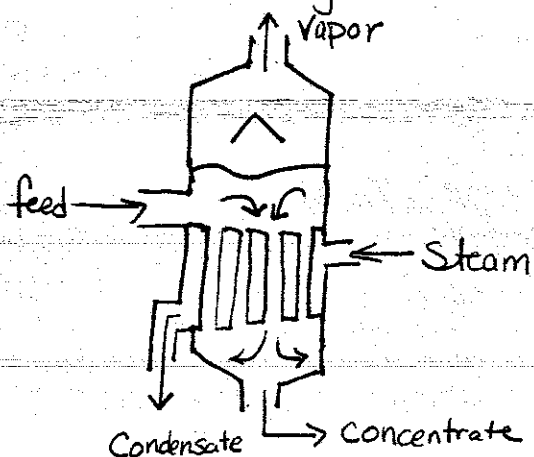
- liquid inside tubes
- Steam condenses on outside
- for sugar, salt, caustic soda.

4) Long tube Verticle type evaporator.
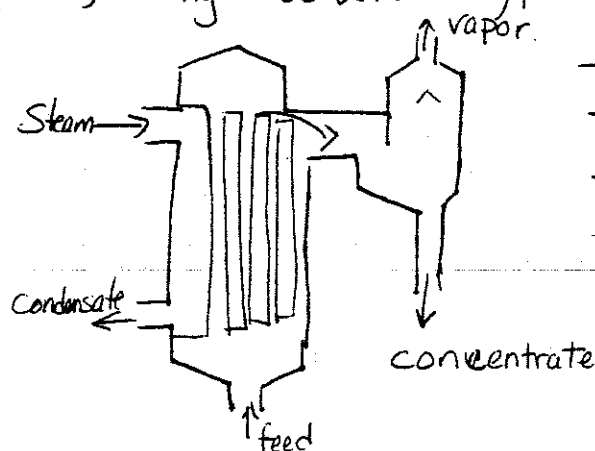
- high liquid velocities
- liquid inside tubes
- Condensed milk

5) Falling Film type evaporator

- Variation of Long tube evap.
  - liq'd feed at top
  - flows down wall as thin film
  - V/L separation at bottom.
  - for heat-sensitive mat'ls (OJ)

6) Forced-Circulation type Evaporator.
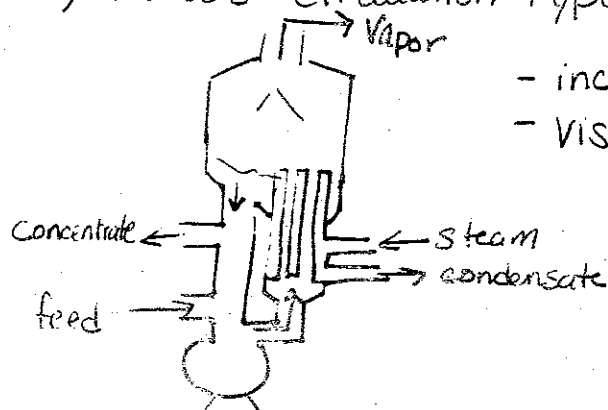
- increase liquid film heat transfer coef
- Viscous liquids.

7. Agitated - film evaporator

    - used to inc. heat transfer on liquid side

      - for heat sensitive viscous mat'ls.

        - rubber latex, gelatin, antibiotics, fruit juice

Method of Operation

1) Single effect evaporators.

    - assumed, completely mixed

    - use $q = UA \Delta T = UA(T_{steam} - T_1)$

    - small operators

    - large capacity inefficient; better to use mult.
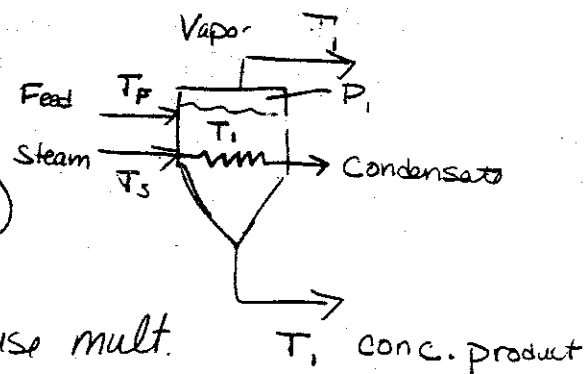
2) Forward Feed mult. effect evap.

      $P_1 > P_2 > P_3$.

    fresh feed added to first effect; same direction w/ steam.

    - used when feed temp high. or if final concentrated prod. is temp sensitive.

    - $T_{BP1} > T_{BP2} >$ etc.

3) Backward feed multiple effect evaporators.

    - feed enters into last effect (coldest)

    - for cold fresh feed.

    - less heat needed to neat smaller amt of liq to higher temps

    - liq. pumps required. b/c flow from low to high P

Drying of Process Mat'l

- ## Wet Bulb Temperature:

- S.S. nonequilibrium Temp reached when a small amt of water is ~~kndy~~ contacted under adiabatic conditions by a continuous stream of gas

B/c Liquid is small, T & Humidity of gas are constant.

makeup H_2O T_W — Thermometer, T_W — T_W

gas T, H — gas (air/water vapor) T, H — Wick

T = dry bulb Temp
T_W = wet " "
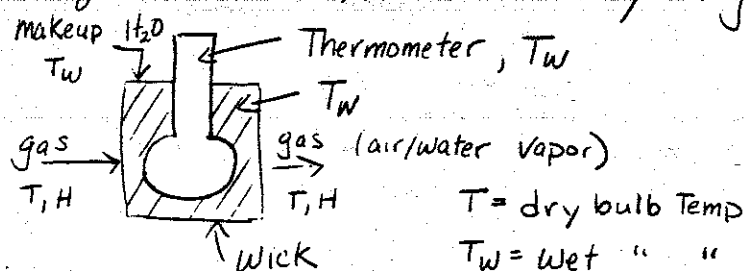
at S.S. water is evaporating to gas stream. The latent heat of evaporation is balanced with convective heat flowing from gas stream at T to the wick at lower temp T_W

$$\frac{H - H_W}{T - T_W} = \frac{-h/M_B K_y}{\lambda_w}$$

$$\frac{h}{M_B K_y} = \text{psychrometric ratio} \sim .95 - 1.005$$

λ_w = latent heat of vaporization @ T_i
H = Humidity @ T
h = convective heat trans. coef
~~M_B = is M.W. of the K, & the air~~
M_B = M.W. of air
K_y = conductive h.t.c.

Note: Wet Bulb determination is often used to determine humidity of an air - H_2O vapor mixture.

Types of Drying

I. Batch or Continuous

A. Tray Dryer
B. Vacuum Shelf Indirect Dryers - for expensive, temp-sensitive, oxidizable mat'ls
C. Continuous Tunnel Dryers - foods
D. Rotary Dryers - granular solids
E. Drum Dryers - for slurries or pastes of solids in fine suspension (Potato → Potato flai
F. Spray Dryers - for light & porous mat'l (Dried Powdered milk)

Typical Rate Drying Curves:
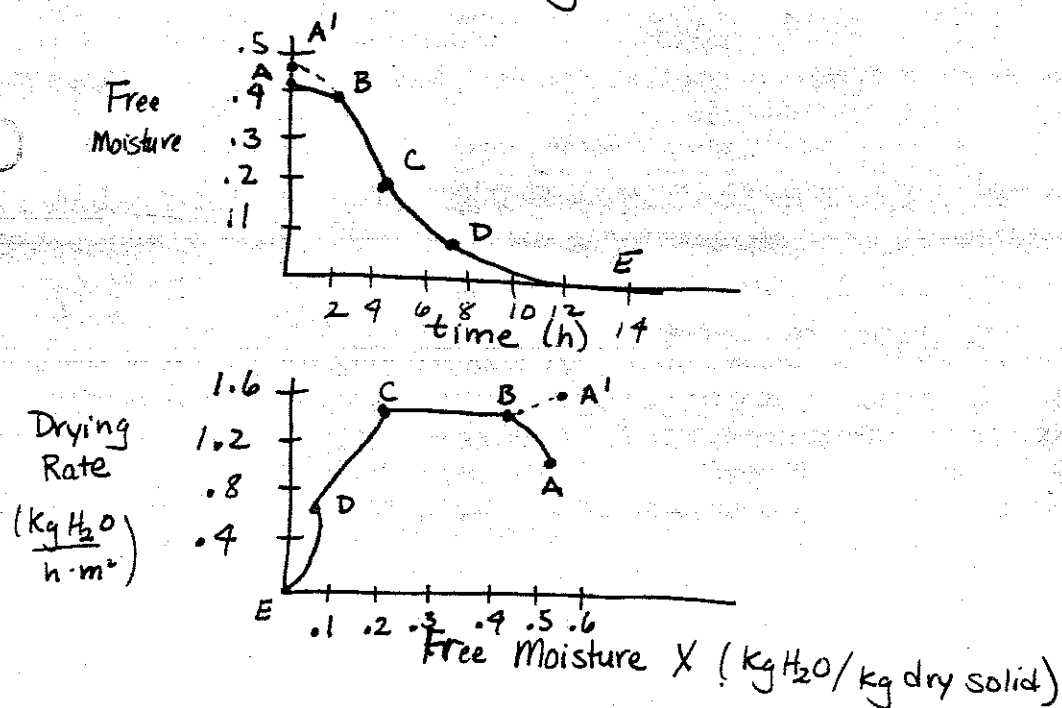
Types of Separation Process & Methods

I. Absorption — gas & liquid phases. Solute A(s) are absorbed from the gas phase into liquid phase. Uses molecular & turbulent diffusion or mass transfer of solute A through stagnant nondiffusing $B(g)$ into stagnant $C(l)$. Example: NH_3 from Air by $H_2O(l)$, SO_2 from flue gases in alkaline solns.

→ Stripping or desorption — opposite of Absorption.
  i.e. — Steam stripping nonvolatile oil (steam contacts oil & small amts of volatile components of oil leave w/ steam)

→ humidification/Dehumidification — pure air & pure $H_2O(l)$

II. Distillation — volatile vapor phase & liquid phase vaporizes.
  Examples: Ethanol/H_2O soln (Ethanol rich vapor)
    — Crude petroleum; fractions of gasoline, Kerosene & heating oils are distill of

III. Liquid-Liquid Extraction — 2 phases are liquid; solute/solutes are removed from one liquid phase to another.
  Examples: Acetic Acid from H_2O by isopropyl ether
    : antibiotics in (aq) fermentation soln by organic solvent.

IV. Leaching - fluid used to extract a solute from a solid
(Extraction) EX: Copper from solid ores by sulfuric acid.
: Vegtable oils from solid soybeans by organic solvents (hexane)
: Soluble sucrose by water from sugar cane + beets

V. Membrane Processing - Separation of molecules by thin, solid membranes.
It controls rate of movement of molecules btw 2 phases.
I.E. : remove Salt from H_2O; purify gases; food processing

VI. Crystallization - Solute components soluble in soln removed by adjusting
one parameter (T or X) there by the solubility of one or more
solute components is exceeded + Crystallize out as solid phase
EX: sugar from soln.; metal salts in processing metal ore soln.

Things to Consider in Separations:

Method	Characteristic Property Difference
1) Distillation	Volatility
2) Crystallization	Melting Point
3) Centrifugation	Density
4) Gas Diffusion	D_{AB}
5) Reverse Osmosis	Pressure; Concentration
6) Liquid-Liquid Extraction	} Difference in Phase Solubility
7) Liquid-Gas Absorption	
8) Filtration	Permeability
9) Electrophoresis Electrodialysis	Charge; Mass

Common Organic Solvents for Aqueous Extraction

MIBK - Methyl Isobutyl Ketone
MEK - Methyl Ethyl Ketone
MEA - Mono ethano amine
DEG - Diethylene glycol

Choosing a Solvent:

1) High selectivity $\neq$ Capacity
2) Regenerable
3) Inexpensive
4) Non toxic, Noncorrosive
5) Immiscible
6) Low Viscosity
7) Does Not form a Stable emulsion with Solute.

Sample Prelim Questions: Separations.

1) How would you get pure H_2O from Sea water

Soln: Multiple Effect Evaporators

Steam

Sea water

Condensate   pure H_2O →

pure H_2O

Conc. Brine.

$* P_1 > P_2 > P_3$

2) How do you separate Air into pure O_2

Soln: Cryogenic Plant.

Pressure Swing Adsorption

O_2 N_2

H_2O

Air

HE₁

Lindy Column

N_2

Low P

3psi

$O_2(l)$

High P

90psi

Unpure O_2

N_2

HE

Note:

1) Ar will build up in O_2 ∴ remove O_2 stream near bott of Low Pressure Co and distill them in a separate column & return pure O_2 into Low Pressure Column

2) Need a Pressure difference b/c the High Pressure colum acts as a Reboiler for the Low P col.

3) How would you remove CH_3Br from air?

$x = .01$ & want $x = 0.002$

Soln: Adsorb CH_3Br with a Heavy Oil (must be non-volatile & inexpensive). Note: CH_3Br is soluble in any non-polar organic Then Strip the CH_3Br/oil with steam; followed by Condensing CH_3Br H_2O

1) Why is distillation done at high Pressure?

   -allows for smaller diameter column & Easy condensation of over head stream, higher Condensation Temperature; less cooling water.

2) How would you remove 1% phenol from H_2O.

   → Liquid Extraction using Benzene, Toluene, CCl_4, or CH_3Cl_3 Solvent then Distillation of Phenol & Solvent.

   | Crystallize phenol. |

3) How do you separate ethanol & H_2O

   - Use distillation but azeotrope @ $x \doteq .95$

   ∴ Azeotropic distillation or Membrane Separation at $x = .95$

Benzene

O, H_2O, EtOH

EtOH
H_2O

Benzene

use high volatile entrainer.

high maximum Azeotrope B.P — Reboile

- minimum Azeotropic B.P. — Condenser

EtOH
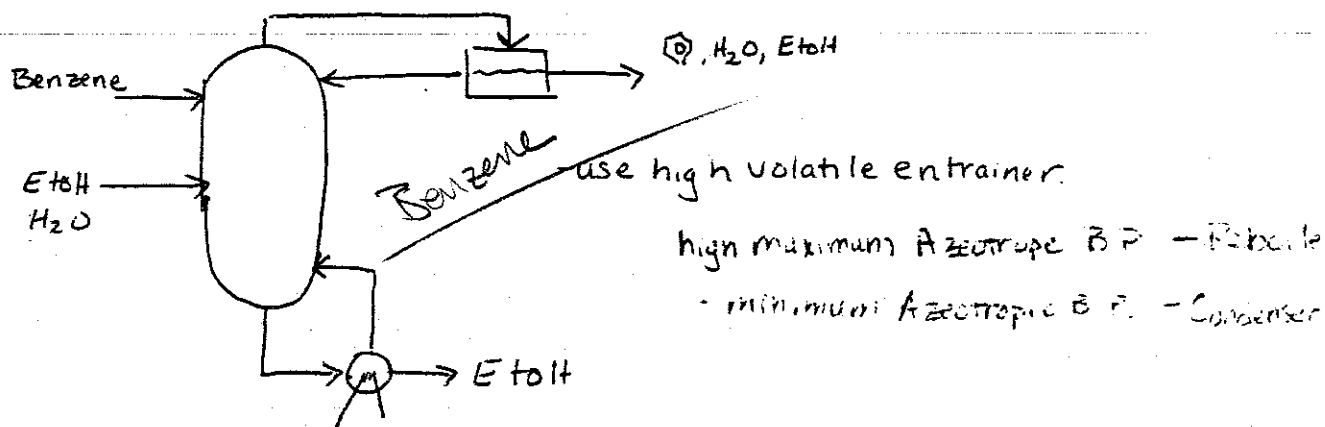
4) How to Separate 2 organic cmpds w/ similiar boiling & melting pts   Membrane

   - Extractive Distillation - uses low volatile substance.

     -Add a solvent which alters the relative volatility of original constituents

5) How do you remove $H_2O(v)$ from Ar(g) to a level of 1ppm if H_2O is orginally at 200ppm (vol%)   Membrane

   -Possible Soln: Drying Agent such as $CaCO_3$

     need to look at equilibrium data

Process Questions : Separations

1) How do you cool a room at 100°F with 120°F water in Phoenix, Arizona ?
   - Phoenix - dry heat, ~0 humidity
   - Use the H_2O and slowly saturate air by misting H_2O
   - Energy used to evaporate the H_2O comes from the air & therefore the Temperature decreases while the Humidity increases

2. What methods to purify polar organics from trace nonpolar
   → depending upon the organic stream Choose a solvent that will not interact with nonpolar ; Use Liquid-Liq Extr
   → the solvent/Organic stream Can then be dist ed.

3) How do you separate CO_2 from Coal gasification byproduct ?
   i) Coal Conversion : use Lurgi gas producer

Coal ½ lb
Coal Lock
membrane here
coal distributor
H_2O
Steam
Cools gases
Steam
1800 - 2100°F
gas out
H_2O
Grate
tar & dust
Air & Steam Feed
Ash Lock
membrane
→ Ashes

Eqns:
$$C + 2H_2 \rightarrow CH_4$$
$$CO + H_2O \rightarrow CO_2 + H_2$$
$$C + CO_2 \rightarrow 2CO$$
$$C + H_2O \rightarrow CO + H_2$$
$$C + O_2 \rightarrow CO_2 + \Delta$$
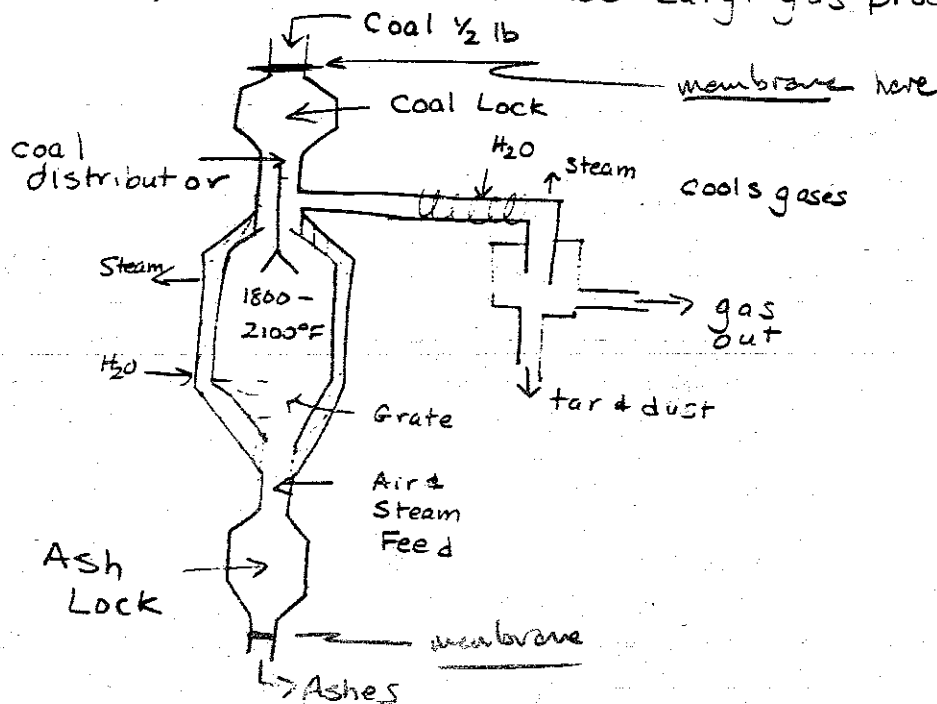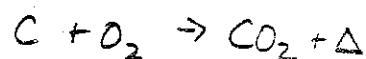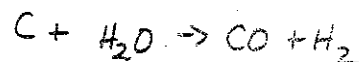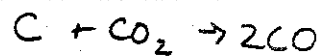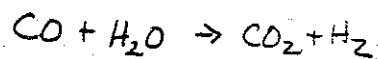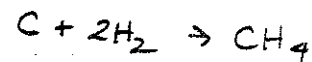
-Separate CO_2 from CH_4, H_2, CO, O_2
  - using absorption in an alkaline solution
  - similiar to removal of SO_2 from flue gases in alkaline soln.
  - follow by distillation of CO_2 from Soln.

4) Remove NH_3 from NH_3-Air System when P<<latm. Also the ΔP is very small and absorption & strippers can't be used.
  → Try dropping Temperature and condense the NH_3 from Air.

5) Remove O_2 from Salt Water.
  a) Look at Thermodynamics
  b) Mass Transfer Resistance
  c) Design Process.

a) Thermodynamics :
  - From Ideal Gas Law increase Temp or decrease Pressure the equilibrium shifts towards the O_2 in Vapor.
  - The Salt soln increases the ionization equilibrium constant, K. ∴ the O_2 will increase its solubility in the solution.
  - Salt may effect the Hydrogen Bonding btw O_2 & H.

b) Mass Transfer Resistance.
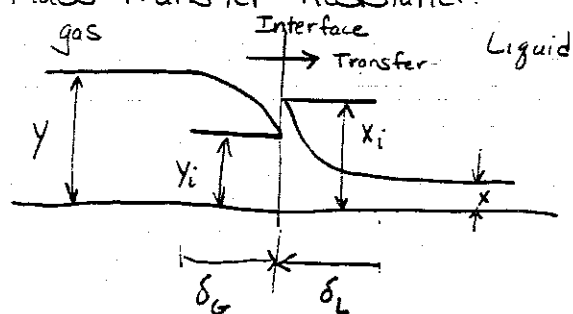
For dilute Solutions :

$$N_A = K_G' (p - p_i)$$
$$= K_L' (C_i - C)$$

or

$$N_A = K_G (y - y_i)$$
$$= K_L (x_i - x)$$

$K_G = K_G' P_T$
$K_L = K_L' P_T$

P = solute partial in bulk gas

P_i = solute partial at interface

K_G = gas phase mass transfer coef.

N_A = Mass Trans

c) Design : Needs to be Economical

- Could put system under vacuum to vent off the O_2 or maybe heat solution and capture O_2 vapor. Be careful not to boil the ~~so~~ solution because of Water Vapor.

- The boiling pt. of Solution is increased in the Sea Water. Compared to pure H_2O

Separations Prelim Review Notes

Outline:
I. Bibliography + Overview of Methods
II. McCabe-Thiele Analysis
III. Continuous Contacting
IV. Miscellaneous Distillation Information
V. Variations on Distillation
VI. Past Prelim Questions

I. Bibliography:

Undergraduate Texts:
—King; Separation Processes
  Henley and Seader; Equilibrium - Stage Separation Operations
  Treybal; Mass Transfer Operations
  Wankat; Equilibrium-Staged Separations
  McCabe, Smith, and Harriott; Unit Operations of Chemical Engineering

Mass Transfer:
—Bird, Stewart, and Lightfoot; Transport Phenomena
  Welty, Wicks, and Wilson; Fundamentals of Momentum, Heat, and Mass Transfer

Unit Design:
—Peters and Timmerhaus; Plant Design and Economics for Chemical Engineers
  Perry; Chemical Engineers' Handbook

Note: The information handed out to first years in 1989
  suggested reviewing King and Peters and Timmerhaus
  Chaps. 1, 2, 3, 9, and 10 for the Process Design section
  of the Prelim.

Overview:

exploit

Separation processes seek to ~~enhance~~ differences in the
physical properties of chemical species to separate them.
Chemical plants typically have more than 50% of capital
investment in separations equipment.
Separations can be broken down into single phase, or
intraphase, separations and multiple phase, or interphase,
separations.
Interphase separations rely on the creation of a second phase
by a separating agent and the subsequent selective distribution
of chemical species between phases. They are generally
energy intensive.
Intraphase separations don't involve the creation of a second
phase, although a second phase may be present. Some rely
on selective distribution of chemical species while others
rely on differences in the response of chemical species to
a driving force.

The following tables give a summary of many separations processes
with references to the Kirk-Othmer Encyclopedia of Chemical
Technology 2nd ed.
Most undergraduate separations texts will have summaries of the
strengths and weaknesses of separations techniques.

II. McCabe-Thiele Analysis : Mass Balances

Single Equilibrium Stage:
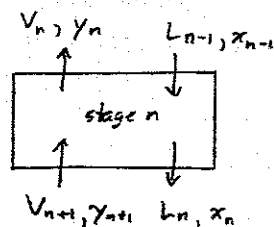
Mass Balances : $L_n + V_n = L_{n-1} + V_{n+1}$

$L_n x_n + V_n y_n = L_{n-1} x_{n-1} + V_{n+1} y_{n+1}$

For CMO : $V_n = V_{n+1}$

$(L_n = L_{n-1})$

Equilibrium : $y_n = f(x_n)$

$L_{n-1}, V_{n+1}, x_{n-1}, y_{n+1}$ are specified.

Feed Stage :
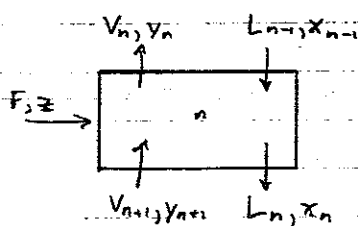
As above, but now including:

Additional term in both mass balances. (F, Fz)

F, z are specified.

Partial Reboiler :
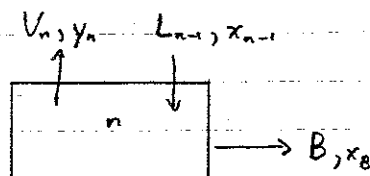
Mass Balances : $B + V_n = L_{n-1}$

$B x_B + V_n y_n = L_{n-1} x_{n-1}$

Equilibrium : $y_n = f(x_B)$

L_{n-1}, x_{n-1} are specified

B or x_B is specified

Total Condenser :
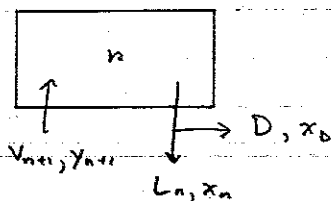
Mass Balances : $D + L_n = V_{n+1}$

$D x_D + L_n x_n = V_{n+1} y_{n+1}$

Equilibrium : none - $y_{n+1} = x_n = x_D$

V_{n+1}, y_{n+1} are specified

D or L is specified

Distillation:

Assumption:

— Constant Molal Overflow — Molar flow rates in vapor and liquid streams are constant in column section (between inlets and outlets). Valid assumption if: a) Column is adiabatic, specific heat changes are negligible compared to latent heat changes, and molar heat of vaporization is independent of concentration, or b) column is adiabatic and saturated liquid and vapor lines on an enthalpy-concentration diagram are parallel. For some systems, such as hydrocarbons, mass heat of vaporization is constant so Constant Mass Overflow is valid.
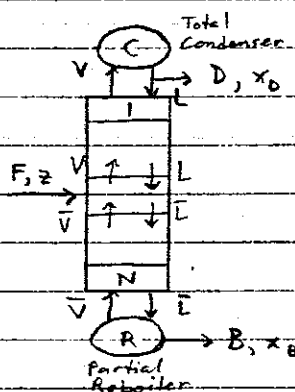
Note: Condenser is not an equilibrium contact, reboiler is an equilibrium contact in __this__ problem
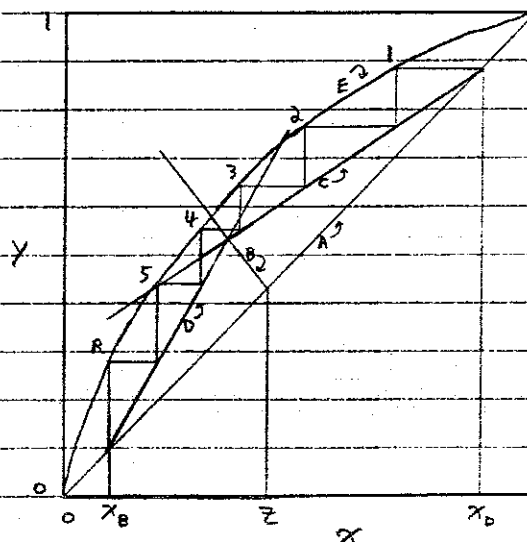
Lines:

A: $y = x$ line

B: Feed line
$$y = \frac{q}{q-1} x + \frac{1}{1-q} z$$
$$q = \frac{\bar{L} - L}{F}$$

C: Upper Operating line
$$y = \frac{L}{V} x + \left(1 - \frac{L}{V}\right) x_D$$

D: Lower Operating line
$$y = \frac{\bar{L}}{\bar{V}} x + \left(\frac{\bar{L}}{\bar{V}} - 1\right) x_B$$

E: Equilibrium line from data or an equation.

Mass Balances:

$$F = D + B$$
$$Fz = Dx_D + Bx_B$$
$$\bar{L} = \bar{V} + B$$
$$V = L + D$$

Observations:

1) 4th stage is feed stage since stage to stage calculations switch from Upper Op line to Lower Op line on 4th stage.

2) Feed stage is optimum feed stage since feed line intersects it.

3) Both Op lines and feed line intersect at single point.

4) Each Op line intersects $y = x$ line at final composition.

Distillation Composition Profiles: (Temperature profile will reflect composition)
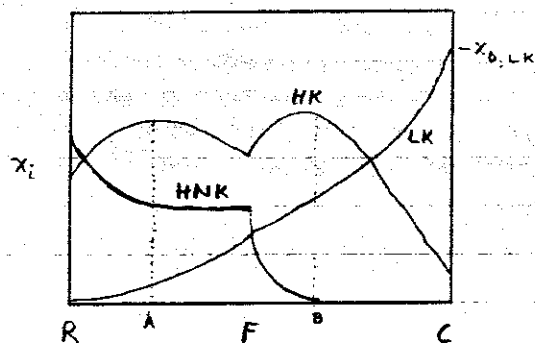
R = reboiler   LK = light key
F = feed   HK = heavy key
C = condenser   HNK = heavy non-key

The split is between the LK and HK. Since there is no LNK, the LK increases monotonically from R to C. The HNK decreases from R to F since it is the least volatile. After the F it drops off rapidly. From the R to A, the HK and HNK form a distillation pair. As one decreases the other must increase. From A to F the pair is the HK and LK so the NK decreases. In the section from F to B, the HK and HNK again form a distillation pair, and finally, from B to C the HK and LK distill.

— The lightest and heaviest components have maxima and minima only at the end points.
— Slopes and curvatures sum to zero. — not rigorous
— Discontinuities at the feed stage.

Batch Distillation:
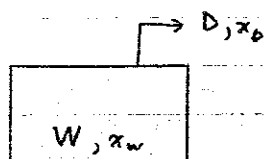
Mass Balance: $-x_D \, dW = d(W x_w) = W \, dx_w + x_w \, dW$

rearrange and integrate from initial to final:

$$\int_{W_o}^{W_f} \frac{dW}{W} = \int_{x_o}^{x_{w,f}} \frac{dx_w}{x_D - x_w} = \ln \frac{W_f}{W_o}$$

x_D is related to x_w by equilibrium or through a multistage tower above the reboiler.

McCabe-Thiele analysis can be used but note that operating lines are constantly changing. Tabulated values of x_D vs x_w can then be integrated.

Stripping and Absorption:

Definitions:
— Stripping is the separation of components from a liquid stream by vaporization into an insoluble gas stream.
— Absorption is the separation of components from a gas stream by absorbing into a nonvolatile liquid stream.
— The insoluble gas or nonvolatile liquid is the separating agent of the operation.

Constant Molal Overflow: CMO is valid if the liquid and gas streams are dilute in the component to be transferred. If not, CMO can be achieved by defining streams in terms of nonvolatile/insoluble flowrates and compositions in terms of mole ratios = moles volatile component/moles nonvolatile carrier

$$Y = \frac{y}{1-y} \quad \text{and} \quad X = \frac{x}{1-x}$$

where Y and X denote mole ratios and y and x denote mole fractions.

If CMO is valid, the operating line will be straight and McCabe-Thiele analysis can be used. Remember that the equilibrium line must be converted to mole ratios if the operating line is in mole ratios.
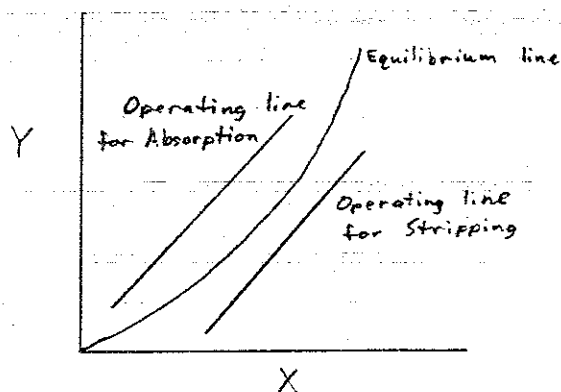
Extraction:

Definitions :

— Extraction is the separation of a solute from one liquid phase by transfer to a second liquid phase.
— Extraction may involve immiscible phases or partially miscible phases.

Immiscible Extraction :

This is analogous to stripping and absorption. Dilute systems can be analyzed using mole fractions. Higher concentrations require use of mole ratios. Higher concentrations can also cause partial miscibility.

Partially Miscible Extraction.

This requires use of a ternary equilibrium diagram. The key to the method of solution is found by noting that, while total and solvent flowrates are not constant in partially miscible extraction, the difference in flowrates of passing streams $\underline{is}$ constant:
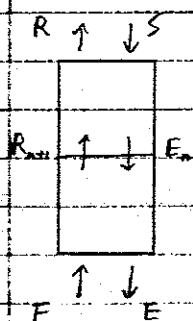
Mass Balance : $F + S = E + R$

or $\quad S - R = E - F = E_n - R_{n+1} = \Delta = constant$

and $E_n x_n - R_{n+1} y_{n+1} = \Delta x_\Delta = constant$

In a ternary system, x_Δ for two components define a difference point. All operating lines in the column pass through this point.

To solve an extraction problem, the compositions of feed, solvent, raffinate, and extract are plotted on a ternary equilibrium diagram (next page), and the difference point found. Stages can then be stepped off by alternating between equilibrium lines (tie lines) and operating lines (all of which pass through the difference point).

This is a poor example; only one equilibrium stage is needed.

F denotes feed, diluent with solute entering
R denotes raffinate, high in diluent exiting
E denotes extract, high in solvent exiting
S denotes solvent, entering

Stages are stepped from F to E along operating line, then back along tie line, down to the raffinate composition, R. Number of traverses on tie lines is number of stages.

III. Continuous Contacting Separations:

Unlike staged separations, where the assumption is that equilibrium or fractional equilibrium is achieved in each stage before phase separation, continuous contactors must be analyzed on a mass transfer basis.
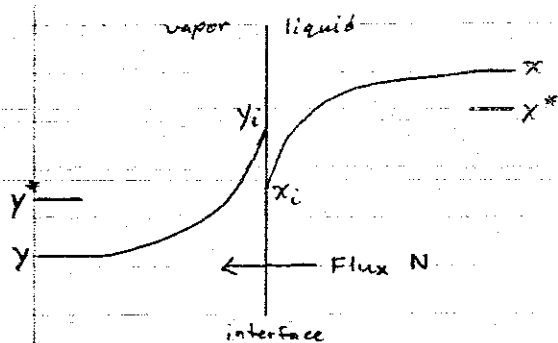
Since interfacial concentrations are not known, analysis is based on bulk concentrations. First, define y^* as the vapor composition in equilibrium with x and x^* as the liquid composition in equilibrium with y. Now write flux equations:

$$N = k_y(y_i - y) = k_x(x - x_i) = K_y(y^* - y) = K_x(x - x^*)$$

rearranging and integrating over the height of the column, h:

$$h = \int_{y_{in}}^{y_{out}} \frac{d(Gy)}{(K_y a)S(y^*-y)} = \int_{x_{in}}^{x_{out}} \frac{d(Lx)}{(K_x a)S(x-x^*)}$$

with CMO:

$$h = \frac{G}{(K_y a)S} \int_{y_{in}}^{y_{out}} \frac{dy}{y^*-y} = \frac{L}{(K_x a)S} \int_{x_{in}}^{x_{out}} \frac{dx}{x-x^*}$$

We then define the height of a transfer unit (HTU) and number of transfer units (NTU):

$$HTU_G = \frac{G}{(K_y a)S} \qquad HTU_L = \frac{L}{(K_x a)S}$$

$$NTU_G = \int_{y_{in}}^{y_{out}} \frac{dy}{y^*-y} \qquad NTU_L = \int_{x_{in}}^{x_{out}} \frac{dx}{x-x^*}$$

therefore: $h = (NTU)(HTU)$

The value of NTU can be calculated with equilibrium data and an operating line. For most systems, CMO or use of mole ratios can be used to give a simple operating line.

The value of HTU is dependent on (Ka). In practice, pilot plant data is used to find HTU from h and NTU, and the pilot column scaled up through a correlation between HTU and diameter. The literature also has data for experimentally determined values of (Ka).

$$\left(\frac{mol}{m^2 \cdot s} \right)$$

IV. Miscellaneous Distillation Information:
Some Distillation Design Correlations:

1) Fenske equation — estimates minimum # of stages for a separation:

$$N_{min} = \frac{\log \left[\frac{(x_{LK}/x_{HK})_D}{(x_{LK}/x_{HK})_B} \right]}{\log \alpha_{LK,HK}}$$

2) Underwood equation — estimates minimum reflux for a separation:

$$R_{min} = \frac{\left[\frac{x_{LK,D}}{x_{LK,F}} - (\alpha_{LK,HK})_F \frac{x_{HK,D}}{x_{HK,F}} \right]}{(\alpha_{LK,HK})_F - 1}$$

3) Gilliland correlation — estimates # of trays for a separation from knowledge of R_{min}, N_{min}, and actual R:

$$\frac{N - N_{min}}{N+1} = 1 - \exp \left[\left(\frac{1 + 54.4 X}{11 + 117.2 X} \right) \left(\frac{X-1}{X^{1/2}} \right) \right]$$

where $X = \frac{R - R_{min}}{R+1}$

4) Kirkbride equation — estimates optimum feed stage location:

$$\frac{N_R}{N_S} = \left[\left(\frac{z_{HK,F}}{z_{LK,F}} \right) \left(\frac{x_{LK,B}}{x_{HK,D}} \right)^2 \left(\frac{B}{D} \right) \right]^{0.206}$$

where N_R = # of stages in rectifying section
and N_S = # of stages in stripping section
$$N = N_R + N_S$$

Crude Petroleum Composition:

	Volume %	EP (°C)	Products
$C_1 - C_4$	1-2	< 30	Natural gas, LPG
$C_4 - C_{12}$	15-30	30-200	Petroleum Ether (C_5, C_6), Ligroin (C_7), naphtha, straight-run gasoline
$C_{12} - C_{15}$	5-20	200-300	kerosene, heating oil
$C_{15} - C_{25}$	10-40	300-400	gas oil, diesel fuel, lube oil waxes, asphalt
$> C_{25}$	nonvolatile	> 400	residual oil, paraffin wax, asphalt

Some Terms to know:

Separation factor: $\alpha_{ij} = \dfrac{K_i}{K_j} = \dfrac{y_i}{x_i} \cdot \dfrac{x_j}{y_j}$, also relative volatility

Reflux: portion of (overhead) product returned to column

Reflux ratio: $R = \dfrac{L}{D}$, ratio of top stream returned to column / product taken off

Limiting conditions: Minimum reflux - infinite stages - operating line touches eq. line
Minimum stages - infinite reflux - operating line is $y = x$

Pinch point: location in column where compositions don't change from stage to stage

Light key: more volatile of the two components between which a distillation split is made. (LK)

Heavy key: less volatile of the split components. (HK)

Light non-key: component more volatile than the light key (LNK)

Heavy non-key: component less volatile than the heavy key (HNK)

Diluent: in extraction, the fluid in which the solute to be extracted is dissolved

Stripping section: section of distillation column below the feed stage

V. Variations on Distillation

Extractive Distillation:

For a system that forms an azeotrope, separation is not possible
across the azeotropic composition. The azeotrope must be broken
by addition of a separating agent which will alter the relative volatilities
of the azeotrope components. The agent is usually less volatile than any
of the components and is introduced near the top of the column. The agent
is selected to reduce the volatility of one of the azeotrope components and bring
it out in the bottoms product. This mixture is then separated in a second column.
— Solvent is chosen on the basis of molecular interactions. Hydrogen bonding
   is the most important, followed by polarity.
— Extractive distillation usually fails to separate isomers. Reactive
   distillation may work.

Azeotropic Distillation:

When the agent in extractive distillation forms a new azeotrope with
the system, it is called azeotropic distillation. If the new (ternary)
azeotrope is heterogeneous in the liquid phase, it is a simple matter
to separate the phases, return one as reflux, and send the other to a
second column. Separation of water/ethanol with benzene is an example.
If the azeotrope is homogeneous, it can sometimes be purified with an
extraction operation or perhaps cooled to the point at which it does
become heterogeneous.
— solvent selection is more difficult than in extractive distillation
   because of fewer suitable solvents: must form azeotrope with
   suitable boiling point and must be heterogeneous or easily washed.
— azeotropic distillation systems with unique solvents are patentable

Reactive Distillation:

Basically, the idea is to perform a reaction in the column, while
driving it towards completion by distilling off the products. Mass
balances must take into account the reaction rate term. Used for
ethyl acetate from ethanol and acetic acid and methyl-tert-butyl ether
from isobutylene and methanol.

Supercritical Fluid Extraction:

— Super critical fluids have densities intermediate to liquids and gases.
— They can achieve high mass transfer rates and dissolve almost as much solute as a good solvent
— Supercritical CO_2 is used in food and pharmaceutical industry
— Recovery of solute is usually easy — drop pressure and solute precipitates
— High pressure equipment is expensive
— CO_2 used to decaffeinate coffee, extract flavor compounds from hops, etc. "natural" process

Making a separation scheme for multicomponent feed streams-
Distillation Sequence Heuristics - Henley and Seader §14.2 :
1) When the adjacent ordered components in the process feed vary widely in relative volatility, sequence the splits in the order of decreasing relative volatility.
2) Sequence the splits to remove components in the order of decreasing molar percentage in the process feed when that percentage varies widely but relative volatility does not vary widely.
3) When neither relative volatility nor molar percentage in the feed varies widely, remove the components one by one as overhead products.
4) When a mass separating agent is used, remove it in the separator following the one into which it is introduced.
5) When multicomponent products are specified, favor sequences that produce these products directly or with a minimum of blending unless relative volatilities are appreciably lower than for a sequence that requires additional separators and blending.

Advantages of Plate Towers:
- Design is more reliable due to easier liquid dispersion
- Can handle wide range of flowrates
- Greater accessibility for cleaning - fluid with soluble solids
- Can be used with interstage cooling if necessary
- Can be designed to handle thermal expansion unlike packing.
- Design of choice for diameters > 4 ft.

Advantages of Packed Towers:
- Better handling of foaming liquids
- Better service for corrosive materials
- Lower liquid holdup
- Lower pressure drops - good for vacuum operation
- Design of choice for diameters < 2 ft.

VI. Prelim Questions:
Questions: (with partial answers)

— What is the lowest temperature water can be cooled to in a cooling tower?

Incoming air will contain a certain amount of water vapor. At any given temperature, the air can hold an amount of water equal to the vapor pressure of water at that temperature. As water evaporates from the stream to be cooled, it drives the water content of the air towards the saturation point. At the same time, it lowers the temperature of the system, lowering the capacity of the air. A simultaneous mass and enthalpy balance is needed to find the equilibrium temperature. Important factors are the temperatures of both streams, heat capacities of both streams, the enthalpy of vaporization of water, the initial water concentration in the air, and the ratio of air flow rate to water flow rate.

Smith &
Hurriot

DF for
evap =
$P_{H2O} - P_{H2O}(T_{WB})$

i.e. we can't
cool below
wet bulb temp

liq T drops
with vaporization

— How would you, being in Phoenix, Arizona, where the temperature is 100°F, cool a room with 120°F water?

Spraying a mist of water into the air will evaporate much of the water into the dry air. The temperature will decrease because of the enthalpy of vaporization.

Prelim Questions: (for you to answer)

— What methods could be used to purify a stream of a polar organic from trace non-polar impurities? Which would you use? why?

    Adsorption?, Membrane?,

— Why is distillation done at high pressure?

    ↑ vapor density, lower D

— Sketch typical temperature and composition profiles in a distillation column.

— How would you control a distillation column

    RR

— How would you remove 1% phenol from water?

    Adsorption

— Outline a method for separating two organic compounds with similar boiling and melting points.

— How would you obtain pure oxygen from air?

— Sketch and describe a multi-effect evaporator. How does the pressure vary through the system?

— How would you separate ethanol and water?

— Suggest several methods for obtaining fresh water from sea water. Which would you use?

— How would you remove water vapor in Ar gas to a level of 1 ppb (by volume) if the water is initially present at a level of 200 ppb?

— What is the reflux ratio and a pinch point?

— Diagram an HCl or SO_2 absorber.

— How do you make pure N_2 from air without cryogenic techniques?

More Questions:

— Develop a process for separating NH_3 from an NH_3-Air gas stream at low pressures ($P << 1$ atm). Because of the low pressure, one cannot afford to have any pressure drop in the process.

— Draw the McCabe-Thiele diagram for a distillation column that uses a chemically reacting absorbent

— You have a continuous distillation setup. What can you do to save energy?

— How would you remove dissolved O_2 from sea water? Suppose you are processing fairly large volumes so that energy intensity is a strong consideration. What thermodynamic variables affect solubility? Where is the mass transfer resistance? What type of unit operation would you use? How would you design it?

— What is a maximum boiling azeotrope? Does it exhibit positive or negative deviations from Raoult's law? If a solution of this type is distilled, will the azeotrope be recovered in the distillate or the bottoms of the column?

Some Separations

Remove trace nonpolars from polar organics

liquid/liquid extraction?

Separate close boiling isomers

try crystalization - eg: ortho & para xylene

Remove O_2 from seawater

warm it up (don't boil) $\Rightarrow$ solubility goes down w/ T
or put under vacuum?

Common Organic Solvents for Aqueous Extraction

MIBK: methyl isobutyle ketone
MEK: methyl ethyl ketone

$$\boxed{(P_i C)} \Rightarrow exp \bigg)_{P_i^S}^{P} \frac{v_i^c \, dP}{RT} \quad \text{condensed phase}$$

C1 Use & Characteristics of Sepn Processes
p26   Classes

sepn factor $\alpha_{ij}^s = \dfrac{x_{i1}/x_{j1}}{x_{i2}/x_{j2}}$ for comps i, j in products $1, 2$

at equilibrium $\alpha_{ij} = \dfrac{K_i}{K_j}$

vapo liquid $K_i = \dfrac{y_i}{x_i} = \dfrac{\gamma_i \, P_i^S \, \varphi_i^S \, \boxed{(P_c)}}{\varphi_i \, P}$

binary $\alpha_{ij}^s = \dfrac{y_i (1-x_i)}{x_i (1-y_i)} \quad \Rightarrow \quad y_i = \dfrac{\alpha_{ij}^s \, x_i}{1 + (\alpha_{ij}^s - 1) x_i}$, at eq $\alpha_{ij}^s = \alpha_{ij}$

C2 Simple Equilibrium Processes
dew / bubble points
adiabatic / isenthalpic flashes
lever rule for binary or ternary
Take advantage of α being weak function of T & P in these calculations

C3 Additional Factors Influencing Product Purities
A) <u>Incomplete Mechanical Sepn</u> of Product Phases
    entrainment makes apparent separation look less than equilibrium
B) Flow Configuration and Mixing Effects
    1) nonuniform bulk concentration (lack of mixing)
        - hurts dissolution of $CuSO_4$ in H_2O from ore
        - helps NH_3 stripping from H_2O on crossflow plate
    2) continuous countercurrent flow or crossflow gives higher than eq sepn
C) Batch Operation

constant molar overflow / L = const, V = const

$$V_p H_p = L_{p+1} h_{p+1} + d h_d + Q_c$$
$$V_{p-1} H_{p-1} = L_p h_p + d h_d + Q_c$$
$$V_p H_p - V_{p-1} H_{p-1} = L_{p+1} h_{p+1} - L_p h_p$$
$$V_p - V_{p-1} = \frac{V_{p-1}(H_{p-1} - H_p) - L_p(h_p - h_{p+1})}{H_p - h_{p+1}}$$

$V_p = V_{p-1}$ IF : 1) $H_{p-1} - H_p = h_p - h_{p+1} = 0$

or 2) $\dfrac{H_{p-1} - H_p}{h_p - h_{p+1}} = \dfrac{L_p}{V_{p-1}}$

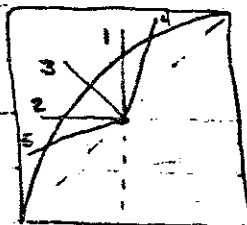for $L/V = const$ $\dfrac{L}{V} = \dfrac{y_{p-1} - y_p}{x_p - x_{p+1}}$

intersection of op lines : $V y_A = L x_A + d x_{Ad}$
$$V' y_A = L' x_A - b x_{Ab}$$
$$(V - V') y_A = (L - L') x_A + F z_{AF}$$
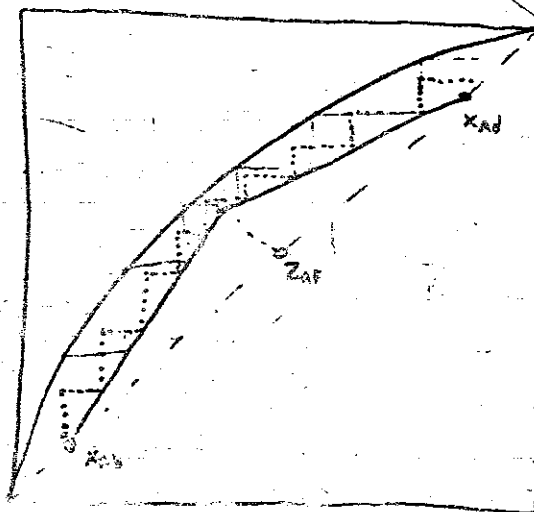$$V_F y_A = - L_F x_A + F z_{AF}$$
$$y_A = \frac{-L_F}{V_F} x_A + \frac{F z_{AF}}{V_F} \quad \text{crosses 45 at } z_F$$

1) sat liq feed
2) sat vap
3) partially vaporized
4) subcooled liquid
5) superheated vapor

Stage to Stage

--- Murphree vapor eff.
$$E_{mv} = \frac{y_{out} - y_{in}}{y^* - y_{in}}$$

C6 Transfer Units for Packed Tower

$$P_A = y_A P \ , \quad C_A = x_A \rho_m$$

$$\frac{V}{A}\frac{dy_A}{dh} = \frac{L \, dx_A}{A \, dh} = \frac{\text{moles } A}{hr \cdot ft^3} \quad \text{into vapor}$$

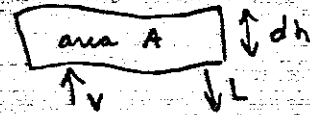$$\frac{V}{A}\frac{dy_A}{dh} = K_G P a \,(y_{Ae} - y_A) \quad ; \quad a = \text{interface area per tower volume}$$

$$h = \frac{V}{A}\frac{1}{K_G P a}\int_{y_{Ain}}^{y_{Aout}}\frac{dy_A}{y_{Ae}-y_A} \qquad K_G \approx \text{constant for gas phase control}$$

$$h = (HTU)_{OG}\,(NTU)_{OG} \ , \quad (HTU)_{OG} = \frac{V}{A K_G P a} \ , \quad (NTU)_{OG} = \int_{y_{Ain}}^{y_{Aout}}\frac{dy_A}{y_{Ae}-y_A}$$
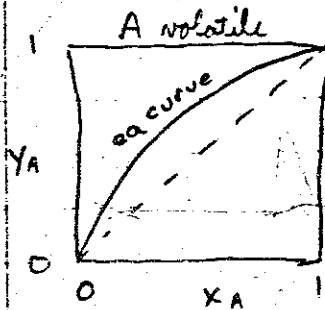
$$\frac{L}{A}\frac{dx_A}{dh} = K_L \rho_m a \,(x_A - x_{Ae})$$

$$h = \frac{L}{A K_L \rho_m a}\int_{x_{Ain}}^{x_{Aout}}\frac{dx_A}{x_A-x_{Ae}} \qquad K_L \approx \text{constant for liquid phase control}$$

$$h = (HTU)_{OL}\,(NTU)_{OL} \ , \quad (HTU)_{OL} = \frac{L}{A K_L \rho_m a} \ , \quad (NTU)_{OL} = \int_{x_{Ain}}^{x_{Aout}}\frac{dx_A}{x_A-x_{Ae}}$$

C5 McCabe-Thiele Distillation

A volatile

eq curve

Rect.: $V_P y_{AP} = L_{P+1} x_{AP+1} + d x_{Ad}$
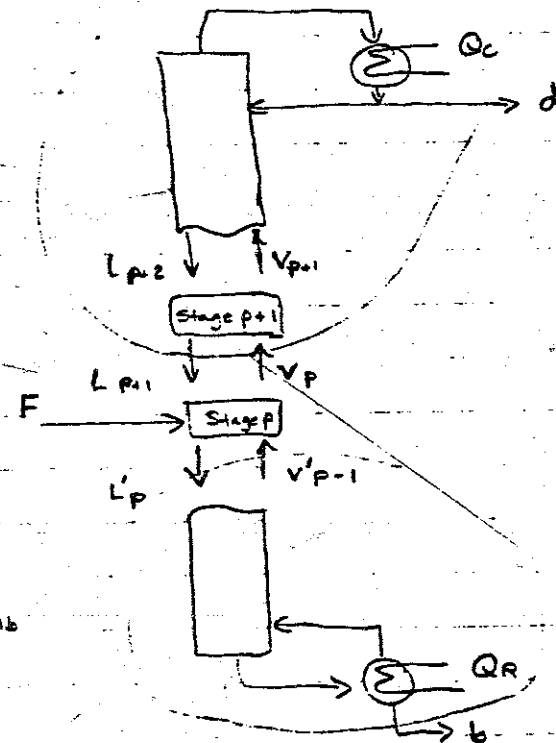
$$y_{AP} = \frac{L}{V} x_{AP+1} + \frac{d x_{Ad}}{V}$$

Strip.: $L'_P x_{AP} = V'_{P-1} y_{AP-1} + b x_{Ab}$

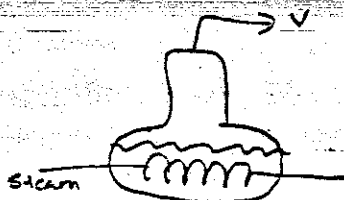$$y_{AP-1} = \frac{L'}{V'} x_{AP} - \frac{b x_{Ab}}{V'}$$

intersection

$$y_{Ai} = \frac{L'}{V'} y_{Ai} - \frac{b x_{Ab}}{V'}$$

$$(V'-L') y_{Ai} = -b x_{Ab}$$

$$y_{Ai} = x_{Ab}$$

C3   Rayleigh batch distillation
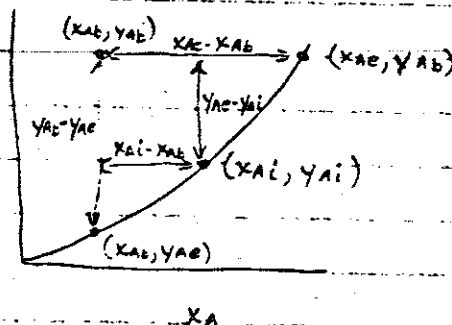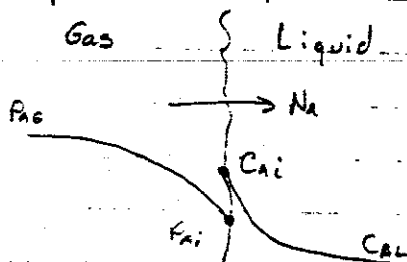

$$dV' = -dL'$$

$$y_i dV' = -d(x_i L')$$

$$-y_i dL' = -x_i dL' - L' dx_i$$

$$L' dx_i = (y_i - x_i) dL'$$

$$\int_{L'_o}^{L'} \frac{dL'}{L'} = \int_{x_{i_o}}^{x_i} \frac{dx_i}{y_i - x_i}$$

$$\ln \frac{L'}{L'_o} = \int_{x_{i_o}}^{x_i} \frac{dx_i}{y_i - x_i}$$

Interphase Transfer

Gas { Liquid

$$N_A = k_G (p_{AG} - p_{Ai}) = k_L (C_{Ai} - C_{AL})$$

overall $$N_A = K_G (p_{AG} - p_{Ae}) = K_L (C_{Ae} - C_{AL})$$

note since $(p_{AG} - p_{Ae}) > (p_{AG} - p_{Ai})$, $K_G < k_G$

relate K_G, K_L and k_G, k_L by linearizing equilibrium relation

to form $P_A = H C_A + b$ ie $\frac{p_{Ae} - p_{Ai}}{C_{AL} - C_{Ai}} = H = \frac{p_{AG} - p_{Ai}}{C_{Ae} - C_{Ai}}$

then $(p_{Ae} - p_{AG}) = (p_{Ae} - p_{Ai}) + (p_{Ai} - p_{AG})$ $(C_{Ae} - C_{AL}) = (C_{Ae} - C_{Ai}) + (C_{Ai} - C_{AL})$

$$\frac{(p_{Ae} - p_{Ai})}{(C_{AL} - C_{Ai})}(C_{AL} - C_{Ai})$$ $$\frac{C_{Ae} - C_{Ai}}{p_{AG} - p_{Ai}}(p_{AG} - p_{Ai})$$

$$-\frac{N_A}{K_G} = -\frac{H N_A}{k_L} - \frac{N_A}{k_G}$$ $$\frac{N_A}{K_L} = \frac{1}{H}\frac{N_A}{k_G} + \frac{N_A}{k_L}$$

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L}$$ $$\frac{1}{K_L} = \frac{1}{H k_G} + \frac{1}{k_L}$$

large H (A slightly soluble in liquid) $\Rightarrow$ $\frac{1}{K_G} \approx \frac{H}{k_L}$ liquid phase control

$\frac{1}{K_L} \approx \frac{1}{k_L}$ k_G unimportant

small H (A highly soluble in liquid) $\Rightarrow$ $\frac{1}{K_G} \approx \frac{1}{k_G}$ k_L unimportant

$\frac{1}{K_L} \approx \frac{1}{H k_G}$ gas phase control

DESIGN

Lyon — How would you separate Air into pure O_2 (cryogenic plant)

Hanson
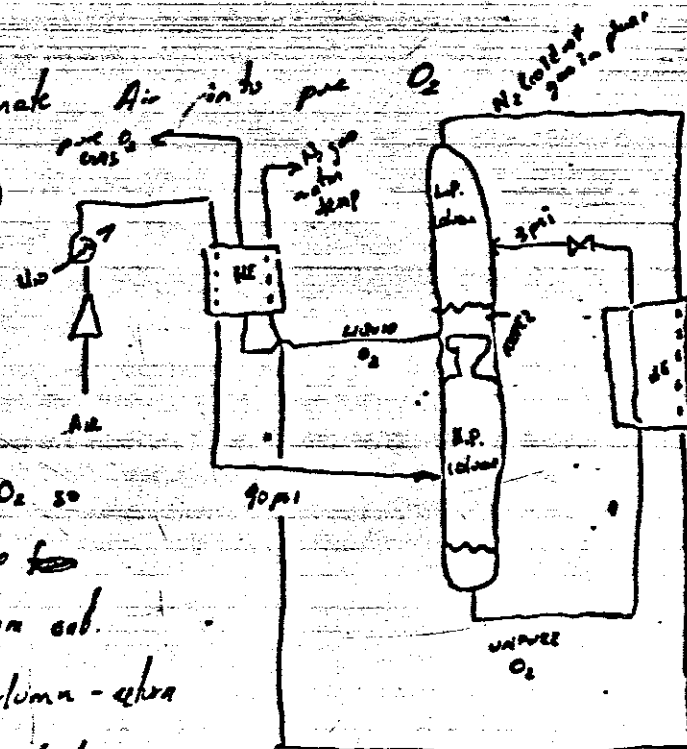
1. NOTE: Argon will build up in O_2 so
pull stream of O_2/Ar gas
near bottom of L.P. column and
distill this in another column - return
O_2 to L.P. column - get rid of
Argon or purify it further (burn O_2 out with H_2)
and sell it.

NOTE 2. The condensor for the H.P. column (lower) acts as the
reboiler for the Low Pressure Column (top). This is why
there is a pressure difference between them.

Foss —
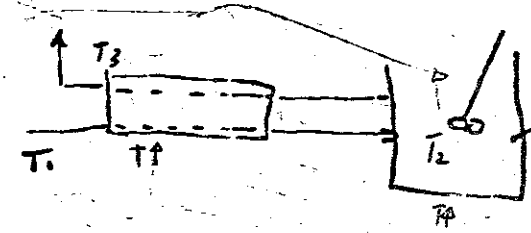
zero order reaction
Exothermic
rate $= k(T)$ (rate of reaction)
$R_v = k_0 exp\left(\frac{-E_a}{RT}\right)$

what would happen if there was a step change in T_1 upward?

Hanson — How would you get pure water from sea water

— multiple effect Evap

pure H_2O

conc. brine

5
$$Pr = \frac{\hat{C}_P \mu}{k}$$

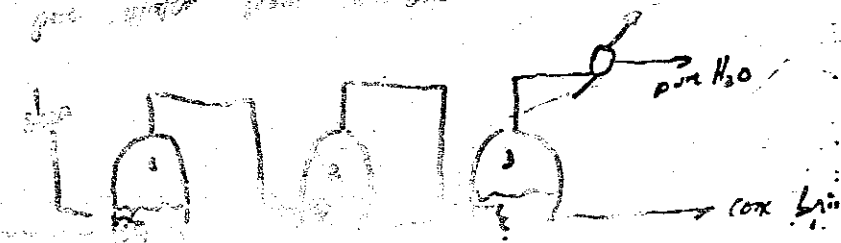|	$\hat{C}_P$	μ	k
air	$.25 \frac{Btu}{lb \cdot °F} = \frac{cal}{g \cdot °C}$	$.02 cp = .0002 \frac{g}{cm \cdot s}$	$.0140 \frac{Btu}{hr \cdot ft \cdot °F/ft}$
H_2O	1	$1 cp = .01 \frac{g}{cm \cdot s}$	$.243 \frac{Btu}{hr \cdot ft \cdot °F/ft}$

$$\frac{Pr_{air}}{Pr_{H_2O}} \approx \frac{1}{4} \qquad \frac{1}{50} \qquad ---- \frac{30}{1}$$

effect on Pr: $\underline{\mu > k \gg \hat{C}_P}$

6 $Sh = Nu_{mass\ tsfr} = \frac{k_c D}{c \, \mathcal{D}_{AB}}$

7 $r_{Ar} > r_{Ne}$ a) $\mathcal{D}_{Ne} > \mathcal{D}_{Ar}$ because $M_{Ne} < M_{Ar}$

$$\mathcal{D}_{AB} = \frac{2}{3\pi^{3/2}} \left(\frac{RT}{2}\right)^{1/2} \left(\frac{1}{M_A} + \frac{1}{M_E}\right)^{1/2} \cdot \frac{1}{(r_A + r_E)^2} \frac{(1/n_A + n'_E)}{V}$$

in a given C, smallest $r_A, M_A \rightarrow$ large $\mathcal{D}$

b) $\mu = \frac{5}{16\pi^{1/2}} \frac{(MRT)^{1/2}}{N_0 (d)^2}$ $\mu_{Ar\ 20°C} = 2.215 \times 10^7 \, P$

$\mu_{Ne\ 20°C} = 3.112 \times 10^7 \, P$

difference in diameter outweighs difference in M

c) kinetic theory gives $C_V = \frac{3}{2} R$ for all ideal monatomic gases

d) $\boxed{Pr = \frac{C_P}{C_P + \frac{1}{2.5} R}}$ Eucken formula for polyatomics suggests $Pr_{Ar} = Pr_{Ne}$

since $C_{P\,Ar} = C_{P\,Ne}$

BSL p257

8 a) Pipeline Pump Sizes

use Bernoulli Eqn $\Delta \frac{1}{2} \langle v \rangle^2 \overset{negligible}{} + g \Delta h + \frac{1}{\rho}(p_2 - p_1) + \hat{W} + \hat{E}_v = 0$

$\hat{E}_{v\,straight} = \frac{1}{2} \langle \bar{v}^2 \rangle \frac{L}{D} f$, $\hat{E}_{v\,fittings} = \Sigma \frac{1}{2} \langle \bar{v}^2 \rangle e_v$

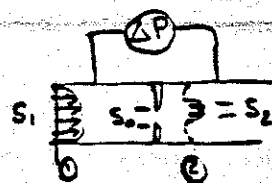$Re \rightarrow f \rightarrow \hat{W} \rightarrow$ pump horsepower

b) Heat Trace / T Profile

expect turbulent flow? with nearly constant T profile

1) $Q_{lost} = UA \Delta T$, U including inner and outer h's

this is conduction to constant outside ambient T

2) may need to consider for convection

9 a) Orifice Meter

cont. $\quad \rho_1 v_1 S_1 = \rho_2 v_2 S_2 \qquad v_2 = \dfrac{v_1 S_1}{S_2}$

Bernoulli $\quad \Delta \dfrac{1}{2} \dfrac{\langle v^2 \rangle}{\langle v \rangle} + \Delta \hat{\Phi} + \int_{P_1}^{P_2} \dfrac{1}{\rho} dp + \widehat{W} + \widehat{E}_v = 0$

$$\dfrac{1}{2\alpha_2} v_2^2 - \dfrac{1}{2\alpha_1} v_1^2 + \dfrac{1}{\rho}(P_2 - P_1) = 0 \qquad \alpha_i \text{ correct for } \dfrac{\bar{v}^2}{v} \approx \bar{v}$$

$$-\dfrac{1}{2\alpha_2}\left(\dfrac{v_1 S_1}{S_2}\right)^2 + \dfrac{1}{2\alpha_1} v_1^2 = +\dfrac{1}{\rho}(P_2 - P_1)$$

$$v_1^2 = \dfrac{(P_2 - P_1)\dfrac{1}{\rho}}{\dfrac{1}{2\alpha_1} - \dfrac{1}{2\alpha_2}\left(\dfrac{S_1}{S_2}\right)^2}$$

$$w \sim v_1 \rho S_1 = S_1 \sqrt{\dfrac{2\rho(P_2 - P_1)}{\dfrac{1}{\alpha_1} - \dfrac{1}{\alpha_2}\left(\dfrac{S_1}{S_2}\right)^2}}$$

based on plate size, $S_0 \qquad w = C_d S_0 \sqrt{\dfrac{2\rho(P_2 - P_1)}{1 - \left(\dfrac{S_0}{S}\right)^2}} \qquad , C_d = .6$

b) Venturi

cont $\quad v_1 S_1 = v_2 S_2$

$$\Delta \dfrac{1}{2} v^2 + \dfrac{1}{\rho} \Delta P = 0$$

$$\dfrac{1}{2} v_2^2 - \dfrac{1}{2} v_1^2 = -\dfrac{1}{\rho} \Delta P$$

$$\dfrac{1}{2} v_1^2 \left[\left(\dfrac{S_1}{S_2}\right)^2 - 1\right] =$$

$$v_1 = \sqrt{\dfrac{\dfrac{2}{\rho} \Delta P}{1 - \left(\dfrac{S_1}{S_2}\right)^2}}$$

c) Pitot Tube
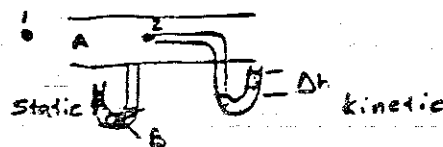
$$\dfrac{1}{2} v_2^2 {}^0 - \dfrac{1}{2} v_1^2 + \dfrac{1}{\rho}(P_2 - P_1) = 0$$

P_1 = static pressure

$$v_1 = \sqrt{\dfrac{2}{\rho}(P_2 - P_1)}$$

10 a) Bernoulli $\Delta \frac{1}{2} \langle v \rangle^3 + \Delta \Phi + \int_{P_1}^{P_2} \frac{1}{\rho} dp + \hat{W} + \hat{E}_v = 0$

b) Hagen Poiseuille $\langle v \rangle = \frac{(P_0 - P_L) R^2}{8 \mu L}$

c) Stokes Law $F_k = 6 \pi \mu V_\infty R$

d) Continuity $\frac{D\rho}{Dt} = -\rho (\nabla \cdot \underline{v})$

e) Navier Stokes $\rho \frac{D\underline{v}}{Dt} = -\nabla P + \mu \nabla^2 \underline{v} + \rho \underline{g}$

11 $NTU_{oc} = \int_{y_{in}}^{y_{out}} \frac{dy}{y_{eq} - y}$., average the driving force to get the separation resulting in $y_{out} - y_{in}$

13

	T	P	T liq		T solid
$\mathcal{D}$	$\sqrt{T}, T^{3/2}$	$\frac{1}{P}$	$\uparrow$ $\frac{\mathcal{D}}{T} = Ae^{-B/RT}$		
μ	$\sqrt{T}$	$\uparrow$	$\downarrow$ $\mu = Ce^{B/RT}$ $\uparrow$		$\uparrow - \downarrow$
k	$\sqrt{T}$	$\uparrow$	$\downarrow$ $\uparrow$		
C_p	$\uparrow$	$\uparrow$	$\downarrow$ $\uparrow$		
h	$\uparrow$	$\uparrow$			
ν	$\uparrow$	$\downarrow$			

14 Reynolds analogy: momentum and heat mechanisms are identical
$\frac{h}{C_p \rho \bar{v}} = \frac{f}{2}$ valid only for $P_r = 1$

Stanton $= \frac{h}{C_p \rho \bar{v}} = St$ not very good in general

Chilton - Colburn: $j_H = j_D = \frac{f}{2}$ for $10000 < Re < 300000$
$0.6 < Pr < 100$
$0.6 < Sc < 100$

$j_H = N_{St} N_{Pr}^{2/3} (\frac{\mu}{\mu_0})^{-14}$
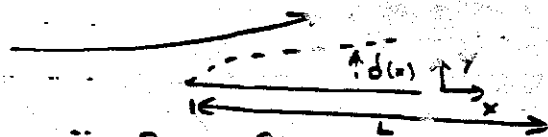
$j_D = \frac{k_c}{\bar{v}} N_{Sc}^{2/3}$

on a limited range in turbulent flow, this empirical relation relates heat, mass, & momentum trsf.

15 Fanning friction factor $f = \frac{\Delta P \times \pi R^2}{(2\pi R L)(\frac{1}{2} \rho v^2)} = \frac{\Delta P}{2 \rho v^2} \cdot \frac{D}{L}$

Moody friction factor = resistance coefficient $= \frac{\Delta P}{\frac{1}{2} \rho v^2} \cdot \frac{D}{L}$

16 Boundary Layer Equations / Ordering .... Denn p 286

cont $\quad \dfrac{\partial v_x}{\partial x} + \dfrac{\partial v_y}{\partial y} = 0$

x mom $\quad \rho\left(v_x \dfrac{\partial v_x}{\partial x} + v_y \dfrac{\partial v_x}{\partial y}\right) = -\dfrac{\partial p}{\partial x} + \eta\left(\dfrac{\partial^2 v_x}{\partial x^2} + \dfrac{\partial^2 v_x}{\partial y^2}\right)$

y mom $\quad \rho\left(v_x \dfrac{\partial v_y}{\partial y} + v_y \dfrac{\partial v_y}{\partial y}\right) = -\dfrac{\partial p}{\partial y} + \eta\left(\dfrac{\partial^2 v_y}{\partial x^2} + \dfrac{\partial^2 v_y}{\partial y^2}\right)$

Nondimensionalize: $\quad \tilde{x} = \dfrac{x}{L}$, $\tilde{y} = \dfrac{y}{\delta}$ $\qquad$ note $\dfrac{\delta}{L} \ll 1$

$\qquad\qquad\qquad \tilde{v}_x = \dfrac{v_x}{U}$, $\tilde{v}_y = \dfrac{v_y}{V}$

$\qquad\qquad\qquad \tilde{p} = \dfrac{p}{\pi}$

cont $\quad \dfrac{U}{L}\dfrac{\partial \tilde{v}_x}{\partial \tilde{x}} + \dfrac{V}{\delta}\dfrac{\partial \tilde{v}_y}{\partial \tilde{y}} = 0$

$\qquad \dfrac{U\delta}{LV}\dfrac{\partial \tilde{v}_x}{\partial \tilde{x}} + \dfrac{\partial \tilde{v}_y}{\partial \tilde{y}} = 0$

if $\dfrac{U\delta}{LV} \gg 1$, neglect $\dfrac{\partial \tilde{v}_y}{\partial \tilde{y}}$ $\Rightarrow$ $\dfrac{\partial \tilde{v}_x}{\partial \tilde{x}} = 0 \Rightarrow \tilde{v}_x \neq \tilde{v}_x(x)$ $\quad$ wrong

$\qquad \dfrac{U\delta}{VL} \ll 1$ $\qquad$ $\dfrac{U\delta}{LV}\dfrac{\partial \tilde{v}_x}{\partial \tilde{x}}$ $\Rightarrow$ $\dfrac{\partial \tilde{v}_y}{\partial \tilde{y}} = 0 \Rightarrow \tilde{v}_y = const = 0$ at surface

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad = 0$ everywhere wrong

$\therefore \dfrac{U\delta}{VL} \approx 1 \Rightarrow \boxed{V = \dfrac{U\delta}{L}}$

$\qquad$ note $\dfrac{\delta}{L} \ll 1 \Rightarrow V \ll U$ as expected

$\qquad\qquad\qquad\qquad\qquad\nearrow V = \dfrac{U\delta}{L}$

x mom $\quad \rho\left(\dfrac{U^2}{L}\tilde{v}_x \dfrac{\partial \tilde{v}_x}{\partial \tilde{y}} + \dfrac{VU}{\delta}\tilde{v}_y \dfrac{\partial \tilde{v}_x}{\partial \tilde{y}}\right) = -\dfrac{\pi}{L}\dfrac{\partial \tilde{p}}{\partial \tilde{x}} + \eta\left[\dfrac{U}{L^2}\dfrac{\partial^2 \tilde{v}_x}{\partial \tilde{x}^2} + \dfrac{U}{\delta^2}\dfrac{\partial^2 \tilde{v}_x}{\partial \tilde{y}^2}\right]$

$\rightarrow \left(\dfrac{\rho U \delta^2}{\eta L}\right)\left(\tilde{v}_x \dfrac{\partial \tilde{v}_x}{\partial \tilde{x}} + \tilde{v}_y \dfrac{\partial \tilde{v}_x}{\partial \tilde{y}}\right) = -\left(\dfrac{\pi \delta^2}{\eta U L}\right)\dfrac{\partial \tilde{p}}{\partial \tilde{x}}$ $\quad \dfrac{\delta^2}{L^2}\dfrac{\partial^2 \tilde{v}_x}{\partial \tilde{x}^2} + \dfrac{\partial^2 \tilde{v}_x}{\partial \tilde{y}^2}$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ negligible

$\dfrac{\delta^2}{\eta U}$ $\quad \dfrac{\rho U \delta^2}{\eta L} \approx 1$ $\quad$ in order for inertial + viscous to be same magnitude

$\Rightarrow \delta = \left(\dfrac{\eta L}{\rho U}\right)^{1/2} = L\left(\dfrac{\eta}{\rho U L}\right)^{1/2} = L\, Re_L^{-1/2}$ $\qquad\qquad$ this is

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ that case

$\dfrac{\pi \delta^2}{\eta U L} \approx 1$ $\quad$ so pressure same mag as inertial + viscous

$\qquad \pi = \dfrac{\eta U L}{\delta^2} = \dfrac{\eta U L}{\text{(}\eta L/\rho U\text{)}} = \rho U^2$

Y mom $\quad \rho\left(\dfrac{UV}{\delta}\tilde{v}_1\dfrac{\partial\tilde{v}_y}{\partial y} + \dfrac{V^2}{\delta}\tilde{v}_y\dfrac{\partial\tilde{v}_y}{\partial\tilde{y}}\right) = -\dfrac{\eta}{\delta}\dfrac{\partial\tilde{P}}{\partial\tilde{y}} + \eta\left(\dfrac{V}{L^2}\dfrac{\partial^2\tilde{v}_y}{\partial\tilde{x}^2} + \dfrac{V^2}{\delta^2}\dfrac{\partial^2\tilde{v}_y}{\partial\tilde{y}^2}\right)$

$\cdot\left(\dfrac{\delta}{\eta}\right)\quad \dfrac{\partial\tilde{P}}{\partial\tilde{y}} = -\rho\left(\dfrac{\delta}{\eta L}\dfrac{\partial\tilde{v}}{\partial\tilde{y}} + \dfrac{\delta}{\eta L^2}\dfrac{\partial\tilde{v}_y}{\partial\tilde{y}}\right) + \eta\left(\dfrac{d^2}{\eta UL^2}\dfrac{\partial^2\tilde{v}_y}{\partial x^2} + \dfrac{\delta}{\eta L^2}\dfrac{\partial^2\tilde{v}_y}{\partial\tilde{y}^2}\right)$
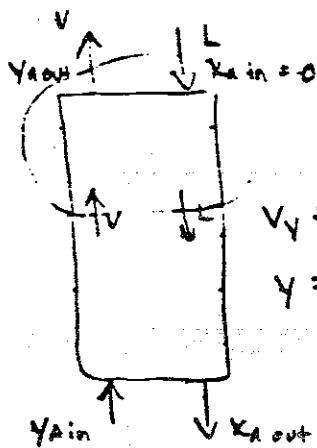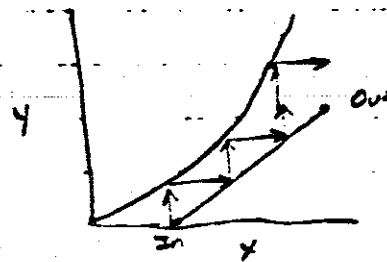
$\dfrac{\partial\tilde{P}}{\partial\tilde{y}} = 0$

$\Rightarrow \quad P = f(x) \quad , \quad \rho\left(v_x\dfrac{\partial v_x}{\partial x} + v_y\dfrac{\partial v_x}{\partial y}\right) = -\dfrac{\partial P}{\partial x} + \eta\dfrac{\partial^2 v_x}{\partial y^2}$

Π | Absorber $\quad A_g \to A_\ell$ $\qquad\qquad$ Stripper $\quad A_\ell \to A_g$
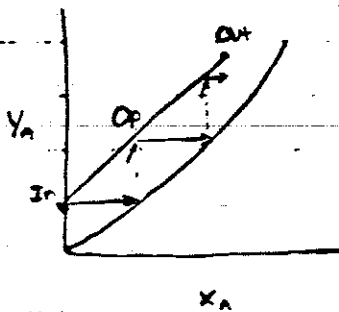
$V_y + 0 = Lx + Vy_{A\,out}$

$y = \dfrac{L}{V}x + y_{A\,out}$

$V_y + Lx_{A\,out}$

$y = \dfrac{L}{V}x - \dfrac{L}{V}x_{A\,out}$

Humidity & cooling towers

all defs. at $P = 1$ atm

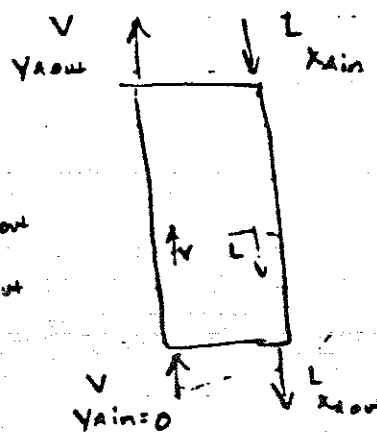$A = H_2O$, $B = Air$, $\bar{P}$ = partial pressure H_2O, P^s = vapor pressure

Humidity, $\mathcal{H} = \dfrac{\text{mass vapor}}{\text{mass dry air}} = \dfrac{MW_A \bar{P}}{MW_B (1-\bar{P})}$

Saturated gas humidity (Vapor, Liq. Equil), $\mathcal{H}_S = \dfrac{MW_A P^s}{MW_B (1-P^s)}$

Relative humidity, $\mathcal{H}_R = 100 \dfrac{\bar{P}}{P^s}$

Air enthalpy, $H = C_{P,B}(T-T_{ref}) + \mathcal{H}\left[\Delta H^{vap} + C_{P,A}(T-T_{ref})\right]$

humidity Chart

dew pt., T_d = temperature at which condensation will occur (given $\mathcal{H}_i$)
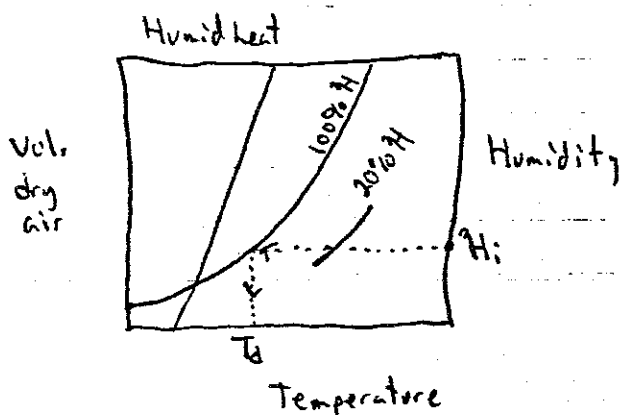
wet bulb temp., T_w is when rate of heat transfer to a water surface = rate of mass transfer away

$K_g \Delta H^{vap}(P^s - \bar{P}) = h_c(T - T_w)$ K_g = mass transfer coeff.
h_c = heat " "

dry bulb, T = air (humid) temp.

Psychrometric charts

The World's top 10 Chemicals

1) Sulfuric Acid, H_2SO_4 90 billion lbs/yr

Manufacture: Sulfur or H_2S is burned in air to form SO_2. Very exothermic.
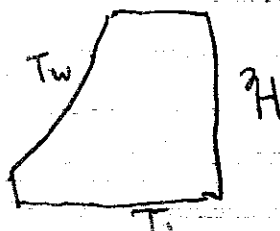 SO_2 is dried & reacted with air over an intercooled – multipass V_2O_5 catalyst reactor. This makes SO_3. The SO_3 is absorbed in H_2SO_4 in a packed tower. This is exothermic. This H_2SO_4 is then diluted – some recycled to absorber – some sent to product. The SO_3 is absorbed in H_2SO_4 ($\sim 98\%$) as opposed to pure H_2O because it has a lower vapor pressure.

Uses : Alkylation units, Fertilizer, metal processing

2) Nitrogen, N_2 52 billion lbs/yr

Manufacture: Distillation of liquid air (Linde process)
   $T_{b,O_2} = -183°C$; $T_{b,N_2} = -195.8°C$ @ $P = 1$ atm
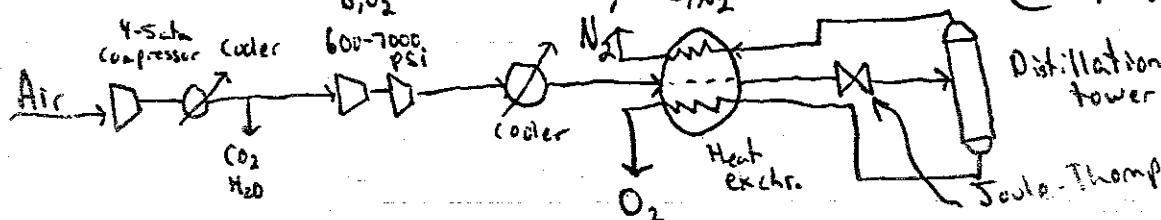
note: The modified Linde cycle used in Industry divides the Column into a low pressure (top) & high pressure sectio

Pressure swing adsorption on a zeolite. At high P, one of the components of air (N_2 or O_2) will adsorb, but not other. Lower P – adsorbed gas desorbs.

Membrane separation – size exclusion
Magnetic methods – O_2 is stronly paramagnetic
Uses: Enhanced oil Recovery, freezing meat, Electronics, inert atmospheres.

3) Oxygen, O_2 37 billion lbs/yr

Manufacture : See N_2 ; Also Electrolytic decomp. of H_2O

Uses: many chemical process - oxidation, Electronics, medical use

4) Ethylene, C_2H_4 36 billion lbs/yr

Manufacture: catalytic cracking of hydrocarbons, or thermal pyrolysis: Endothermic rxn.
Thermal pyrolysis at latm & 1300-1600°F of petroleum fractions (largely C_6's) gives from 6-40% Ethylene Recovery in low pressure distillation columns - for removal of heavy HC's. low temp, high P. columns for CH_4, H_2 removal & C_3s, C_4s

Uses: Polymers - polyethylene, polyvinyl chloride, polystyren polyethylene terephthalate (2Liter coke bottles); Antifreeze

5) Ammonia, NH_3 34 billion lbs/yr

Manufacture: Haber process : H_2 from thermal reforming of Natural gas w/ steam. N_2 from air after O_2 removed in furnace.
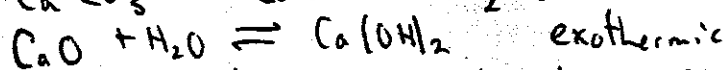← water gas shift rxn comes in here
N_2 & H_2 in a ratio of 1:3   is sent at 550°C, 200-350 atm over doubly promoted iron catalyst. recirculation, & bleeding of inerts is required. Need either refrigeration or scrubbing to collect NH_3 .   Exothermic rxn

Uses: Fertilizer, explosives, refrigeration, paper pulping

6) Lime, $Ca(OH)_2$ 32 billion lbs/yr

Manufacture: Calcination ~~(burning in the absence of A)~~
of limestone. $CaCO_3 \Longleftrightarrow CaO + CO_2$ (a)
               $CaO + H_2O \rightleftharpoons Ca(OH)_2$ exothermic
limestone must be crushed & calcined at 1700-2450°F
the CO_2 must be removed quickly as rxn (a) is reversible
rotary Kilns are used. 6-12ft in diameter x 60-400ft long

Uses: Metallurgy, soap, waste water treatment

7) Sodium Hydroxide, NaOH   24 billion lbs/yr

Manufacture: produced by electrolysis of NaCl sol'ns

Uses: Chemical production, rayon, soap, pulp & paper

8) Chlorine, Cl_2 23 billion lbs/yr

Manufacture: Also made by electrolysis of NaCl
sol'ns
        $2NaCl + 2H_2O \xrightarrow{\bar{e}} H_{2(g)} + Cl_{2(g)} + 2NaOH$
Made in diaphragm cells. Cl_2 made on anode, H_2
(& NaOH) made at cathode.
        With graphite anodes some CO_2 is produced.
Cl_2 with water vapor (inevitably released in production) is very
corrosive. It must be dried with H_2SO_4, then it is
liquefied (100psi, ~40°c) & stored.
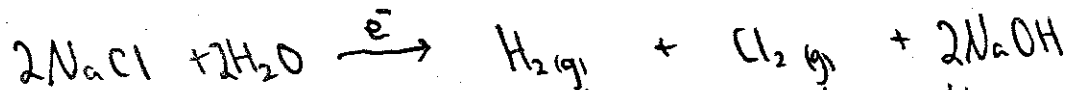
Uses: Vinyl chloride, pulp & paper bleaching, water treatment,
chlorinated ethanes, bromine production from sea water.

9) Phosphoric Acid, H_3PO_4 23 billion lbs/yr

Manufacture: liquid elemental Phosphorous is burned   at ~1000°F to form P_2O_5, this is hydrated in a spray tower & mists are collected in an electrostatic ppt. ~ this method produces "clean" phosphoric acid for uses other than fertilizer. when the H_3PO_4 doesn't have to be particularly pure, the wet process is used:

best absorp. occurs in a sol'n of H_3PO_4 ~ as in H_2SO_4

$$Phosphate\ rock \ + \ H_2SO_4 \rightleftharpoons CaSO_{4(s)} + H_3PO_4$$

Partial purification — removal of F, Ca, Fe, Al, SO_4 — is performed by evaporative concentration.

Uses: Fertilizer, dicalcium phosphate (Animal feed preparation)

10) Propylene, $CH_2 = CH-CH_3$ 20 billion lbs/yr

Manufacture: produced as side product in manufacture of gasoline, or. Ethylene.

Uses: Alkylation with isobutane to raise octane levels in gas. Polypropylene

In your free time investigate production of HCl, HNO_3, benzene, P-Xylene, Acetic Acid, The water gas shift rxn.

13 Feasibility Survey

The purpose of this survey is to preliminarily indicate the probable success of a project and to show what additional information is necessary to make a complete evaluation. Important items to consider are the following:

1. Raw materials (availability, quantity, quality, cost)
2. Thermodynamics and kinetics of chemical reactions involved (equilibrium, yields, rates, optimum conditions)
3. Facilities and equipment available at present
4. Facilities and equipment which must be purchased
5. Estimation of production costs and total investment
6. Profits (probable and optimum, per pound of product and per year, return on investment)
7. Materials of construction
8. Safety Considerations
9. Markets (present and future supply and demand, present uses, new uses, present buying habits, price range for products and by-products, character, location, and number of possible customers)
10. Competition (overall production statistics, comparison of various manufacturing pocesses, product specifications of competitors)
11. Properties of products (chemical and physical properties, specifications, impurities, effects of storage)
12. Sales and service (method of selling and distributing, advertising required, technical services required)
13. Shipping restrictions and containers
14. Plant location
15. Patent situation and legal restrictions

Process Development

Program to obtain additional data as needed by indications from the feasibility survey.

Process Design (preliminary)

1. Look at all possible manufacturing processes
2. Establish bases for design in order to eliminate flowsheet options (eg. product specifications, fraction of the year that plant will be in operation, temperature of the cooling water, available steam pressures, fuel used, value of the by-products, etc.)
3. Prepare simplified flow diagrams showing the processes and deciding on the unit operations involved.

    <u>Note</u>: preliminary material balances at this point may eliminate some of the alternative cases.
4. Select equipment using material and energy balances
5. Preform an economic evaluation

p32 ## Factors in process comparison

1. Technical factors
    (eg. Batch vs. Continuous, process flexibility, etc.)
2. Raw materials
    (eg. availability, handling problems)
3. Waste products and by-products
    (eg. amount, environmental)
4. Equipment
5. Plant location
    (eg Climate, transportation, labor)
6. Costs
7. Time factor
    (completion deadline, value of money)
8. Process considerations
    (eg. technology available, consistency of product within company)

<u>General Design Considerations:</u>

I Plant location
    1. Raw Materials
    2. Markets
    3. Energy availability
    4. Climate
    5. Transportation facilities
    6. Water supply
    7. Waste disposal
    8. Labor supply
    9. Taxation and legal restrictions
    10. Site characteristics
    11. Flood and fire protection
    12. Community factors

II Plant Layout (can be important in construction and manufacturing costs)

III Plant Operation and Control
    1. Instrumentation
    2. Maintenance

IV Utilities

V Structural Design (foundation for the equipment and vibrating machinery)

VI Storage

VII Materials Handling

VIII Waste Disposal

IX Federal and State Environmental Regulations

X Air pollution abatement
    1. Particulate removal
    2. Noxious gas removal

XI Water Pollution Abatement
    1. Physical Treatment
    2. Chemical Treatment
    3. Biological Treatment

XII Solid Waste Disposal
    1. Recycling and chemical conversion
    2. Incineration
    3. Pyrolysis (w/o O_2)
    4. Land fill

General Design Considerations cont

XIV Thermal Pollution Control

XV Health and Safety
1. Safety Regulations
2. Chemical Hazards
3. Fire and Explosion Hazards
4. Personnel Safety
5. Noise Abatement

XVI Patents
1. Patentable Inventions
2. Patent Applications
3. Foreign Patents
4. Interferences
5. Infringement
6. Assignment of Patent Rights

p 302 ch. 9 Profitability

p 294 rate of return $= \dfrac{profit\ (annual)\ 100\%}{investment\ cost}$

eg. process cost $1,000,000 and the annual profit is $50,000

$$rate\ of\ return = \frac{50,000\ (100\%)}{1,000,000} = 5\%$$

Note: Treasury bonds pay $\approx 7\%$; thus ror should be >7%

discounted cash flow (takes into account time value of money)

apply discount factor $d_n = \dfrac{1}{(i+1)^n}$ to find future value of profit

i = rate of return
n = # years

ex.
Initial fixed capital investment = $100,000
working capital investment = $10,000
service life = 5 years
salvage value at end of service life = $10,000

Year	predicted cash flow
0	(110,000)
1	30,000
2	31,000
3	36,000
4	40,000
5	43,000

solve iteratively for i

$$(30,000)(1+i)^4 + (31,000)(1+i)^3 + (36,000)(1+i)^2 + (40,000)(1+i) + 43,000 = S$$

$$S = (110,000)(1+i)^5 - 10,000 - 10,000$$

<u>Net present worth</u>   find present value of cash flows and
          subtract the initial investment

<u>Capitalized costs</u>   useful for comparing alternatives $= \dfrac{C_R(1+i)^n}{(1+i)^n - 1} + V_S$

C_R = replacement cost

V_S = salvage value

<u>payout period</u> $= \dfrac{\text{depreciable fixed-capital investment}}{\text{avg. profit/yr + avg. depreciation/yr}}$
(no interest)

= minimum length of time theoretically necessary
to recover the original capital investment
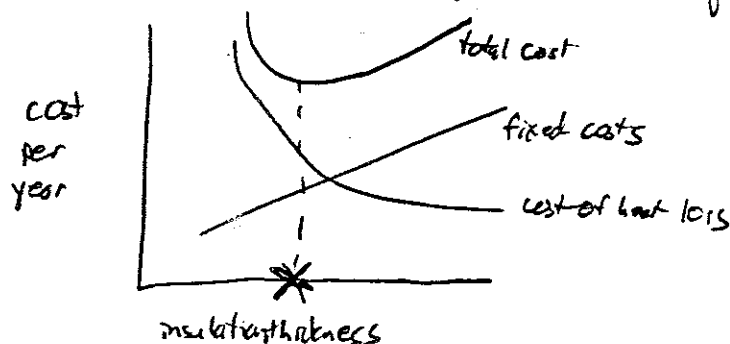
<u>continuous interest</u> : replace $(1+i)^n$ with e^{rn}

eg. $d_n = \dfrac{1}{e^{rn}}$

p357 ch. 10 <u>Optimum Design and Design Strategy</u>

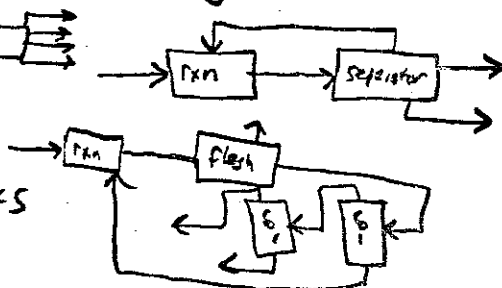take minimum of cost vs. parameter equation or graph

eg.

(linearize non-linear equations)

Procedure for process design:

1. input - output
2. recycle structure
3. separation system
4. heat-exchanger networks
   (design above the pinch)

Equipment costs from <u>Douglas Conceptual Design of Chemical Processes</u>

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<u>Heat exchangers</u>: $C_A = C_{A,BC}\left(\dfrac{A}{A_{bc}}\right)^{0.65}$ $\boxed{BC = \text{Base case}}$

$$Q = FC_p\Delta t = UA\Delta T_{lm}$$

<u>Isothermal plug-flow reactor</u>: $V = \dfrac{F}{k\rho}\ln\dfrac{1}{1-x}$ (first order isothermal)

$$C_R = C_{R,BC}\left(\dfrac{V_R}{V_{R,BC}}\right)^{0.63}$$

<u>Furnaces</u>: $C_F = C_{F,BC}\left(\dfrac{Q_F}{Q_{F,BC}}\right)^{0.78}$

<u>Compressors</u>: $C_C = C_{C,BC}\left(\dfrac{B_{hp}}{B_{hp,BC}}\right)^{0.93}$ $\quad B_{hp} = \text{power/efficiency}$

$$Power = \dfrac{3.03\times10^{-5}}{\gamma}\dfrac{P_{in}F_V}{60\rho}\left[\left(\dfrac{P_{in}}{P_{out}}\right)^{\gamma}-1\right]$$

$$\gamma = \left(\dfrac{C_p}{C_v}-1\right)\dfrac{C_p}{C_v}$$

(isentropic compression of an ideal gas)

<u>Distillation Columns</u>: $C_{sh} = C_{sh,BC}\left(\dfrac{N}{N_{BC}}\right)^{0.862}\left(\dfrac{D_{ia}}{D_{ia,BC}}\right)^{1.066}$ $\quad N = \#\ trays$

additional data From Guthries

1) When you make syn gas from coal, what are the products? Are the reactions endothermic or exothermic? How would you separate CO_2 from the gaseous product?

Feed (wt%): C-70.2, H-4.6, N-1.0, S-3.6, O-10.5, Ash-10.1

products = CH_4, C_2H_6, C_3H_8, C_4H_{10}, CO_2, NH_3, H_2S

exothermic?

separate in scrubber with base

2) How do you make sulfuric acid?
" " " sodium hydroxide?

3) You want to extract mechanical energy from geothermal steam which contains one percent incondensible gases CO_2, H_2S, NH_3. What exit T and P would choose? Would you get rid of the incondensibles? How?

4) In the Haber process $3H_2 + N_2 \rightarrow 2NH_3$
✓ Is rxn reversible?
✓ " " exothermic? Why?
How do you calculate K w/o experimental data?
How does K depend on temperature?

5) What is the lowest temperature water can be cooled to in a cooling tower?

View factor

6) Why does frost not form under a tree when it is on the grass all around the tree.

7) With 60°F cooling water + 100 psig steam, devise a process to provide water ~32°F without refrigeration.

7) Answer: Use cooling tower to lower 60°F to ~45°F. Use venturi with steam to lower pressure over pool of water, H_2O evaporates getting ΔH_{vap} from surrounding liquid lowering the temperature.

100 psi
steam
ambient
low P
d
d > 32° to provide hydraulic hea
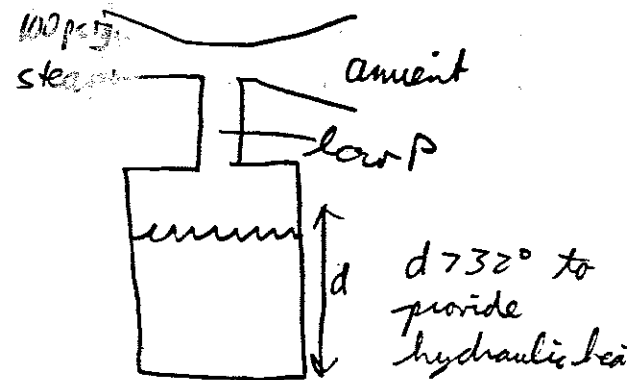
8) Suppose superheated steam were available with composition 99% H_2O and 1% CO_2. Outline a process to derive the most work or energy possible from this steam. How could you further decrease outlet pressure below ambient for a turbine? What should you do with the CO_2?

1) How would you go about estimating the costs of a distillation column, pumps, or heat exchangers?