

Natural Gas Purification

Impurities: H_2O , H_2S

Methods: Compression; Treatment w/ Drying Substances;

Adsorption; Refrigeration

WATER

Compression: ① Compressor, ② Cooling system to condense H_2O

Drying Substances: Glycols - high H_2O affinity, low cost, chem. stability, low freezing, low solv. action for nat'g. gas

Molecular Sieves - (in processes w/ water dewpoints,

$\theta = 90 \text{ to } -100^\circ C$ ($230 \text{ to } -290^\circ F$)

Adsorption: refrigerated by counter-current flow of hot gases

Packed towers w/ Activated Alumina; Barite

counter-current flow

of gas & reagent

Silica gel

Regenerator for H_2SO_4

dehydrating reagent

H_2SO_4

Concentrated sol'n's of $CaCO_3$ or Sodium thiosulfite

Refrigeration

Gas passed over refrigerated coils (costly unless own power - steam available and will be wasted otherwise)

→ (cont)

Q H₂S removal (and CO₂ removal)

Chemical Solvents: Monoethanolamine (MEA), DEA, Diisopropanolamine, hot K₂CO₃, slurry of highly reactive Fe compound.

Physical Solvents: Methanol, propylene carbonate, PEG dimethyl e
...

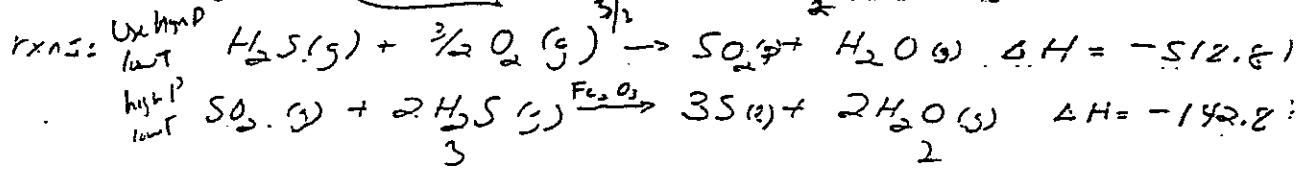
Dry Bed or Spent: Hydrated Iron Oxide-coated wooden chips

Some better for H₂S, some for CO₂; choice depends on impurity composition

If removing both CO₂ and H₂S:

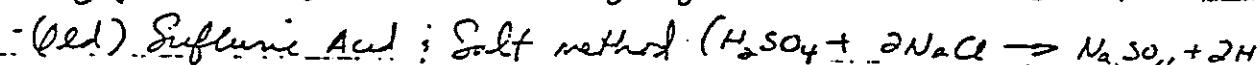
< 10-36% MEA, 45-85% diethylene glycol, remainder in water

H₂S recovery → (Claus process)



Hydrochloric Acid (Muriatic Acid \leftarrow Commercial Grade)
HCl Soln
used by metal, chemical, food, & petroleum industries

Sources: - By-product of chlorination of hydrocarbons.



(New) Hydrogen: Chlorine combustion method.

Chlorination of hydrocarbons:

- evolves much heat (control necessary)

- after unreacted hydrocarbons removed,

HCl absorbed w/ water.

Synthetic (H₂ & Cl₂)

- Both available very pure from electrolytic manufacture of NaOH

- $H_2 + Cl_2 \rightarrow 2HCl$ Equilibrium very far to right

Can get 99% HCl Gas under correct control of operating conditions.

Rxn highly exothermic; spontaneous once initiated.

- Further purification: absorb in water $\Rightarrow \Delta H = -1625 \text{ kJ/kg}$ HCl absorbed

- Aqueous soln stripped under slightly elevated pressure

\hookrightarrow strong gaseous HCl \rightarrow dehydrated to 99.5% dehydrated HCl upon cooling to -12°C

$$\frac{\text{Mass}}{\text{Vol}} = \frac{\text{Mol}}{\text{Vol}} = \frac{P}{RT}$$

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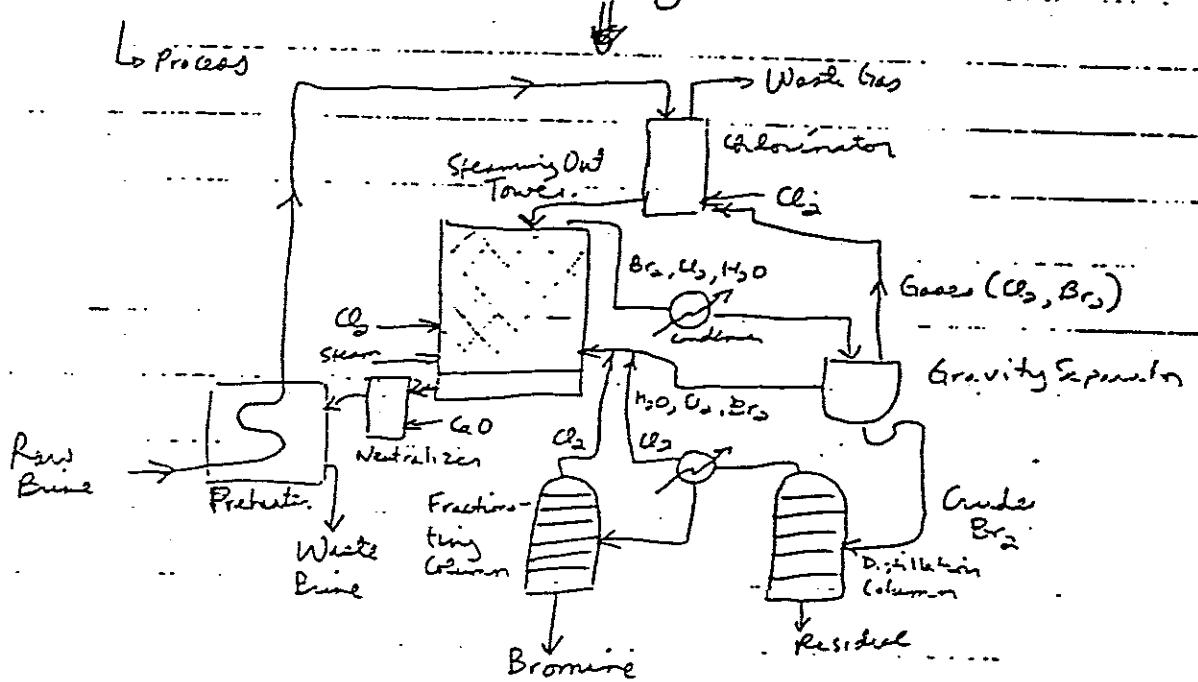
Bromine \rightarrow heavy, dark red liquid

Uses :- (major, but decreasing) ethylene dibromide for lead oxide removing
anti-knock fluids

- laboratory reagents
- flame retardant
- alkali bromides (lithography, sedatives)

Sources: $2\text{NaBr} + \text{Cl}_2 \rightarrow 2\text{NaCl} + \text{Br}_2$ (air-blowing from sea)

Salt Brines: $\xrightarrow{\text{Extraction}}$; $\xrightarrow{\text{Steaming out}}$



Crude Bromine purified by: - redistillation or

- passing vapor over iron filings which hold back Cl_2 impurity.

Iodine → violet vapor

- from kelp → kelp-burning process
(^{to iodates})

- present sources: nitrate fields, brine wells

Uses: organic compounds, KI, NaI, other inorganics;

catalyst for chlorination of organics; alkali iodides;

antiseptic

Fluorine - pale greenish-yellow gas

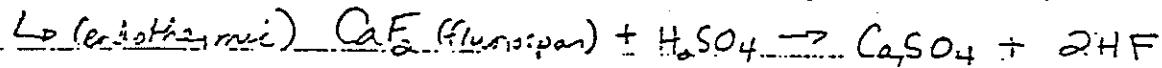
F-containing minerals: CaF_2 fluorite, fluospar, fluocapatite, cryolite

↳ uses: HF - "hydrofluoric acid" (gas manufacture), Freon.

Teflon (tetrafluoroethylene polymer.)

F_2 gas - from electrolysis of KHF_2

HF (both aqueous - if absorbed in H_2O - and anhydrous - if liquefied).



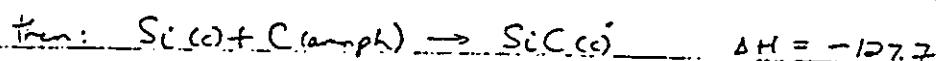
- Prepared in heated kilns

- Concentrations of 60% + can be handled in steel @ low T's (^{w/o} corrosion)

Silicon

(Possibly)

First step in SiC production: $\text{SiO}_2(s) + 2\text{C}(\text{graphite}) \rightarrow \text{Si} + 2\text{CO} \Delta H = +606\text{ kJ}$



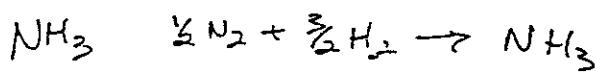
Electrolytic process: ends of trough (electrodes) connected to central graphite heating core.

Warning on this process → don't get too hot ($> 2040^\circ\text{C}$!) or silicon

will volatilize and artificial graphite will be made

↳ if want silicon, take vapors to condenser, then crystallize

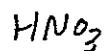
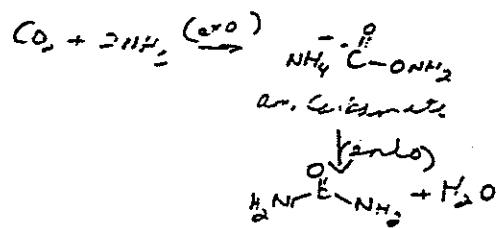
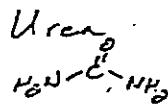
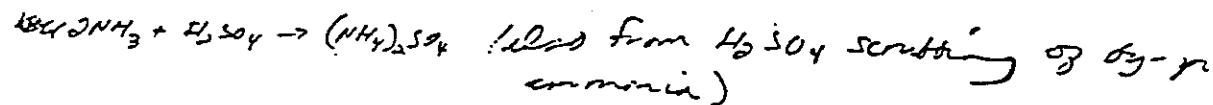
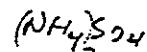
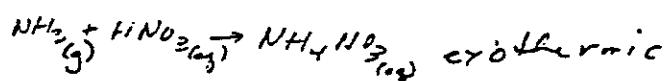
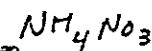
Nitrogen Industries



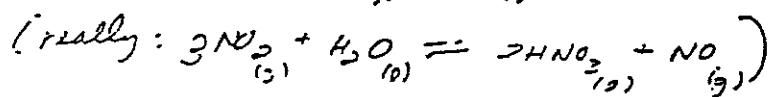
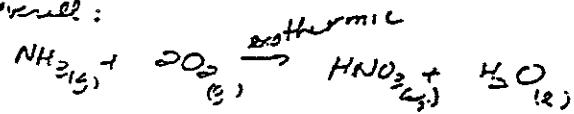
exothermic

Ferrooxides catalyst (mixed)

Recycle (major) equilibrium to left
 NH_3 removed by refrigeration



(strong oxidizer) overall:



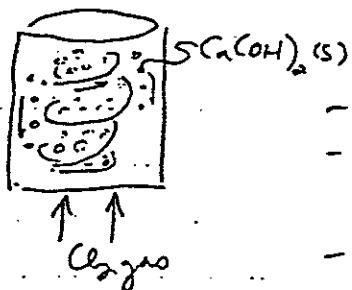
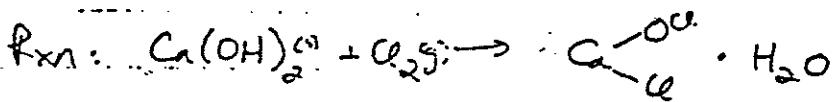
AMMONIA

- Most made synthetically, some mined (Chilean salt peter)

NH₃ gas used as: Fertilizers; in acid testing; paper pulp dying; manufacture of nitric acid, urea, nitrates, nitr compounds, hydroxylamine, hydrazine; etc as a refrigerant

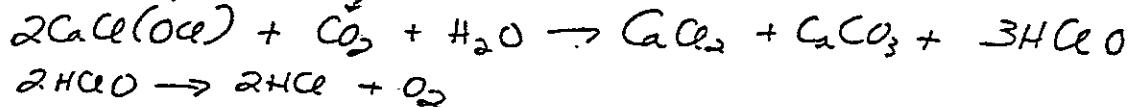
Raw materials: air, water, hydrocarbons (more complex w/cost)

Bleach → problems: instability, lots of inert material



- Countercurrent orientation
- Solid lifted by blower, falls in path of gas.
- Rxn carried out at $< 50^\circ\text{C}$

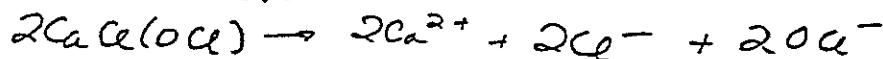
In air: decomposition absorbed from air



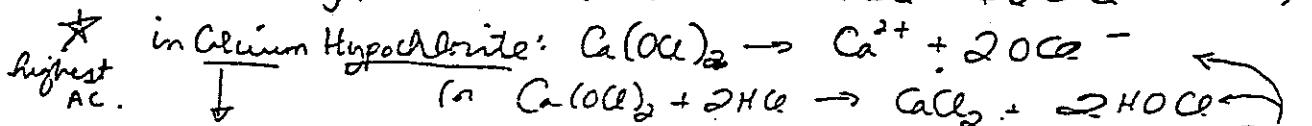
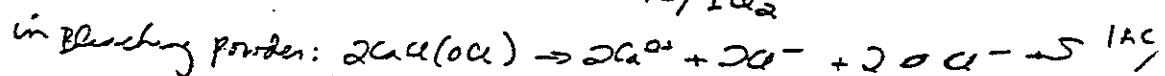
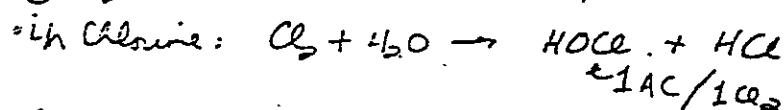
On standing: decomposition



Dissolved in Water:



Oxidizing agent, but measured in AVAILABLE CHLORINE %



to make this (2 ways)

- 1) Chlorination of $\text{Ca}(\text{OH})_2$; separation of $\text{Ca}(\text{OCl})$ then settling out w/ NaOH sol'n.
- 2) Under refrigeration, formation of salt $(\text{Ca}(\text{OCl})_2 \cdot \text{NaOCl} \cdot \text{NaCl} \cdot 12\text{H}_2\text{O})$ (chlorination of mix of NaOH & $\text{Ca}(\text{OH})_2$); reacted w/ chlorinated lime slurry; filtered to remove salt; dried \rightarrow stable product, 65-70% CaCl

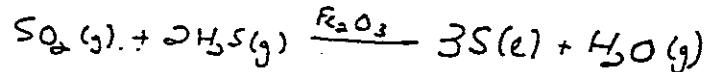
Advantages: 2x stronger than bleaching powder, i.e. $\text{Li}^+ + \text{O}^-$

Sulfur / Sulfuric Acid

Ores: Pyrite (FeS_2), sphalerite (ZnS), chalcopyrite ($CuFeS_2$)
 nat'l gas, petroleum: H_2S
 MINED - Frasch process. \rightarrow 3 nested pipes:
 (large pipe) 1) Hot, pressurized H_2O & melts sulfur deposits
 (med. pipe) 2) Melted sulfur pushed w/ water pressure.
 (small pipe) 3) Compressed hot air decreases S density, pushes it out of well.

from FUEL GASES

- 1) H_2S produced during natural, coke-oven, petroleum. Gas purification:
 removed w/ ethanolamine or $LiCO_3$ sol'n, heating to regenerate H_2S .
- A) Burned ($H_2S(g)$) + $\frac{3}{2} O_2(g) \rightarrow SO_2(g) + H_2O(g)$ $\Delta H = -518.8 \text{ kJ}$
 for SO_2 to make H_2SO_4
- B) Claus process. (rxns: above for $SO_2(g)$)



$$\Delta H = -142.8 \text{ kJ}$$

H_2SO_4

oxidizing and dehydrating agent \rightarrow used to absorb H_2O after certain processes.
 Sold as H_2SO_4 in H_2O solution, or SO_3 in H_2SO_4 (oleums).

Rxns:

- (1) $S(l) + O_2(g) \rightarrow SO_2(g)$ $\Delta H = -298.3 \text{ kJ } 225^\circ\text{C}$
- (2) $SO_2 + \frac{1}{2} O_2 \rightleftharpoons SO_3(g)$ $\Delta H = -98.3 \text{ kJ } 225^\circ\text{C}$
 $K_p = \frac{P_{SO_3}}{P_{SO_2} P_{O_2}^{\frac{1}{2}}} \quad \left. \begin{array}{l} \text{higher w/ T} \\ \text{but rxn rate lower.} \end{array} \right\} \text{tradeoff}$
- (3) $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$ $\Delta H = -130.4 \text{ kJ } 225^\circ\text{C}$

Equilibrium in (2) is of interest. Increased by removing SO_3 in scrubber and returning remaining reactants to converter.
Conversion: over V_2O_5 catalyst (77% in diatomaceous earth)
 Double absorption plants \rightarrow up to 99.8% conversion.

Contact Process: } for Making H_2SO_4

Raw materials: Sulfur \rightarrow high purity, molten S sprayed onto furnace w/ burners $\rightarrow SO_2$ gas out: 8-12%

Sulfide Ores \rightarrow burned in fluidized beds or toasters

- SO_2 dried (to prevent corrosion) in towers w/ 93-98% H_2
- Waste heat \rightarrow steam generation
- $SO_2 \xrightarrow{\text{catalyst}}$ converter; 4 stages, cooling between stages to increase conversion \rightarrow w/o double absorber \rightarrow up to 98% conversion
w/ double abs \rightarrow thru absorbing tower betw. 3rd & 4th stages.
- SO_3 absorption: 98.5-99%. H_2SO_4 most efficient agent due to its low vapor pressure; must condense/dilute recycling acid
Cannot use H_2O because acid mist (i.e. possible to absorb) results

Towers lined w/ acid-proof brick (H_2SO_4 will corrode steel!)

Sulfuric "Waste" Acid Recovery:

- if sufficiently clean and concentrated: atomized, burned to SO_2 (i.e. other gas SO_2 converted to SO_3 to H_2SO_4 by contact process.)
- Concentration
 - Heating w/ steam coil or underfiring cast iron pots (98%)
 - Air-blown concentrator (Hot air evaporates water in several stages; counter-current - air bubbled through acid.)
Mist removed in venturi/cyclone separator (93% acid)
 - vacuum concentrator; acid under vacuum indirectly steam heated; vapors ^{any toxic} condensed for recovery.

Design

Hydrogen

→ from hydrocarbons and/or $H_2O \rightarrow$ decomposed

► Electrolytic Method

- iron cathode

- nickel-plated iron anode (plating reduces O_2 overpot'l)

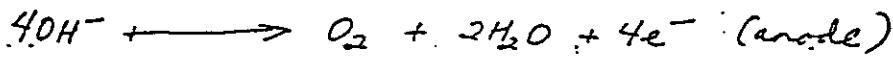
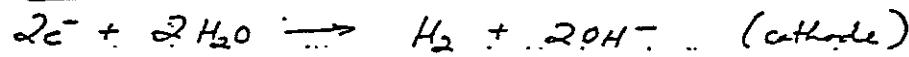
- 15% NaOH solution electrolyzed. (also: salt brine)

- 2.0-2.25 V required (above 1.23 V theoretical potential
because of overpotential of H₂ on electrodes)

= T ≈ 60-70 °C

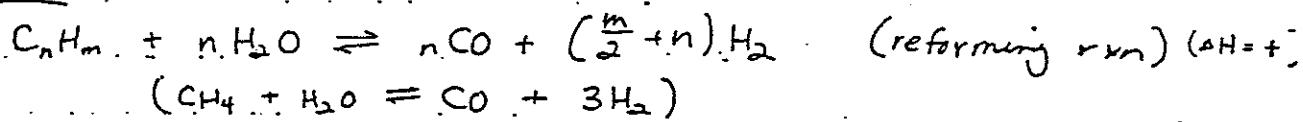
= Produces ~ 99.7% pure H₂

% cell rxns:



► Steam-Hydrocarbon Reforming Process (#1 manufacturing process for H₂)

Catalytic rxn. of steam and hydrocarbons ^{or} commonly: CH₄, C₂H₆, C₃H₈
rxns (rapid & right catalys.)



Process: hydrocarbon vaporized, desulfurized

→ mixed w/ steam, reformed over Ni catalyst (T ≈ 815 °C) in combustion furnace
(to completion: high T, low P, excess steam) → CO, H₂, CO₂ out.

→ gases cooled, more steam added, → to CO converter, passed over iron-oxide catalyst
↑ 370 °C
→ gases cooled again, passed thru 2nd stage CO converter. ↑ 90-95% CO conv.

→ gases cooled, scrubbed (to remove CO₂) w/ monoethanolamine (Girbotol absorber)

(2nd stage CO converter here, followed by 2nd stage Girbotol.)

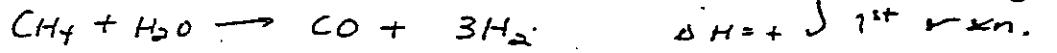
► Partial Oxidation (#2 process)

use: natural gas, refinery gas, hydrocarbon gas mixtures

* can use: liquid feedstocks of gas oil, diesel oil, heavy fuel.

Process: non-catalytic partial combustion of feed w/ O_2
in presence of steam in combustion chamber
@ flame temps. of $1300 - 1500^\circ C$

rxns (w/ CH_4 as primary component of feed.):



Product gas cooled by direct- H_2O quench (Carbon removed from quench water or disposed of.)

Remaining steps same as w/ reforming: } Water-gas shift & etc
} CO_2 removal w/ monolith alumina methanation.

► Other Processes

- Coal Gasification (water-gas, producer-gas)

- Ammonia cracking → advantage: N_2 is inert, no separation needed

- vaporizing liquid NH_3 , heat to $870^\circ C$, pass over active catalyst,
cool in heat exchangers (vaporize incoming NH_3 ..)

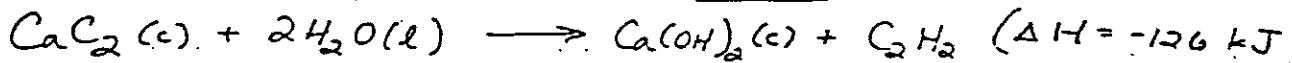
Makes: 1 volume N_2 , 3 volumes H_2 .

(1)

Design # 48

How to recover/acetylene from inorganic compounds
Shreve's p124.

Traditional method of manufacture: Reaction:



2 methods:

1) Wet. (batch Carbide-to-water)

- in cylindrical water shell w/ hopper & feed facilities on top
- Carbide fed to H_2O @ measured rate until exhausted
- $\text{Ca}(\text{OH})_2$ discharged as lime slurry, ~90% H_2O

2) "Dry generation" (large-scale industrial continuous process)

- 1 kg H_2O per 1 kg CaC_2 (molar ratio $\text{H}_2\text{O}/\text{CaC}_2 \approx 3.6$)
- ΔH_{rxn} (6.2 MJ/ ft^3 CaC_2) dissipated by excess H_2O vaporization
- by-product (lime) left dry, easily handled. \rightarrow some recycled to carbide furnaces.
- Conditions: $T < 150^\circ\text{C}$, $P < 204 \text{ kPa}$
- Continuous agitation to prevent overheating.

Never methods of manufacture: Pyrolysis / cracking of CH_4 or liquid hydrocarbon fuels.

Issue: @ high temps where CH_4 will decompose to C_2H_2 , competing rxn is decomposition to elements
 \rightarrow need: very short residence time, very hot rxn T, rapid quenching w/ oil or water

Selective solvent for C_2H_2 : e.g. dimethyl formamide

Uses of acetylene: - high welding temp. when used w/ O_2

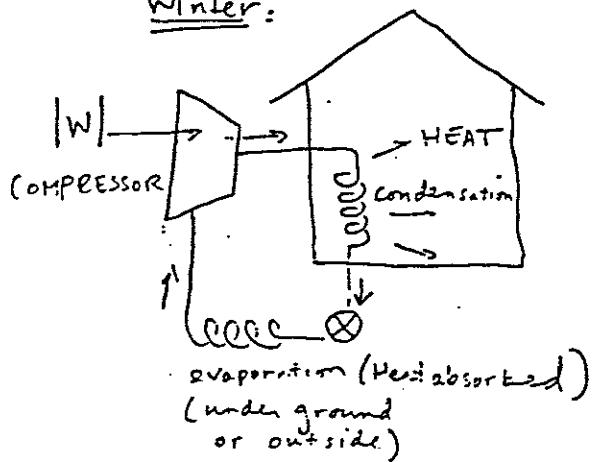
- manufacture of chloroprene and (its polymer) neoprene (mostly from acetylene)

- manufacture of vinyl chloride, acrylonitrile, polyvinyl pyrrolidone, TCE, acetic acid (also manufactured from ethylene, other sources)

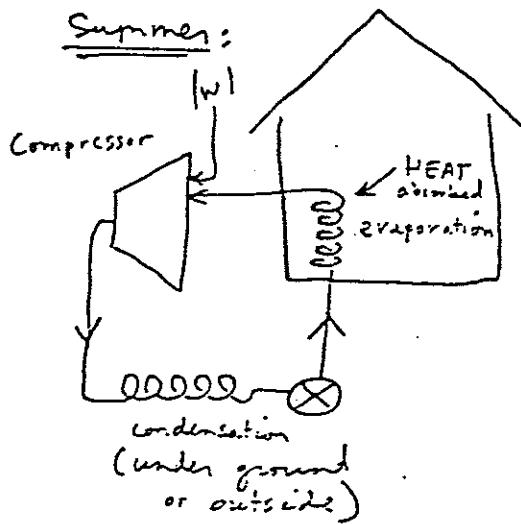
①
► Design # 15

Heat pump: reversed heat engine.

Winter:



Summer:



Winter VS. Summer: flow of refrigerant, direction of
compressor REVERSED.

ENERGY INPUT: electric power to run compressor

tradeoff: cost of electricity vs. cost of burning fuel
for compressor in a heater

$$\text{Coefficient of performance} : \frac{|Q_{cl}|}{|W|} = \omega$$

minimum power requirements from Carnot Heat pump.

Equations: $|W| = |Q_{hl}| - |Q_{cl}|$

$$\frac{|Q_{cl}|}{|Q_{hl}|} = \frac{T_c}{T_h}$$

$$\omega = \frac{|Q_{cl}|}{|W|} = \frac{T_c}{T_h - T_c}$$

→ if know desired cooling rate,
and T_h and T_c available/desired,
can get $|W|$.

► #20

HCl gas stream: absorb w/ water → dilute acid stream
neutralize w/ base (e.g. NaOH) → $\text{H}_2\text{O} + \text{NaCl}$ st

N_2 stream: rid of trace impurities, vent to atmosphere.

$$Q = \int_{R_1}^{R_2} 2\pi r N_Z(r) dr = 0$$

Design # 40 ①

Pure N_2 from air w/o cryogenic techniques?

- uses of N_2 :
- inert atmosphere (requirements: dry, <10 ppm O_2 content)
 - for refrigeration (temps as low as $-210^\circ C$)
 - manufacture of ammonia (new source is air, not natural)
 - diluent to control rxn. rates

Normally produced from air by liquefaction and rectification in double column. \rightarrow Cryogenic technique.

Oxygen purified/separated non-cryogenically through Pressure Swing Adsorption

(Ref: Davis, Chem. Eng. V 79 N. 23 p 28 (1972))

Rough idea of process:

- Molecular sieve (zeolite) as adsorbent to separate g.o.s from ambient temp. compressed air.
- Adsorption + regeneration steps
 - ↑ ↑
 - vessel pressurized, Depressurization, purging, partial repressurization
 - compressed air fed until adsorbents
 - reach capacity.
- No cryogenic equipment necessary; entire separation effected by pressure swing.

Issue

Would have to find good adsorbent ^{selective} for nitrogen.

Another (possibly better) option possibility: membrane separation.

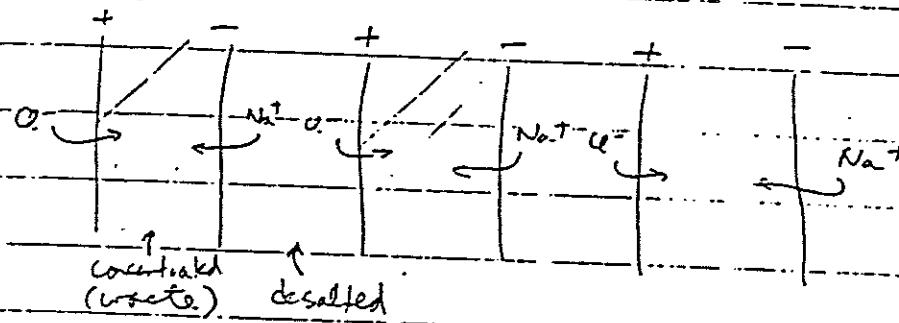
Shreve's Chemical Process Industries

Manufacture

- Acetic Acid.
 - Acetone
 - ✓ Ammonia >
 - Benzene
 - ✓ Chlorine
 - Ethanol
 - EO (Ethylene Oxide)
 - Formaldehyde
 - ✓ Hydrogen
 - HCl
 - HCN
 - HF
 - ✓ Methanol CO $12H_2$
 - Nitric Acid
 - Polyethylene
 - Phenol
 - Phosphoric Acid
 - NaOH
 - Styrene
 - Sulfur
 - ✓ Sulfuric Acid >
 - Urea
 - Vinyl Chloride
 - Zinc
 - Silicon
 - Iodine
 - Bromine
 - O_2 , H_2 , CO_2 separations from air
 - Dry Ice.
 - Cl_2 , F_2
 - Sun Gas
- ✓ Nitrogen (Sep from air w/o cryogenics)
- ✓ Acetylene
- Soda Ash (Na_2CO_3)
- Caustic Soda ($Ca(OH)_2$)

Water Desalination

Electrodialysis -



Ion removal: 20 - 60% per stack

Also: reverse polarity of membranes periodically to prevent scale buildup.

Reverse Osmosis

Pressure > osmotic pressure forces pure water out of salt water stream thru semi-permeable membranes.

Membranes: Bundles of capillaries

Spiral-wound sheets

Mat's Cellulose acetate (brackish water)

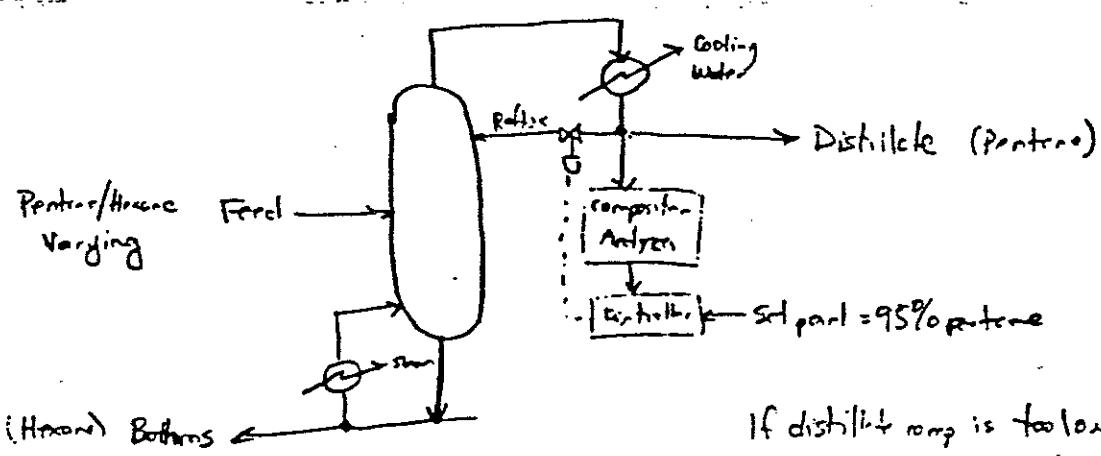
Polyamide (seawater)

Water deionization → ion exchange (cation & anion, in series or simultaneously.)

(periodically necessary to regenerate ion-exchange resin.)

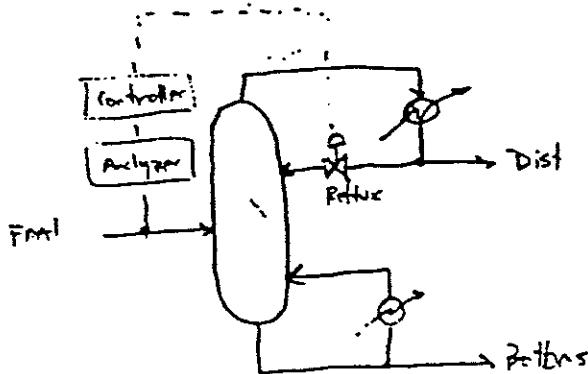
PROCESS CONTROL OF A DISTILLATION COLUMN

a) Simple Feed back

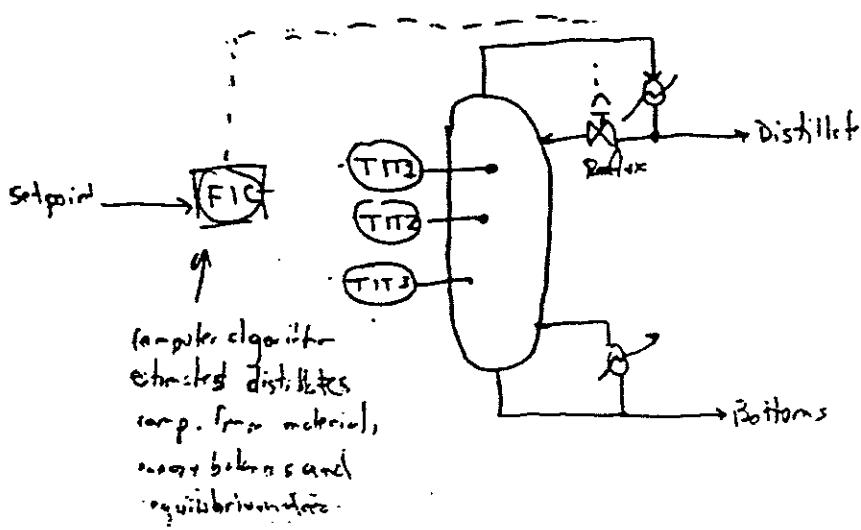


If distillate temp is too low, open reflux valve

b) Feed forward



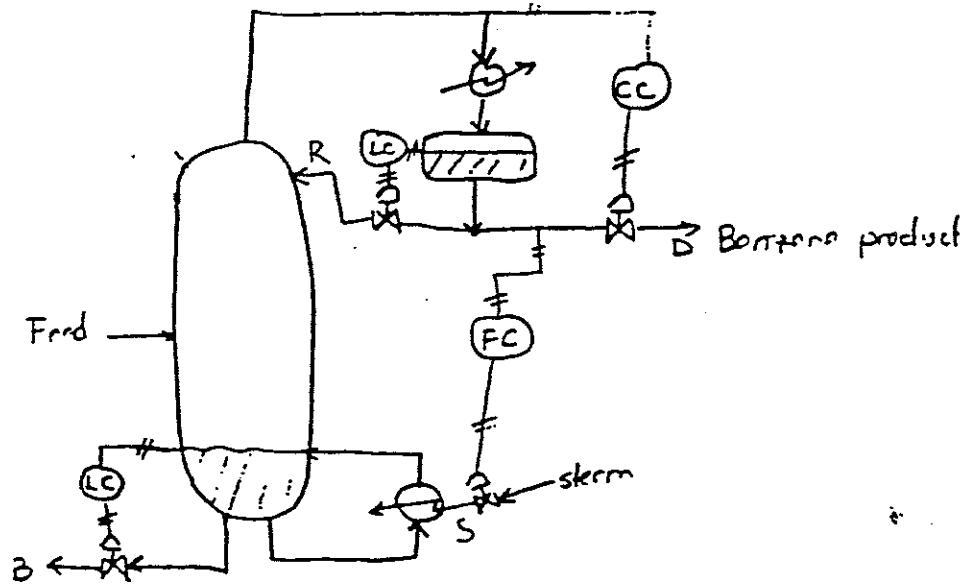
c) Inferential



Benzene Column control

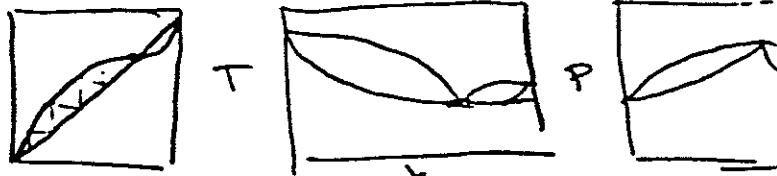
- Control variables:
- 1) Benzene product purity
 - 2) Fractional recovery of benzene in overhead product (distillate rate)
 - 3) Liquid level in overhead accumulator
 - 4) Liquid level at bottom of column.

- Manipulated variables:
- 1) Distillate rate, D
 - 2) Reflux rate, R
 - 3) Stern flow rate, S
 - 4) Bottoms flow rate, B



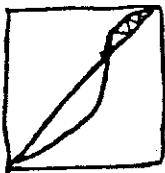
Azeotropes

For minimum boiling azeotrope, total pressure is greater than vapor pressure of either comp't. Thus, in distillation, the azeotropic mixture would be the overhead product



For maximum boiling azeotrope, the azeotropic mixture is bottoms product. because the minimum total pressure is below the vapor pressures of the pure comps'.

Here



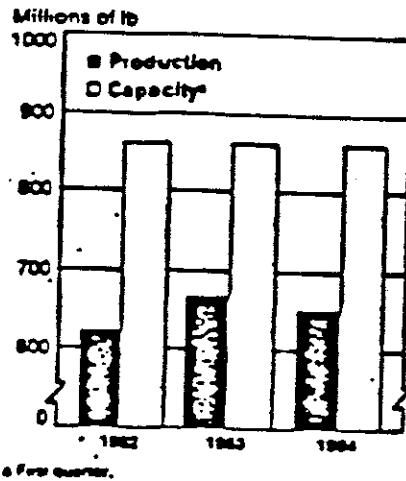
Azeotropes limit the separation that can be achieved by ordinary distillation techniques. It is possible in some cases to shift the equilibrium by changing the pressure sufficiently to 'break' the azeotrope, or move it away from the region where the required separation must be made.

Key Polymers

Acrylic

- Production off a bit
- Capacity on hold
- Prices steady

PRODUCTION/CAPACITY



HOW MADE

Polymerization of acrylonitrile, a product of the reaction of ammonia and propylene.

MAJOR END USES (U.S.)

Apparel 65%, home furnishings 30%, industrial 5%

FOREIGN TRADE

Exports—to decline to under 150 million lb in 1984; imports—to rise to about 20 million lb

PRICES

3-denier staple for apparel 90 cents to \$3.10 per lb; discounting significant

COMMERCIAL VALUE

\$500 million for production, 1984

After a good recovery in 1983, acrylic fiber production will decline slightly in 1984. The major cause of this year's slump in production is the same as that for all of the synthetic fibers: production growth problems—imports of products of these fibers, mainly in the form of apparel. For acrylic fibers, rising imports of apparel and a decline in exports of the fiber itself combine to have a greater effect than for the other important synthetic fibers.

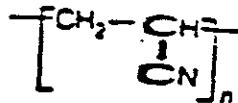
In 1984, production of acrylic fibers probably will be down 3% from its 1983 level to about 850 million lb. Most industry analysts expect this to be the top end of what will be produced this year. However, their forecasts of production range from 830 million to 870 million lb.

Capacity to make acrylic fibers generally is holding level. Minor debottlenecking is taking place but won't add significantly to capacity. Estimates of capacity range from 810 million to 870 million lb a year, depending on the fiber denier.

If capacity is about 860 million lb and if production reaches 850 million lb, then the average plant operating rate in 1984 will be more than 75%. This operating rate will be slightly below the average for the chemical industry this year. In addition, it will be well below the recent historical high for acrylic fibers of 81% in 1980 when production was more than 780 million lb from about the same capacity.

The operating rate in 1983 was a couple of percentage points higher at nearly 78%. This could be the best operating rate of the next few years, unless some major technical development or fashion change aids acrylic fibers, according to some industry observers. This low operating rate and the prospect of slowing demand could continue to put pressure on acrylic fiber prices.

Imports of apparel made of acrylic fibers are reducing domestic use and production of this fiber. Imported women's sweaters this year could ac-



Polyacrylonitrile

count for half of U.S. sales, possibly as much as two thirds. Imported men's sweaters lag women's in their share of sales, making up some third to one half of the total U.S. market. Thus, imports may account for half of U.S. retail sweater sales in 1984. Sweaters currently account for about 15% of acrylic fiber use.

Fashion, too, is influencing demand for acrylic fibers in sweaters. Cotton is staging a comeback in sweaters as well as in many other apparel items, many of which don't contain acrylic fibers.

Gains in use of acrylic fibers in several areas of activewear or sportswear offset some of the losses in demand in sweaters caused by imports. Socks, long an important use of acrylic fibers, continue to be strong this year with good gains except for the lowest-priced, so-called "tube" socks, which increasingly are being made of cotton. Demand for active wear is in even better shape because of the growing interest in sports and physical fitness.

Some of acrylic fibers' old standbys, however, aren't doing so well and may decline fairly rapidly in their share of the fiber use. Craft yarns, for example, are weak now for reasons that are unclear except for an assumption that today fewer people knit at home. Acrylic fiber blankets, long considered aesthetically pleasing substitutes for more expensive wool blankets, are in a slump, partly because of market capture by lower-cost polyester fiber blankets. Carpet use continues to decline because of competition from polyester and nylon fibers.

Clearly, what acrylic fibers need is some fashion or technical development to make them the preferred fiber, regardless of cost, in present or new uses. These fibers also need some relief from imports of apparel. As a result, the small decline in production in 1984 could be repeated next year and each year thereafter for some time unless acrylic fibers get a new market to spur their use.

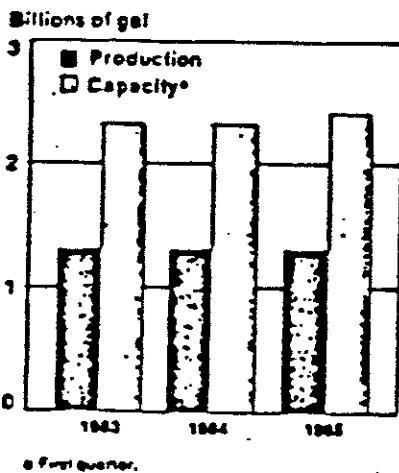
Key Chemicals



Benzene

- Production flat
- Capacity holding
- Prices firming

PRODUCTION/CAPACITY



MAJOR PRODUCERS

Amoco Oil, Arco Chemical, Coastal Corp., Exxon Chemical, Gulf Oil Products, Shell Oil, Sun Oil

HOW MADE

Separated from aromatic streams from refineries, olefin plants, coke ovens; dehydrogenation of toluene

MAJOR DERIVATIVES (U.S.)

Ethylbenzene 50%, cumene 20%, cyclohexane 15%, ethiline 5%

MAJOR END USES (U.S.)

Syntetic plastics 35%, phenolic resins 20%, nylons 15%

FOREIGN TRADE

Exports—small, remaining at about 20 million gal in 1985; imports—slipping to 150 to 160 million gal in 1985

PRICES

List price \$1.17 per gal

The best news to come to benzene producers this year is a slight firming of prices. Beyond that, it's a pretty ho-hum outlook for benzene: Production probably will not grow appreciably, nor will capacity rise further following the addition of a new Sohio plant at the end of 1984.

The price firming, however, may not do enough for benzene producers. Spot prices for benzene, reflecting only a part of total sales, increased in small increments beginning in January. By early March, they were above the list price, which had dropped significantly in 1984.

These spot prices reflect mainly demand factors and feedstock conditions beyond those in the chemical industry. The spot price rise went along with firming of gasoline prices, and was related to the value benzene has in gasoline both as a volume component and as an octane contributor to the total pool octane value. Some minor effect was felt from the drawdown of benzene inventories in 1984 and from anticipated improved demand for some end products of benzene.

During 1984, benzene prices fell more than 30 cents a gal, or nearly 20%, because of stagnant demand, lower prices for some derivatives, large inventories, and declines in crude oil prices. Spot prices ranged slightly below list prices during the second half of the year, further hurting profits from recovery and selling of benzene.

That situation changed during the first quarter of 1985. Now, questions are developing as to whether these price increases, small as they are, will hold for the rest of the year. Benzene demand in the second quarter probably will be as good as in the first quarter. Later on, demand may weaken, pulling down production as inventories build.

Benzene production for all of 1985, therefore, likely will end up about the same as in 1984, at 1.3 billion gal. This hold on production could mean that a slight decline will occur in the

operating rate for total nameplate capacity, but it ~~essentially~~ will remain about the same 55% rate that it been the past two years.

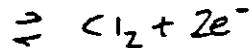
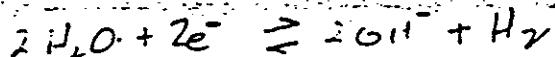
Nameplate capacity, much of ~~it~~ is in or closely attached to refineries, has been considered to be overstated. ~~But~~ sufficient aromatic streams could be obtained, then nameplate capacity might nearly reached. But ~~even so~~, capacity could be overstated because of long shut downs at steel mills and refineries, ~~which~~ are not expected to be run again. In addition, several large benzene units currently are shut down, with questions a future operation concerning some them.

Some small amounts of capacity have been scrapped, but during fourth quarter of 1984, Sohio Chemical started up its new unit with nameplate capacity of 115 million gal a year. The actual net gain in capacity for 1985 operation is hard to pin down but probably ~~at least~~ two thirds of Sohio's new unit capacity should added to the total.

Part of benzene capacity is attached to steam crackers where benzene separated from the pyrolysis gas fraction of their product stream. Typically, benzene produced in steam crackers has accounted for about 20% of production, ~~or~~ a bit more. The other part of benzene supply—imports could decline a bit in 1985 unless domestic prices rise. As U.S. sell prices declined during 1984, imports also declined because of little or profit to traders in benzene. This year imports could supply at least 10% U.S. benzene demand, but certainly not more than 25%.

None of the major uses of benzene will show much gain in demand during 1985. One—styrene—because of parts of polymers, could decline slightly. The result, then, for benzene will be a year of minor change in production and a struggle to squeeze a bit profit from a slight price firming.

Key Chemicals



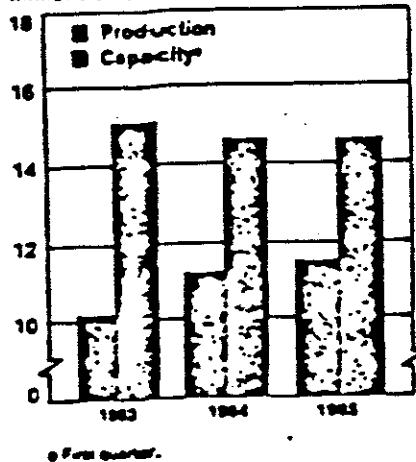
NaOH

Caustic soda

- Production rising
- Capacity stable
- Prices stronger

PRODUCTION/CAPACITY

Millions of tons



MAJOR PRODUCERS

Diamond Shamrock, Dow Chemical, Occidental Chemical, Olin, PPG Industries, Vulcan Materials

HOW MADE

Electrolysis of NaCl brine

MAJOR DERIVATIVES (U.S.)

None taking more than 5% of consumption

MAJOR END USES (U.S.)

Chemical manufacture 50%; pulp and paper manufacture 20%

FOREIGN TRADE

Exports—declining to about 1.7 million tons; imports—rising to about 500,000 tons in 1985

PRICES

List prices at Gulf Coast plants \$175 per ton; prices higher at other locations

In addition to the obvious coproduct situation, caustic soda production is rising for many of the same economic reasons as chlorine. Strength in the economy increases the demand for chemicals that are made using caustic, either as a source of sodium ions or as a processing aid, such as in neutralization.

Production growth for finished caustic in 1985 will be slightly less than will be reported for chlorine. Caustic output will be up less than 3% to 11.5 million tons, after a 10% rise in production during 1984.

The difference in the growth between chlorine and caustic is caused by the differences in their sources and in their final processing. Although different processes and brines can be used to make chlorine, caustic soda comes almost entirely from electrolysis of sodium chloride brine. Not all of the caustic soda in solution from the electrolysis cells is finished or concentrated to the usual commercially available solutions of 50% or 70% or made into dry caustic. This unfinished caustic is used as a neutralizing agent in other units at the same plant site where it is made.

Capacity to produce caustic is greater than capacity to produce chlorine because of the stoichiometry of the electrolysis. But it is not changing at all, other than as a result of efficiency improvements to the cells. (Chlorine capacity changes slightly more than does caustic capacity because of sources of chlorine other than sodium chloride brine.) Because exports of caustic—now slowing—are a proportionately larger part of demand, less pressure to expand capacity exists than that for chlorine.

Plant operating rates this year will be nearly the same as 1984: about 78% of nameplate. This includes some small amount of capacity shutdown. At this level, it seems unlikely that any shutdown capacity will be restarted anytime soon or that any new capacity will be built.

The export markets for caustic, accounting for about 10% of production, are a special cause for concern to chlor-alkali producers. The export business rebounded in 1983 and continued strong in 1984, reaching 1.3 million tons. This was close to the record set in 1979. But currently sliding exports will continue to slide as chlor-alkali industries develop in countries with much-lower-cost energy.

Imports of caustic into the U.S. are rising from countries other than the traditional ones, such as Canada. These imports come from countries that have lower energy costs, either direct or subsidized, and that are attracted by the strong dollar. The greater imports plus lower exports reduce the favorable trade balance.

This trade-balance effect tends put pressure on caustic prices, which were raised in 1984. So far, prices, though discounted significantly from list prices, have held up. Prices could go higher, according to some industry sources, because caustic may have to carry a larger share of the production cost of an electrochemical unit, which is 1 ton of chlorine and about 1.1 tons of caustic. Caustic's share of an electrochemical unit will rise because of possible softer chlorine demand if shipments of PVC ease during the second half of 1985.

Demand strength for caustic comes mainly from the big catch-all use category—chemicals manufacture. Often, caustic used in chemicals simply passes through the process and is regenerated. But some caustic is lost in most processes requiring constant addition. A similar situation exists for pulp and paper manufacturing.

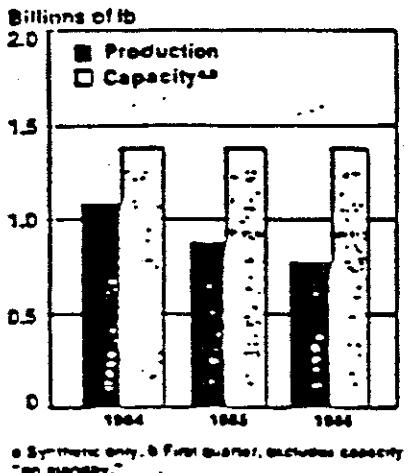
Demand for caustic in 1985 will remain strong enough to keep production rising another year, even in the face of a less favorable trade balance. With net exports possibly slowing, U.S. demand growing slowly, chlor-alkali producers will have the same struggle with profitability that they have had.

Key Chemicals

Ethanol

- Production off steeply
- Capacity on hold
- Prices level

PRODUCTION/CAPACITY



MAJOR PRODUCERS

Eastman Chemical, U.S.I. Chemicals,
Union Carbide

HOW MADE

Synthetic—direct hydration of
ethylene; otherwise fermentation

MAJOR DERIVATIVES

Acetic acid (vinegar) 10%, esters
10%, ethers 10%

MAJOR END USES

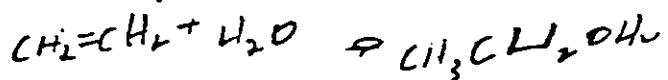
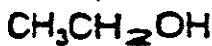
Solvents 55% (85% including
derivatives), food 10%

FOREIGN TRADE

Exports—declining to less than 10
million lb; imports—rising to more
than 500 million lb

PRICE

\$1.80 per gal



Synthetic ethanol production (excluding beverage alcohol), which has been declining rapidly in recent years, is expected to continue its slump through 1986 and possibly later. Any reversal of this situation will depend on a tight control of imports. This year imports of both synthetic and fermentation ethanol likely were several times U.S. output.

The import problem is far worse for producers of fermentation ethanol, which is used in gasoline mixtures for motor fuel, than it is for producers of synthetic ethanol. However, in 1985 a considerable—but impossible to estimate accurately—quantity of synthetic ethanol arrived from Saudi Arabia.

Some imported fermentation ethanol goes to uses formerly supplied by synthetic ethanol, including uses in some solvents and as intermediates for various chemicals. Rising imports of both fermentation and synthetic ethanol caused this year's rather steep decline in output of synthetic ethanol. Production in 1985 will do well to reach 900 million lb, down about 20% from 1984 output of more than 1.1 billion lb. For the first three quarters of 1985, preliminary figures show production of about 730 million lb on an annualized basis. Often, however, a surge in synthetic ethanol production occurs during the fourth quarter. This makes a higher annual total likely.

The decline in production of synthetic ethanol forecast for 1986 will be about half that expected for 1985. Next year's output could total 800 million lb, but probably will be less, if imports continue at current levels or rise slightly.

Falling capacity utilization is hurting the three synthetic ethanol producers. For 1985, the average operating rate is estimated to be less than 65% of nameplate capacity, and for 1986, it is predicted to be less than 60%. This downward trend indicates that some capacity might be shut down. However, a number of producers have captive uses for their ethanol, allowing

them to keep units operating. But, the make-or-buy decisions looms over producers, especially if they have a more profitable use for the ethylene consumed in the ethanol.

Some synthetic ethanol will continue to be needed for certain cosmetic and pharmaceutical solvents in which odor is critically important. Slightly more than half of U.S. synthetic ethanol is used as a solvent, and, of this, about 30% goes into cosmetics. Fashion influences make demand forecasts difficult in cosmetics. Over the near term, growth is predicted to be modest—less than 5% annually.

Other solvent uses of ethanol such as in coatings and inks are under pressure from lower-cost imported material. In certain proprietary uses, only synthetic ethanol will do the job, but in most uses, fermentation ethanol is acceptable. In some applications, especially coatings, isopropyl alcohol also provides competition. Growth in these other solvent applications will remain modest; for most it will be less than 5% annually.

Ethanol is used to make a wide variety of chemicals, with ethyl acrylate, vinegar, various glycol ethers, ethylamines, and ethyl acetate ranking among the larger users. Each of these products has various uses as well, of which none have strong growth prospects. Because of the inroads of fermentation alcohol, all a group the various chemical uses of synthetic ethanol probably will show a small decline next year, as they are showing in 1985. Use in glycol ethers is especially vulnerable owing to concern over their possible toxicity.

The small growth expected in the aggregate of ethanol's chemical and solvent end uses will be obscured by the rise in its consumption as a motor fuel. If imports of ethanol for fuel use continue to rise in 1986, they still will be diverted into nonfuel uses, which is what caused the declines in production of synthetic ethanol in 1985 and is expected to cause them in 1986.

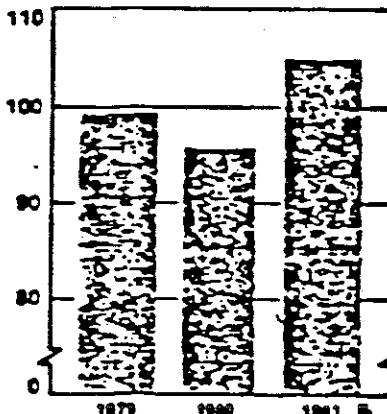
Key Chemicals

Hydrogen

- Production recovering
- Market expanding
- Prices up

PRODUCTION

Billions of cu ft*



* Excluding captive production.

HOW MADE

Steam reforming of natural gas
Captive gas shift

MAJOR USES

Chemical processing 63%,
metallurgical uses 37%

FOREIGN TRADE

Negligible

PRICES

88 cents per 100 cu ft in 13,000-gal
lots (liquid)

COMMERCIAL VALUE

About \$150 million for total merchant
production, 1981

Hydrogen has been one of the bright spots in the U.S. industrial gas business—that is until last year. In 1980, however, hydrogen production fell 3.2% from 1979 levels. This is quite a change from the gas's 10-year growth rate of about 8%.

This growth rate, alone, however, did not make hydrogen's reputation for profitability. Rather it was the relative lack of competition and modest growth of producing capacity that has made the chart hydrogen a good product to be in. And producers believe that the growth rate will increase—to as much as 10% per year.

There are essentially only three producers of liquid hydrogen in the U.S.—Union Carbide, Air Products and Airco, the U.S. subsidiary of Britain's BOC International. Union Carbide and Air Products dominate the market.

Merchant hydrogen is just a small part of all of the hydrogen produced in the U.S. Some industry experts have estimated that total production of hydrogen far outstrips any other industrial gas on a cubic-foot basis. This is because many users of hydrogen produce their own gas for captive use. These sources of hydrogen are largely unknown and thus not counted in the government production figures. Therefore, no one knows just how much hydrogen is produced or even how many producers there are. This segment has been estimated to be at least as much as 10 times as large as merchant hydrogen output, however.

Merchant hydrogen production suffered last year because it is closely tied to two highly cyclical products. About 63% of merchant hydrogen production goes to chemical processing for such products as plastics, pesticides, and chemical intermediates. The other 37% goes to metall processing where it is mixed with nitrogen to form blanketing atmospheres.

Since both chemicals and metals suffered last year, it is no wonder that merchant hydrogen production declined. In fact, merchant hydrogen production is a lagging indicator for the economy. Last year hydrogen production did not start to decline until after the recession had begun.

And since the chemical and metal economies have not yet recovered, neither has the hydrogen production. U.S.

production of hydrogen was off 3.8% through the first four months of 1981 to 32.1 million cu ft. This number is only roughly correct, since it takes into account some hydrogen gas that is sold on the merchant market. It rather should be used as an indication of the way the market is going.

The price for hydrogen seems to be increasing, although price seems to be uncertain, too. Since, like other industrial gases, contracts include widely varying prices, the average for the industry is largely unknown. The best guess is that hydrogen currently is selling at about 98 cents per 100 cu ft in 13,000-gal lots. This excludes equipment and shipping charges. Other estimates have put the price about 10 cents higher. However, these prices are discounted and, further compounding the problem, in some cases energy charges apply.

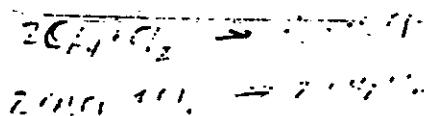
But, if it is assumed that the current list price is 98 cents, this represents an increase of about 7.7% from a year ago. It also means that the price of hydrogen has increased almost 30% in the past three years.

Even though there is discounting now, the small number of producers almost guarantees a more orderly marketplace for hydrogen than for other industrial gases. For one thing, there is not the spate of new capacity as in the three other gases. Merchant hydrogen capacity is still about 128 tons per day, the same as it was at this time last year, according to industry sources.

Two new plants will be coming on stream to serve the U.S. market. Air Products' new plant at Sarnia, Ont., although not a U.S. plant, will be sending most of its products into U.S. markets. This plant will come on stream sometime this year, and will be the first new capacity serving U.S. markets since 1979. Union Carbide also is building new capacity at Niagara Falls, N.Y., which will be on stream in 1982.

Transportation costs also are becoming problematical. In the past, liquid hydrogen has been shipped up to miles from the plant. Although it is possible to do this, producers feel that they had better look to ways of cutting this overhead. They say that in the future plants will be built closer to areas where the merchant hydrogen is needed.

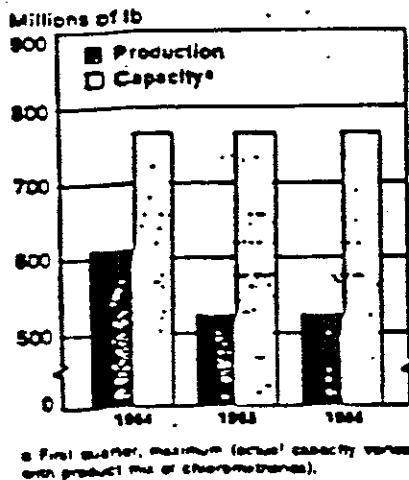
Key Chemicals



Methylene chloride

- Production to hold
- Capacity variable
- Prices steady

PRODUCTION/CAPACITY



MAJOR PRODUCERS

Diamond Shamrock, Dow, LCP Chemical, Vulcan

HOW MADE

Chlorination of methane;
hydrochlorination of methanol, then
chlorination of methyl chloride

MAJOR END USES

Paint remover 30%, solvents 20%,
degreasing agent 10%, chemicals
manufacturing 10%, blowing agent
5%

FOREIGN TRADE

Exports—about 50 million lb;
Imports—about 50 million lb

PRICE

About 35 cents per lb

Methylene chloride producers have cut output drastically in 1985, and prospects for improvement in 1986 are slim. Compounding the problem, the Environmental Protection Agency has begun its long-awaited study on the possible risks of cancer from exposure to methylene chloride, which is used largely as a solvent.

Current estimates put production of methylene chloride in 1985 at about 520 million lb, or slightly less. That figure is about 15% less than last year's output of 607 million lb estimated by the U.S. International Trade Commission. However, the annualized 1985 production for the first three quarters totals 510 million lb. If the final 1985 estimate is increased as much as was the final 1984 figure over the preliminary estimate, then 1985 production could be as much as 550 million lb. Thus, output would be down only about 10% from 1984.

Production of all four chloromethanes—methylene chloride, methyl chloride, chloroform, and carbon tetrachloride—is down, but not uniformly, from levels in 1984 when recovery from the recession reached its peak. The reason for irregular changes in output is the flexibility that manufacturers have in running plants to make whichever chloromethane is most in demand. Capacity estimates for methylene chloride are the maximum that can be produced, partly at the expense of output of other chloromethanes. Based on this maximum capacity, the 1985 average operating rate for methylene chloride plants is 68% of nameplate.

Manufacturers of methylene chloride would like to increase output this year and need to offset anticipated lower production and sales of chloroform. This decline in sales will result from the modification of a DuPont chloroform plant that will make DuPont nearly self-sufficient in its supply of the material to make dichlorodifluoromethane, used as a refrigerant and in manufacturing fluoropolymers.

Demand for methylene chloride is forecast to remain nearly stagnant in 1986. The end uses are expanding very little and may well shrink, depending on how the public views the results of the EPA toxicity study. Most uses of methylene chloride depend on its solvent properties; relatively small quantities are used as chemical intermediates.

The largest solvent use of methylene chloride is in paint removers. For several years this use grew rapidly as methylene chloride replaced other solvents that cause under air pollution control regulations. However, growth has abated recently because demand for paint removers is rising slowly and capture of the markets held by other, older paint remover solvents is almost complete. If more concern develops over toxicity, use in paint removers could decline steeply after 1986.

The second largest use of methylene chloride, that as a propellant in aerosol preparations, also has grown little. Methylene chloride took over much of the market from fluorocarbon propellants because of concern about damage to the atmospheric ozone layer. Methylene chloride apparently causes little damage to the ozone layer because it decomposes relatively rapidly in air. For the near term, growth in this use of methylene chloride will follow closely that of the population and will vary as a result of changes in use of hair sprays and other aerosol products.

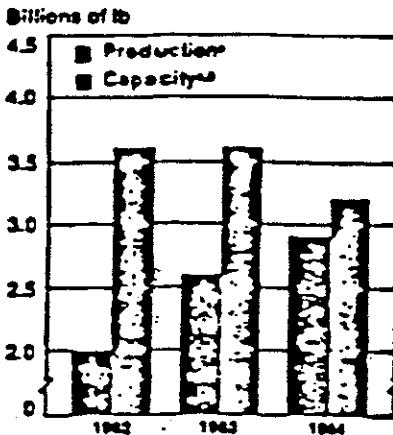
The other uses of methylene chloride also rely on its solvent properties. Those include industrial cleaners and degreasers, which depend on trends in industrial operations. For example the shift to less metal processing in making automobiles and other durable goods tends to reduce demand for methylene chloride. A host of small solvent uses account for a large part of consumption, but none of these are increasing fast enough to help much in stemming the general decline in use of methylene chloride.

Key Chemicals

Phenol

- Demand higher
- Capacity to rise
- Prices up

PRODUCTION/CAPACITY



HOW MADE

Peroxidation of cumene (isopropyl benzene) and cleavage to phenol and acetone

MAJOR DERIVATIVES (U.S.)

Resins (mostly with formaldehyde as comonomer) 40%, Bisphenol A 20%

MAJOR END USES (U.S.)

Adhesives 80%, plastics 20%

FOREIGN TRADE

Exports—to hold at about 100 million lb in 1984, imports—small and holding around 25 million lb

PRICES

List prices 36 to 39 cents per lb, discounts still significant

COMMERCIAL VALUE

\$1 billion for production, 1984

This year phenol will join that small, but growing, group of organic chemicals whose excess capacity is about used up. Production of synthetic phenol in 1984 could exceed 3 billion lb, surpassing the 2.95 billion lb record set in 1979.

Since 1979, considerable changes have occurred for phenol. Nameplate capacity has continued to rise and exceeded 4 billion lb in 1981. Then following a severe decline in production during the recession to about 2 billion lb in 1982, capacity also dropped.

Monsanto is the latest to leave the phenol business, dropping 500 million lb from the 1983 capacity list. Minor debottlenecking offset a part of this shutdown capacity, but the current total, at about 3.2 billion lb, will be strained if 3 billion lb of phenol are produced in 1984.

Even if production falls a little short of the 1979 high this year, the average operating rate for plants on stream as the year began will be 90% for all of 1984. But some help is coming. By the end of this quarter, Georgia-Pacific will be putting some 157 million lb of capacity on stream in a plant that has been shut down for several years.

Additional debottlenecking is going on as well, which will add a bit to phenol capacity and help the snug supply. These small expansions could total between 100 million and 200 million lb when added up by the end of 1985.

List prices for phenol have risen so far in 1984 and some discounts have been taken off. This has helped to raise the previous low returns on sales of phenol and its derivatives. (Merchant sales account for about half of the production of phenol, although for some producers, sales are very small.) Considering current and expected returns on sales, producers still are unlikely to build new plants. A producer would require a large captive use to justify a plant, with any

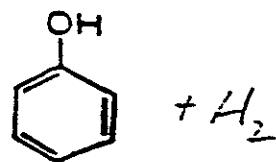
phenol for sale as incremental production.

Capacity additions by debottlenecking may be all that will be needed for several years. If 1984 production reaches 3 billion lb, it will be just 3.4% above the previous high. This tiny growth means that for the past five years production of phenol languished—hardly an incentive to build new capacity. Therefore, small capacity additions likely will be enough to get through 1985 when demand again might slow as the economy cools.

Exports, of course, are a potential outlet for additional product made in the U.S. Currently, exports of phenol probably will amount to about 100 million lb, about the same as last year. Exports could be reduced to meet internal demand, but exporters have some investment in special handling equipment for phenol cars which they would like to keep earning some return. New foreign plants also could cut into exports.

Adhesives—particularly those made with formaldehyde—for the housing market account for a major share of the consumption of phenol. This market depends heavily on housing demand. But, even if housing demand slows next year and, in turn, demand falls for plywood made with phenol-based adhesives, enough demand remains in other phenol uses for it still to have a good year. Inventory changes in plywood have some influence on adhesive demand, which could cause temporary swings in phenol demand as plywood inventories are liquidated and then rebuilt quickly.

Other applications for phenol are much smaller, and many also are connected with housing and with auto production. They also are partly responsible for pushing phenol production to capacity limits this year, but they, too, would decline if the economy slows. After many poor years, the many uses are making a very good year for phenol.



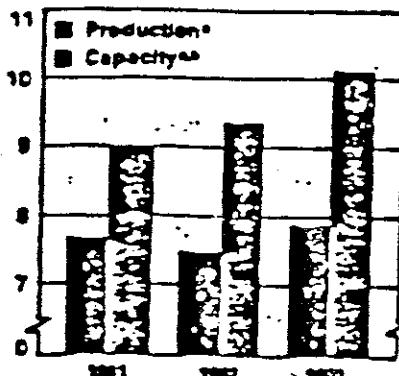
Key Polymers

Low-density polyethylene

- Demand rebounding
- Capacity growing
- Prices still low

PRODUCTION/CAPACITY

Billions of lb



* Includes linear low-density polyethylene. * From quarter, includes some shut-down capacity not subjected to restraint.

HOW MADE

Polymerization of ethylene at high and low pressures aided by catalysts and initiators

MAJOR FABRICATED FORMS (U.S.)

Film, largely for packaging, 85%; coatings 10%; injection molding 5%

FOREIGN TRADE

Exports—large, but may drop to less than 1 billion lb in 1983; imports—less than 40 million lb

PRICES

List prices 28 cents per lb and up; discounts varied and sizable

COMMERCIAL VALUE

\$2.5 billion for production, 1983

Low-density polyethylene weathered the recession a little better than expected and will make a run for record U.S. production this year. Producers have enough confidence that capacity expansions continue, mostly in the new, linear low-product type. Still, plant use rates and profitability aren't very good, and the resin's important export market is due for a drop.

Production of low-density polyethylene declined just 3% in 1982 from 1981 to 7.5 billion lb. For 1983, production could bounce back to a new high of 7.8 billion lb, possibly more if linear low-density polyethylene demand reaches optimists' expectations. The record is 7.8 billion lb in 1978.

Both production and sales of this polymer ran above the expected 1982 rate of gain in the latter part of 1982. This unsustainable pace apparently was due to inventory building as interest rates declined and buyers all through the sales chain, from polymer producers to end-product distributors, believed they saw a business pickup. However, analysts say this growth rate, more than 12% for December 1982 over December 1981, can't be maintained for 1983 as a whole.

Plant capacity for low-density polyethylene continued to grow in 1982. This growth equals the net of plant additions for conventional and linear low-density polyethylenes minus permanent shutdowns in conventional plants. The largest addition in 1982 was Exxon Chemical's plant at Mont Belvieu, Tex., with capacity of 600 million lb per year of linear low-density polyethylene.

Other additions and subtractions brought total nameplate capacity to 10.1 billion lb as 1983 began, up 8% from a year earlier. Of additions due in 1983, the vast majority will be accounted for by Eastman Chemicals and Mobil Chemical, which are building the last of the conventional low-density plants in the U.S. In addition, process technology improvements will add some linear low-density capacity, and there will be some shifting of older high-density units to make this form of polyethylene.

Not all of this capacity actually is producing. At least 500 million lb currently is shut down and not expected to operate again, at least at the present locations. Probably another 500 million

lb, possibly more, of capacity is temporarily shut down. All shut-down capacity uses the older, high-pressure technology, whose economics have been eclipsed dramatically by the newer-pressure processes.

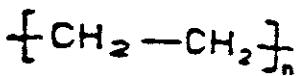
Subject to market demand, sort temporarily shut-down capacity might be converted to make linear low-density material. However, costs of conversion compared to costs of new plants, costs of conversion of high-density polyethylene plants, make forecasts a most impossible given the outcome of current capacity excess.

The likely result: In 1983, unless a unusual demand surge comes along, that more than 1 billion lb of capacity remains idle. If production reaches 7 billion lb, remaining capacity will run a very decent 87%. Counting all shutdown capacity, the plant-use rate for a year will drop to 78% from 81% in 1982. The recent though in plant use was 83% in 1978.

On the market side, U.S. uses of low-density polyethylene, counting all resin forms, will have roughly the same pattern as in recent years, with film dominating. Growth in film use will account for most of the production gain excluding inventory building. This favors linear low-density material, which goes largely into films. Further help for films will come from quality improvements.

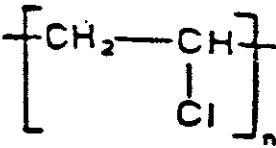
Outside the U.S., low-density polyethylene faces a different picture. A with many other U.S. chemicals, export will suffer because of the high value of the dollar and competition from new foreign plants with lower-cost feed stocks. After reaching almost 1.1 billion lb in 1982, close to the all-time high in 1980, exports of low-density polyethylene are forecast to drop 10% to about 1 billion lb in 1983.

The export drag will combine with competition for U.S. sales to take a toll on profitability and lead to more plant shutdowns. Efforts to raise polyethylene prices seem continuous but with little result. Enough new capacity will become available in 1983 that the pricing/profitability relationship will remain much like 1982, the only a respectable volume increase. Since this plastic will have a large volume, it may not be able to find a financial reward.



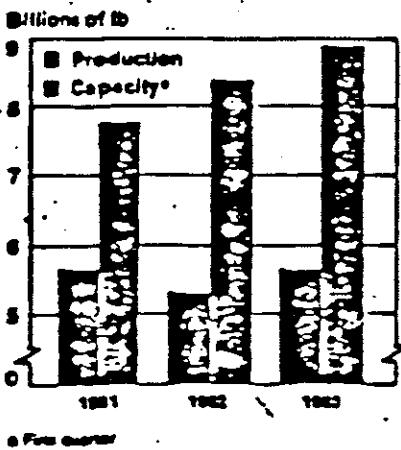
Key Polymers

Polyvinyl chloride



- Demand recovering
- Capacity shaking out
- Prices turning up

PRODUCTION/CAPACITY



HOW MADE

Polymerization of vinyl chloride by suspension, emulsion, bulk, or solution processes initiated by free radicals

MAJOR FABRICATED FORMS (U.S.)

Extrusions, nearly two thirds pipe 64%; calendered sheet, film 10%

FOREIGN TRADE

Exports—declining to about 500 million lb in 1983; imports—staying about 50 million lb

PRICES

List prices unsettled, starting at 28 cents per lb; discounting large

COMMERCIAL VALUE

\$1.5 billion for production, 1983

Signs of recovery finally are coming through for polyvinyl chloride, but it will take some time for this plastic to recover from the tumultuous times of the early 1980s. In 1983, even with a moderate production rebound powered by an improved construction market, polyvinyl chloride plants will bump along at only 64% of nameplate capacity.

The result will be a continued shakeout in this business, with more plants closing and more producers heading for the exit. In this respect, PVC is starting the new business cycle far different than in the late 1970s, when plant use strained the limit at 87% of capacity in 1979 and expansions rolled on and on.

PVC gets these wild cyclical changes in part because it is the thermoplastic most tied to the gyrating construction market, which takes a bit more than half of total U.S. PVC output. If home furnishings and other consumer items used around the house were included, construction's share of PVC demand would be still greater.

Unfortunately, at the beginning of a business recovery as at present, PVC lags construction because of the multi-stage pipeline extending back from construction sites to plastic extruders to resin producers. This "fine-fit" time can account for as much as half a year, depending on perceptions of demand strength at different stages of the pipeline.

Currently, these perceptions indicate strong coming PVC demand in construction. Spurred by lower interest costs, these assessments call for renewed inventory building and increased PVC production, continuing a trend begun in late 1982. For 1983, output now is heading back to the 1981 level of 5.7 billion lb, possibly higher by 100 million to 200 million lb. This increase of 8% or higher still would leave PVC shy of its 1979 record of 6.1 billion lb.

As 1983 began, operable PVC plant capacity totaled 6.9 billion lb per year, but probably 1 billion lb of this was not running. How much shut-down capacity eventually will restart is difficult to estimate; not much will be tempted out under current financial conditions.

Later this year, startup decisions obviously will depend on PVC prices, including the differential between polymer

and monomer prices. At this time efforts are under way to raise PVC prices. Part of the reason is that monomer prices are being pushed up under pressure from price hikes in raw material chlorine. With such cost pressure from the rear and with a moderate demand increase in front, PVC producers seem likely to get some price hike during 1983.

If, however, resulting price increases of a few cents per lb are not enough to cause shut-down PVC production units to restart, actual operating capacity c. 8 billion lb will run at 71%. If production reaches 5.9 billion lb, the operating rate could rise to 74%. But, if all available capacity were included in the computation, operating rates would range from 64 to 86%.

At these levels of operation, PVC profitability is tenuous. Price increases could help, along with greater volume, but the question remains: Is there enough money in PVC to justify development work to broaden uses of this thermoplastic? Small producers probably cannot finance projects such as developing new compounds aimed at light and weather resistance—for example, in construction uses of siding and windows. These producers also can be at a cost disadvantage compared to larger producers integrated back to vinyl chloride and maybe chlorine. Hence shut-down capacity at these small producers is more likely to remain closed this year and possibly never restart.

Besides the expected demand improvement in the construction market, some upturn will come in the many other uses, such as consumer products, electrical items, and packaging. However, none will outdistance construction in percentage growth.

The export market, which last year took about 10% of production, is expected to fall in 1983. One big reason is higher prices, up from bargain levels in 1982. Offsetting PVC exports for integrated producers may be an increase in exports of the polymer precursors ethylene dichloride and vinyl chloride.

Without much help from exports, in 1983 PVC will ride largely on the fortunes of the U.S. construction business. Basics have improved a lot here, so benefits for PVC will take a while especially on the bottom line.

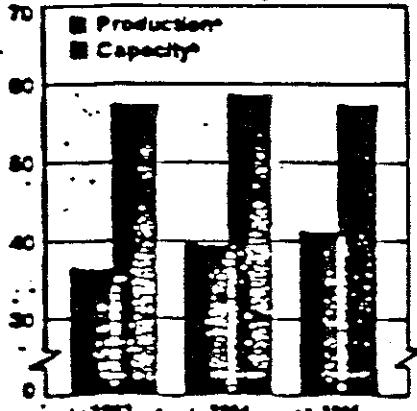
Key Chemicals

Sulfuric acid

- Production up modestly
- Capacity off again
- Prices slightly higher

PRODUCTION/CAPACITY

MILLIONS OF TONS, 100% H₂SO₄



MAJOR PRODUCERS

Allied, Du Pont, Monsanto, Olin,
Stauffer Chemicals

HOW MADE

Sulfur dioxide made by burning sulfur or recovered from smelting, oxidized, and reacted with water

MAJOR DERIVATIVES (U.S.)

None more than 5% of production

MAJOR END USES (U.S.)

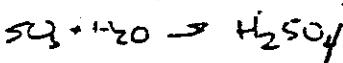
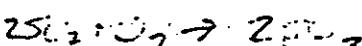
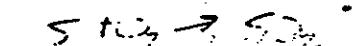
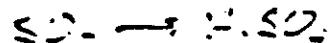
Fertilizer manufacturing 70%,
metals processing 10%

FOREIGN TRADE

Exports—could rise to 150,000 tons
in 1985. Imports—remaining around
800,000 tons in 1985

PRICES

List for smelter acid, \$20 to \$50
per ton; for virgin acid, \$35 to
\$85 per ton



Prospects for sulfuric acid in 1985 are for a further non decline in capacity, a small gain in production if fertilizer and industrial uses are up slightly, and the usual price pressure, minimizing profitability in spite of marketers' best efforts.

Output of sulfuric acid—the largest-volume chemical produced in the U.S.—is expected to increase modestly this year to 41.0 million tons (expressed as 100% product) following a substantial rise in 1984. This slowing of growth is to be expected in a year in which economic expansion has been slowing. But causes of the slowdown this year are more than simply the general level of the economy. They include slowing of exports of phosphate fertilizers, which consume 30% of the largest share of sulfuric acid.

Actual increase in 1985 sulfuric acid production could be less than 1 million tons of 100% H₂SO₄, or about 2% over 1984 production of 39.8 million tons. However, a small increase is normally expected for such a major-volume product after a large gain in the preceding year. The 1984 production gain was more than 3.4 million tons measured as 100% acid, a 9.3% increase over 1983 output.

Capacity to make sulfuric acid declined during 1984. Part of the net decline of about 500,000 tons came as a result of a shutdown of a major copper smelter, ending its production of by-product acid. Other smelter acid capacity is expected to be either completely shut down or drastically reduced during 1985. Some virgin acid production, going mostly to various industrial uses such as steelmaking, also has been shut down and more will be closed down this year. Offsetting the declines in smelter by-product acid and acid produced for industrial uses will be minor gains in capacity used to make phosphoric acid for fertilizers.

As 1985 began, estimated U.S. smelter capacity to make sulfuric acid from its various sources—including burning of sulfur, recovery from smelt-

er operations, and roasting pyrites—about 57.5 million tons of 100% acid. Most of this capacity will be available for production during 1985. Thus, a average capacity utilization rate for all plants will be a bit over 71%.

In addition to acid production from the various sources, some 350,000 tons will be added to the supply as net of imports over exports. The major source of imported sulfuric acid is Canada and much of this is smelter acid (because of pollution regulation sulfur dioxide can't be released to atmosphere, and so is converted to sulfuric acid). The major destination of U.S. exports of the acid is Mexico—mostly smelter acid eventually used in diverse small applications such as automobile batteries.

Imported sulfuric acid, most heavily sold from the upper Midwest to the northeastern U.S., keeps pressure on prices for merchant acid. Other price pressure comes from recovered sulfur, which is moved to markets as quickly as possible from desulfurization units at refineries and gas processing plants. The result is a wide range of prices for sulfuric acid.

In 1984, prices for elemental sulfur, especially Frasch sulfur, rose about 17% as three price increases for Frasch sulfur accounted for a total of \$25 per long ton, bringing the terminal price at Tampa, Fla., to \$147.50 per ton after discounts. Merchant acid prices also rose, but not by this much because of the large overcapacity. Large gain in phosphate fertilizer exports with accompanying higher prices allowed captive sulfuric acid producers to pass on part of their increased costs of sulfur during 1985.

Sulfuric acid's major captive uses—some 70% of production, in making phosphoric acid and other fertilizer materials, will not grow much in 1985. The other uses of sulfuric acid, such as in metals processing, petroleum refining, and manufacture of many different chemicals, also will grow slower this year.

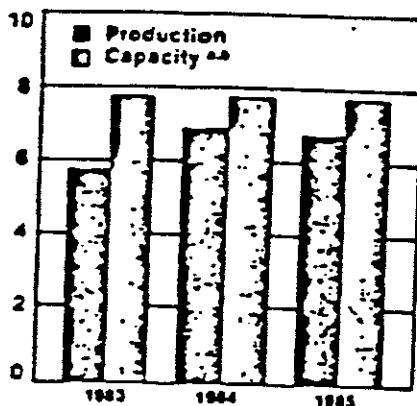
Key Chemicals

Urea

- Demand may rise
- Capacity on hold
- Prices under pressure

PRODUCTION/CAPACITY

Millions of tons



MAJOR PRODUCERS

CF Industries, Columbia Nitrogen, Farmland, Union Oil, Williams Cos. (Agrico)

HOW MADE

Reaction of ammonia and carbon dioxide under pressure.

MAJOR DERIVATIVES (U.S.)

Urea-formaldehyde resins 5%

MAJOR END USES (U.S.)

Fertilizers 80%, animal feeds 10%, adhesives and plastics 5%

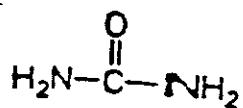
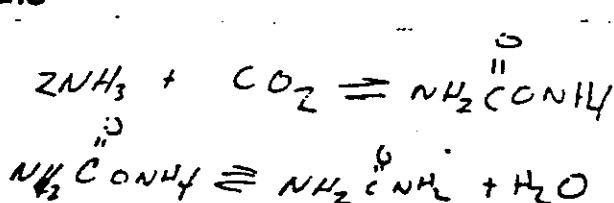
FOREIGN TRADE

Exports—may rise slightly to above 1.25 million tons in 1985.

Imports—rising rapidly to around 2.5 million tons in 1985.

PRICES

List prices about \$150 per ton on Gulf Coast



The outlook for production of urea in 1985 holds uncertainties similar to those for ammonia. These uncertainties could be extended as well to other high-nitrogen-content fertilizers that often compete with urea and ammonia.

At this time, however, urea production, inventories, and selling conditions are running about normal for this time of the year. Changes could come in all of these factors, caused by changes in demand, as a better idea of the success for fertilizer sales develops this spring along with the outlook for housing, which is the major nonagricultural end use for urea.

Based on early forecasts, urea producers will not have nearly so good a year in 1985 as they did last year; in 1984, production of urea reached an estimated 6.9 million tons, up some 19% from 1983. In 1985, production probably will be down slightly, less than 5%, to the 6.5 million to 6.7 million ton range.

Forecasts for 1985 urea production attempt to take into account U.S. consumption of urea and the net difference between imports and exports. The domestic consumption of urea will depend on many of the usual conditions, starting with weather, actual applied costs relative to similar costs of other fertilizer nitrogen sources, and planted acreage.

Weather, while not so absolute a factor as cost, can heavily influence urea use. If the spring weather provides generally dry and relatively easy-to-work fields, anhydrous ammonia will be used more heavily than urea. Urea-ammonium nitrate solutions rank in between.

The costs of applied fertilizer nitrogen to farmers and planters rank first, as might be expected, in most decisions of which material to use. Shifts in prices of ammonia and urea at plant sites bring even larger swings in prices that farmers pay. Therefore, substitution could become important, especially as farms get larger and purchases of fertilizer and the cost of its

application account for large amounts of money to the individual farmer.

Prices of nitrogen fertilizers are strongly affected by the trade situation. Imports of urea have risen rapidly and may exceed 2.5 million tons in 1985. As is the case with ammonia, imports of urea from countries with large, low-cost supplies of natural gas offer many benefits to the exporting countries. Generally, hard currency is obtained, and the gas is exported in a profitable form in contrast to little or no use as yet in the producing country. Plant operating problems have limited some countries' urea exports to the U.S. in the past, but now perhaps experience has reduced these problems.

Exports of urea from the U.S., especially to the Far East, continue at higher levels than were anticipated some years ago. However, they are well down from the peak of nearly 2 million tons set in 1980, with rough estimates for 1985 at about 1.25 million tons.

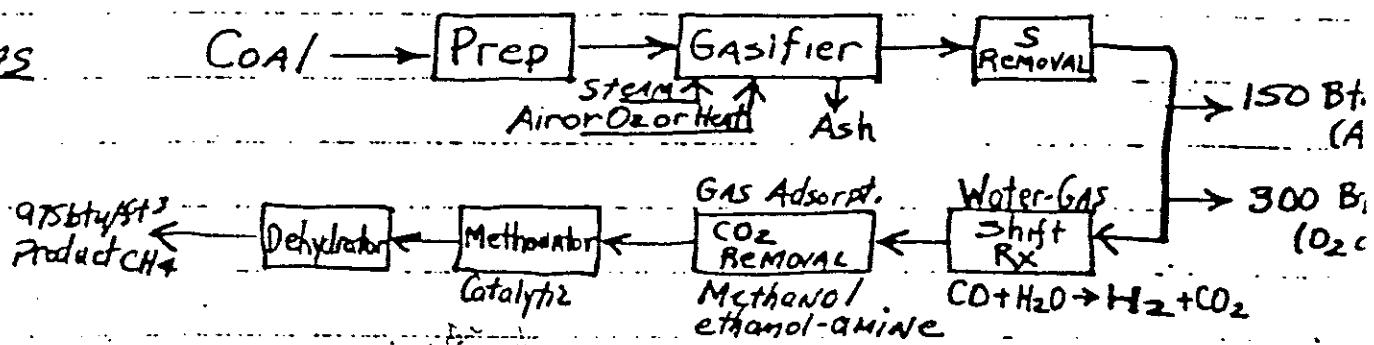
This net trade imbalance of about 1.25 million tons of urea in 1985 will keep plant operating rates lower than desirable for good profitability at about 85% of nameplate capacity. Some of the small plants either will continue their current shutdowns or will be shut down after the main fertilizer season is over. This will indeed be true for those that depend on an adjacent ammonia plant for a supply of carbon dioxide.

The feed and industrial markets for urea take about 15% of U.S. consumption. Feed use always faces strong price competition from other sources of nitrogen such as molasses, so probably will not grow much if at all. Industrial uses are dominated by urea-formaldehyde resins used as adhesives for particle board for interior construction, especially for housing—a use that may remain unchanged or decline slightly in 1985.

Urea, then, will have a slightly down year with production declining after a good recovery in 1984.

PRELIM - PROCESS

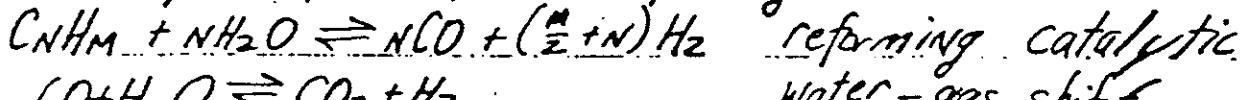
SYN GAS



CO₂ - Flue Gas, Fermentation, Lime Kiln. (Absorption) (Scrubbing)

(H₂)

Electrolysis of H₂O, Steam Reforming of Carbonaceous Materials



Purification - CO water-gas shift, scrubbing, catalytic Methanation, CO₂-H₂S Solvent Scrubbing, Absorption

→ Boiling = -193°C
→ Critical = -195.8°C
→ Triling = -195.8°C

Cryogenic

O₂/N₂ - liquefaction and rectification of air

2 columns, Lower Column - High Pressure (Condenser N₂)
Upper - Low Pressure (Reboiler - O₂)



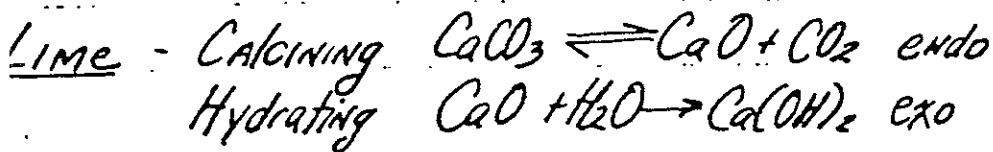
Acetylene - Pyrolytic Cracking of Natural Gas $2CH_4 \rightarrow C_2H_2 + 3H_2$

SO₂ - Burn S or by roasting of Metal Sulfides

CO - Cryogenic purification of Synthesis gas with H₂ as by product

N₂O - $NH_4NO_3 \xrightarrow{\text{exo}} N_2O + 2H_2O$, caustic purification for nitric acid
dichromate for nitric oxide

PRELIM - PROCESS



I₂ - electrolysis of fused chlorides or aqueous alkali metal chlorides

Bleach - $\text{Ca}(\text{OH})_2 + \text{Cl}_2 \rightarrow \text{CaOCl}_2 \cdot \text{H}_2\text{O}$ $\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaOCl} + \text{HCl}$
 50°C. countercurrent, pass Cl₂ through a rotating cylinder with inner lifting blades, shower the solid in gas path.

H₃PO₄ - $\text{Pt} + \text{O}_2 \xrightarrow{\text{H}_2\text{O}}$, phosphate + H₂SO₄ (major use of H₂SO₄)

NH₃ - $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightleftharpoons \text{NH}_3$, high P, Low T, [Fe catalyst], e

HNO₃ - $\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{NO}$
 Pt, Rh, Gauze catalyst

sulfur bearing ores, smelters, refineries
 $\text{H}_2\text{S} + \frac{3}{2}\text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O}$ exo
 $\text{SO}_2 + 2\text{H}_2\text{S} \xrightarrow{\text{Fe}_2\text{O}_3} 3\text{S} + 2\text{H}_2\text{O}$ exo

SO₂ - smelter gases, elemental
 $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$ exo [catalytic diazotization w/ V₂O₅]
 $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_3$ exo, $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$

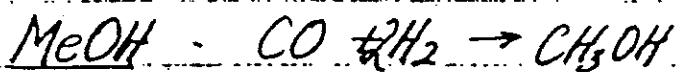
ICl - by product in chlorination of hydrocarbons, salt + H₂SO₄, combustion of H₂+Cl₂, 9NaCl + 2SO₂ + O₂ + H₂O → 2Na₂SO₄ + 9HCl

ethylene - thermal and catalytic cracking of hydrocarbons

OH - electrolysis of NaCl

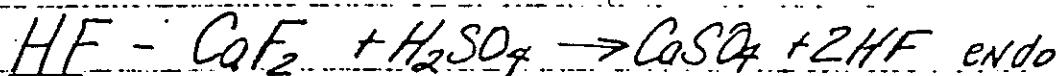
PRELIM - PROCESS

Formaldehyde = catalytic oxidation of MeOH



EtOH - hydration of ethylene

Acetic Acid - oxidation of acetaldehyde, fermentation



BELEM - Process

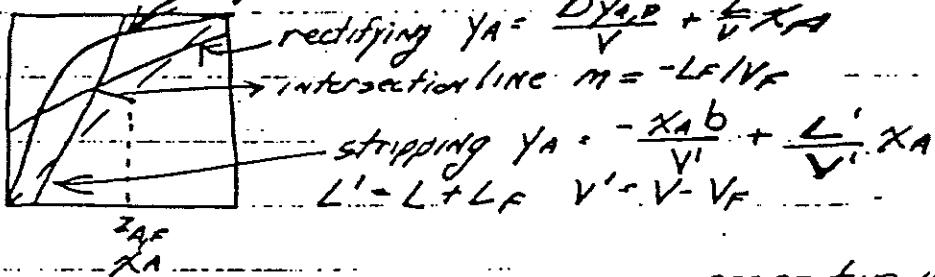
$$\text{separation factor } \alpha_{ij} = \frac{x_{ij}/x_{ji}}{x_{ie}/x_{je}}$$

best for reduction of separation agent and purity ^{staging} COUNTER > CROSS > COCURRENT

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

TACABE-Thiele Diagram

Constant Molal Overflow



limiting conditions MINIMUM reflux (∞ stages) with equilibrium
MINIMUM stages (∞ reflux) operating $y = x$

Multistage Batch Distillation

$$-\ln \frac{b'}{F'} = \int_{x_{A,F}}^{x_{A,D}} \frac{dx_A}{x_{A,D} - x_{A,b}}$$

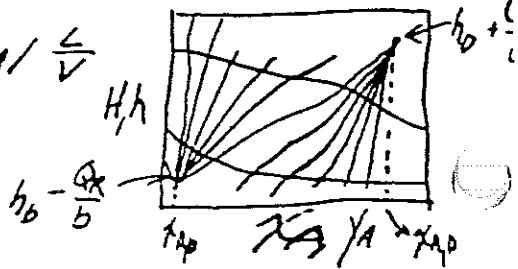
constant reflux ratio ($x_{A,D}$ varies)

constant $x_{A,b}$ (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 $\frac{L}{V}$

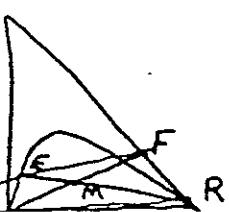


Liquid-Liquid Extraction

$$R-S = F-E$$

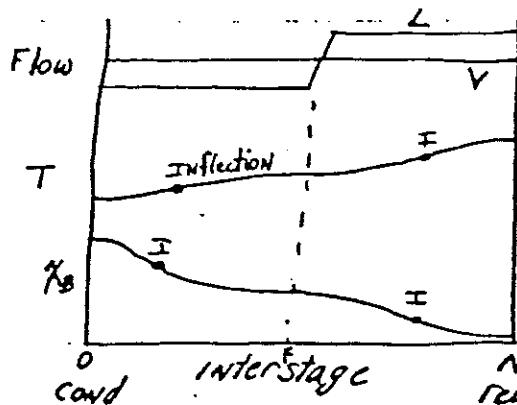
tie lines w/ equilibrium

use difference point for operating

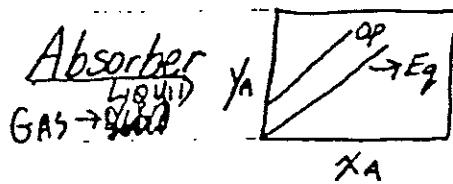


PRELIM - PROCESS

Patterns of change



saturated liquid feed
T profiles in a columns reflect co. while interstage fl. reflects enthalpy b.
refl (IN Absorber + S1 opposite)



(Henry's Law) dilute Minimum solvent by assuming heat effects absorbers - heat up satur strippers - cool down

Extractive Distillation - adding a solvent serves to volatilize one component over another, useful when close b.p. (low vola)

Azeotropic Distillation - similar but solvent forms azeotrope which is volatile.

Minimum Stage Requirement $N_{\text{MIN}} = \frac{\log [(X_A/x_b)_d / (X_A/x_b)_b]}{\log d_{AB}}$

Stages versus reflux correlation Gilliland

Stage Efficiency - Murphree - change equilibrium curve

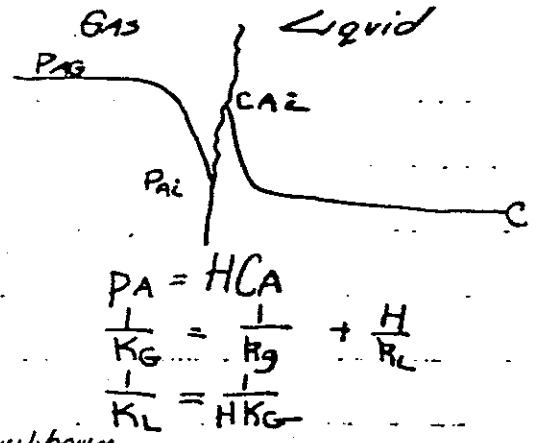
Extraction - selectivity, recoverability, Distribution coefficient, Capacity, solvent solubility, density, interfacial tension

Prelim - Process

Mass Transfer - molecular diffusion, convection, turbulent mixing

$$N_A = -CD_{AB} \nabla X_A + X_A (N_A + N_B)$$

$$\text{Chilton-Coburn: } j_0 = j_H = \frac{f}{2}$$



$$N_A = K_G (P_{AG} - P_{AE}) = K_L (C_{AE} - C_{AL})$$

$$= R_g (P_{AG} - P_{AL}) = R_L (C_{AE} - C_L)$$

$$P_A = HCA$$

$$\frac{1}{K_G} = \frac{1}{R_g} + \frac{H}{R_L}$$

$$\frac{1}{K_L} = \frac{1}{H_K}$$

Counter Current Contactors

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

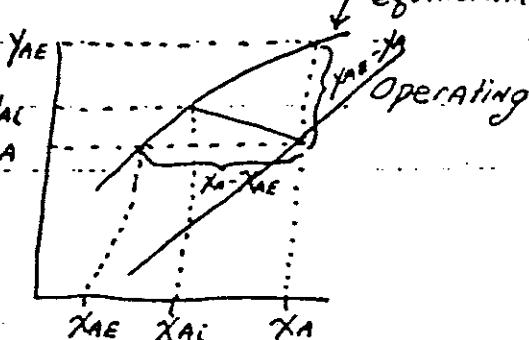
$$h = \frac{V}{A} \int_{y_{A,in}}^{y_{A,out}} \frac{dy_A}{K_G P_a (y_{AE} - y_A)}$$

GAS PHASE Control

$$(NTU)_{OG} = \int_{y_{A,in}}^{y_{A,out}} \frac{dy_A}{y_{AE} - y_A} = \frac{h A K_G P_a}{V}$$

$$(NTU)_{OL} = \int_{x_{A,in}}^{x_{A,out}} \frac{dx_A}{x_{AE} - x_A} = \frac{h K_p m_A A}{L}$$

Liquid Phase Control



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

$$(HTU)_{OL} = \frac{L}{h K_p m_A A}$$

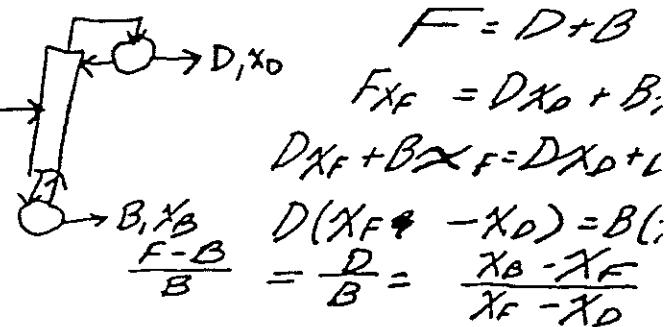
$$h = (HTU)_{OG} (NTU)_{OG}$$

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

PRELIM PROCESS

SEPARATE Similar MP & BP L-L Extraction, Azeotropic Distillation.
Cool Water at 150°F Cooling Tower (Wet Bulb Temp) (Adiabatic Satn.)
Remove H₂O (200 ppm) to 1 ppb in Ar⁷ Tw⁶² - 185.7°C (Cryogenic, Skypac Adsorb.)
Remove 1% phenol from H₂O - 150 Amyl acetate L-L extraction
Ethanol + H₂O

DISTILLATION Column CONTROL
monitor x_B, x_D change reflux ratio $r = \frac{V}{D}$, thus changing D/B.



COST ESTIMATION

Scaling $a = b = \left[\frac{C_A P(a)}{C_B P(b)} \right]^{0.6}$

- | Pipe fitting → nom id | Material ↓ |
|---|------------|
| 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 concentrated soln remains. Usually removal of H_2O from ag. soln
- typical Examples:
aqueous solns of: sugar, NaCl, NaOH, glycerol, glue, milk, + OJ.
Also for Seawater \rightarrow Drinking H_2O .

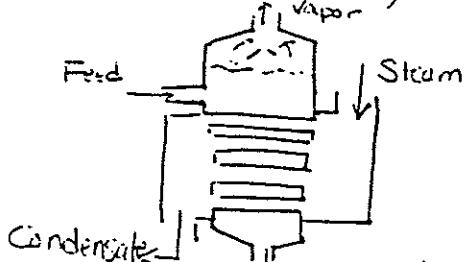
A. Processing Factors:

1. Concentration of liquid
- usually low, viscosity $\sim H_2O$, 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 Cryst may occur.
4. Temp Sensitive mat'l (ie biological)
5. Foaming or frothing (ie. Skim milk) - foam accompan. of vapor + entrainment losses occur.
6. Pressure + Temp (Remember: P + T_{BP} of soln + and as soln conc increases T_{BP} may rise.)
- Sometimes operate under 1 atm or vacuum
7. Keep in mind - Scale deposition + mat'l construction

B. Types of Evaporators:

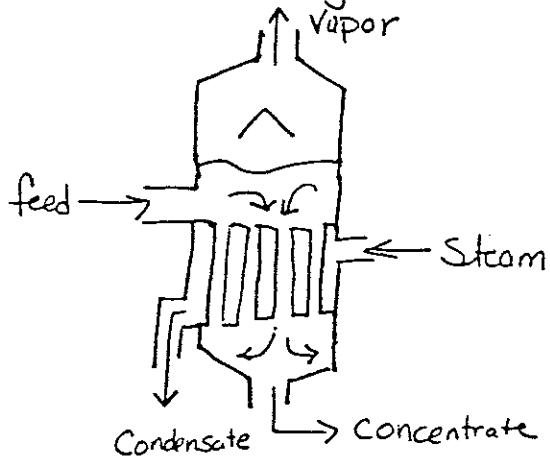
1. Open Kettle

2. Horizontal-tube, nat'l circulation evaporator



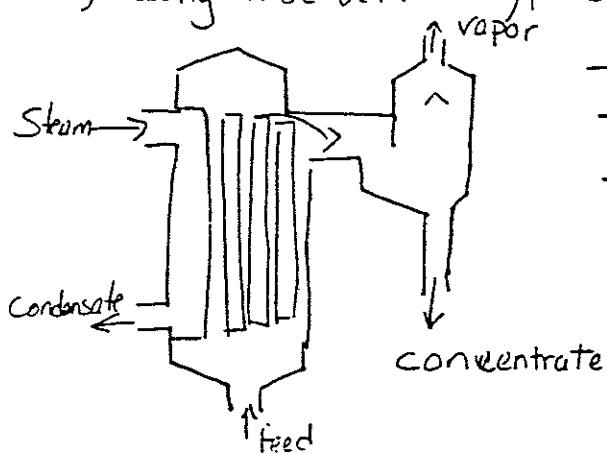
- Cheap
- nonviscous lig w/ high heat trans.
- no deposit scale
- continuous operation.

3.) Vertical type nat'l circulation evaporator.



- liquid inside tubes
- Steam condenses on outside
- for sugar, salt, caustic soda.

4) Long tube Vertical type evaporator.

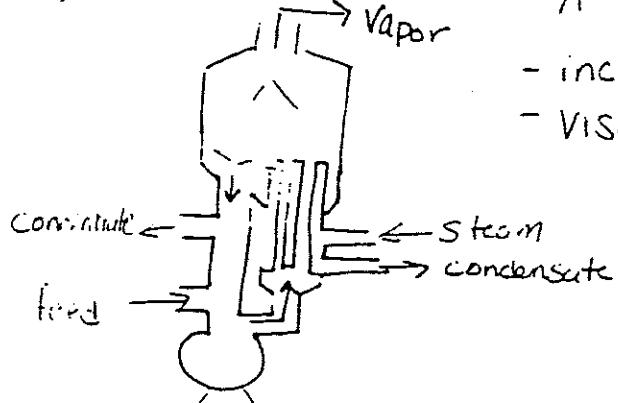


- high ~~low~~ liquid velocities
- liquid inside tubes
- Condensed milk

5) Falling Film type evaporator

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

6) Forced - Circulation type Evaporator



- increase liquid film heat transfer coeff
- viscous liquids

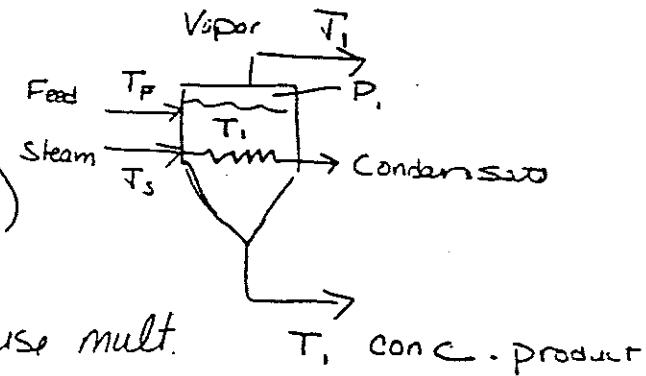
7. Agitated-film evaporator

- used to inc heat transfer on liquid side.
- for heat sensitive viscous mat'l's.
- rubber latex, gelatin, antibiotics, fruit juice.

Method of Operation

1) Single effect evaporators

- assumed, completely mixed
- use $g = UA \Delta T = UA(T_{steam} - T_i)$



- Small operators
- large capacity inefficient; better to use mult.

2) Forward Feed multiple effect evap.

$$P_1 > P_2 > P_3$$

fresh feed added to first effect; same direction w/ stream

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

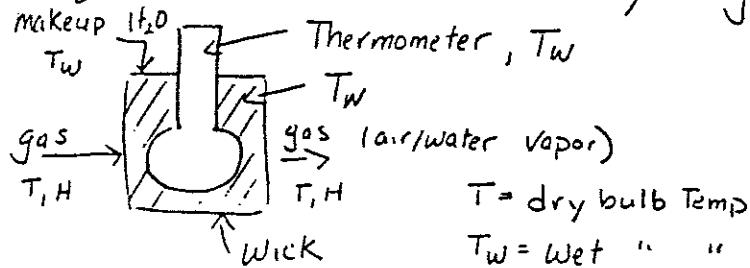
$$T_{BP1} > T_{BP2} > \dots$$

3) Backward feed multiple effect evaporators.

- feed enters into last effect (coldest)
- for cold fresh feed.
- less heat needed to heat smaller amt of lig to higher temps
- lig pumps required b/c flow from low to high P

Wet Bulb Temperature:

- S.S. nonequilibrium Temp reached when a small amt of water is ~~water~~ contacted under adiabatic conditions by a continuous stream of B/C Liquid is small, T + Humidity of gas are constant.



At S.S. water is evaporating to gas stream. The heat of evaporation is balanced with convective heat flowing from gas stream at T to the wick at lower temp T_w

$$\frac{H - H_w}{T - T_w} = \frac{-h/M_B K_y}{\lambda_w}$$

$$\frac{h}{M_B K_y} = \text{psychrometric ratio}$$

$$\sim .95 - 1.005$$

Note: Wet Bulb determination is often used to determine humidity of an air-H₂O vapor mixture.

λ_w = latent heat of vaporization
 H = Humidity @ T
 h = convective heat trans.
 ~~M_B = M.W. of air~~
 M_B = M.W. of air
 K_y = conductive h.t.c.

Types of Drying

I. Batch or Continuous

A. Tray Dryer

B. Vacuum Shelf Indirect Dryers - for expensive, temp sensitive, oxidizable materials

C. Continuous Tunnel Dryers - foods

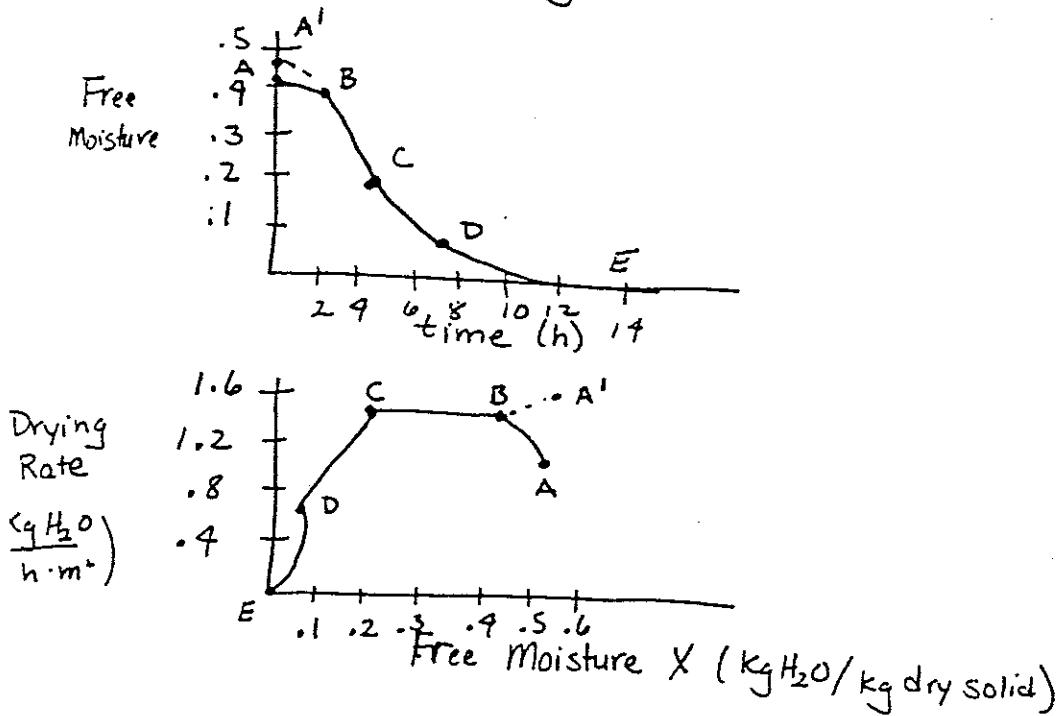
D. Rotary Dryers - granular solids

E. Drum Dryers - for slurries or pastes of solids in fine suspension (Potatoes \rightarrow potato)

F. Spray Dryers - for light & porous material (Dried Powdered Milk)

Typical Rate Drying Curves:

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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(l) into stagnant C(l). Example : NH₃ from Air by H₂O(l), SO₂ from flue gases . n alkaline salts
→ stripping or desorption - opposite of Absorption
i.e. - Steam stripping nonvolatile oil (steam contacts oil + small amounts of volatile components of oil leave w/ steam)
- humidification / Dehumidification - pure air + pure H₂O(l)
- II. Distillation - volatile vapor phase + liquid phase vaporizes.
Examples: Ethanol / H₂O(s):n (Ethanol rich vapor)
- Crude petroleum: fractions of gasoline, Kerosene + heating o. 1: arm distn
- III. Liquid-Liquid Extraction - 2 phases are liquid; solute/solutes are removed from one liquid phase to another.
Examples: Acetic Acid from H₂O by isopropyl ether
: antibiotics . n (g) fermentation solns by organic solnt.

- IV. Leaching** - fluid used to extract a solute from a solid
 (Extraction) Ex: Copper from solid ores by sulfuric acid.
 : Vegetable 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 b/w 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_{ox}) thereby 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:

<u>Method</u>	<u>Characteristic Property Difference</u>
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	Charge; Mass
Electrodialysis	

Common Organic Solvents for Aqueous Extraction

MIBK - Methyl Isobutyl Ketone

MEK - Methyl Ethyl Ketone

MEA - Mono ethanamine

DEG - Diethylene glycol

Choosing a Solvent :

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

Separations Prelim Review Notes

Topics:

- 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*

Weltz, 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 is suggested reviewing King and Peters and Timmerhaus Chapters 1, 2, 3, 9, and 10 ~~for the Process Design section of the Prelim.~~

Overview:Explains

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 separation 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.

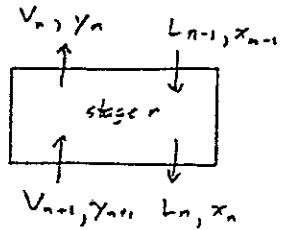
Intraphase separations don't involve the creation of a second phase, although a second phase may be present. Some rely on selective distribution of chemical species while others rely on differences in the response of chemical species to a driving force.

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:



$$\text{Mass Balances: } L_n + V_n = L_{n-1} + V_{n+1}$$

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

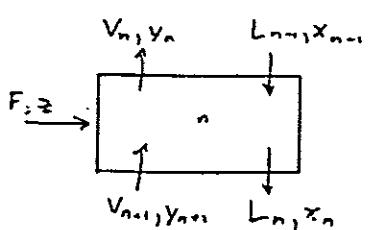
$$\text{For CMO: } V_n = V_{n+1}$$

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

$$\text{Equilibrium: } y_n = f(x_n)$$

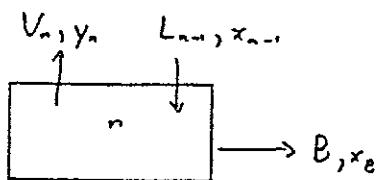
$L_{n-1}, V_{n+1}, x_{n-1}, y_{n+1}$ are specified.

Feed Stage:



As above, but now including:
Additional term in both mass balances. (F, Fz)
 F, z are specified.

Partial Reboiler:



$$\text{Mass Balances: } B + V_n = L_{n-1}$$

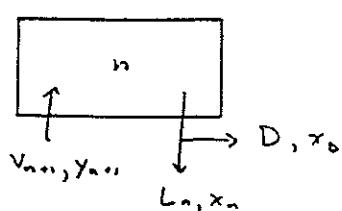
$$Bx_e + V_n y_n = L_{n-1} x_{n-1}$$

$$\text{Equilibrium: } y_n = f(x_e)$$

$$L_{n-1}, x_{n-1} \text{ are specified}$$

$$B \text{ or } x_e \text{ is specified}$$

Total Condenser:



$$\text{Mass Balances: } D + L_n = V_{n+1}$$

$$Dx_e + L_n x_n = V_{n+1} y_{n+1}$$

$$\text{Equilibrium: } \underline{x_{n+1}} = y_{n+1} = y_n = x_e$$

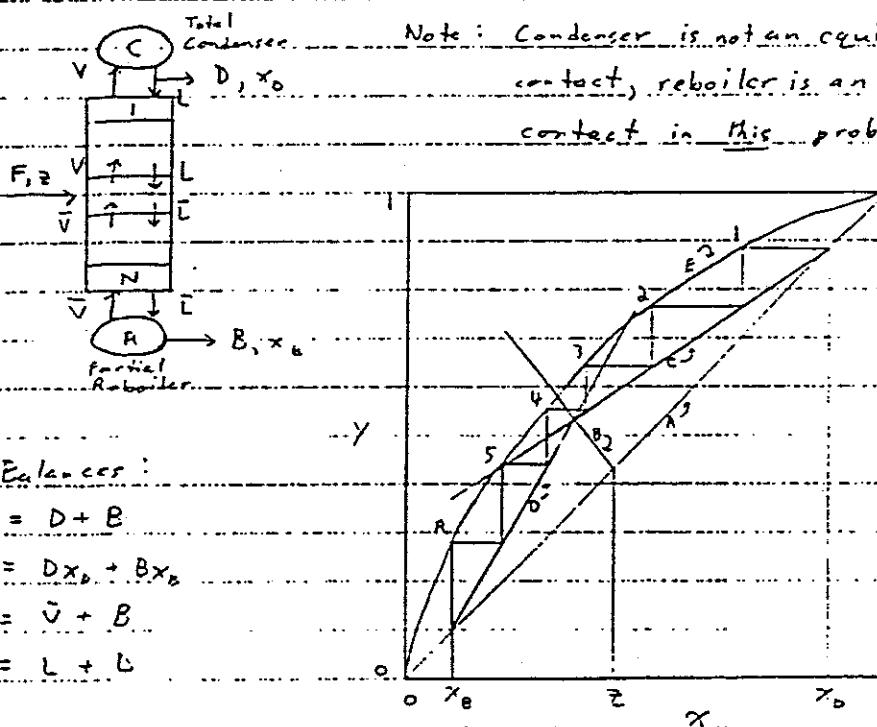
$$V_{n+1}, y_{n+1} \text{ are specified}$$

$$D \text{ or } L \text{ is specified}$$

Distillation:

Assumption:

— Constant Molar 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 generated 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

Mass Balances:

$$F = D + B$$

$$F_z = D x_0 + B x_B$$

$$\bar{V} = \bar{L} + B$$

$$V = L + B$$

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.

Lines:

A: $y=x$ line

B: Feed line

$$y = \frac{a}{q-1} x + \frac{1}{q-1} z$$

$$z = \bar{F}$$

C: Upper Operating line

$$y = \frac{L}{V} x + (1 - \frac{L}{V}) x_0$$

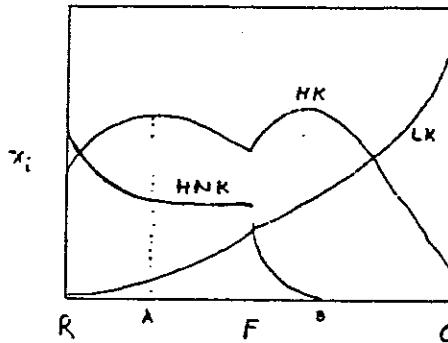
D: Lower Operating line

$$y = \frac{\bar{L}}{\bar{V}} x + (\frac{\bar{L}}{\bar{V}} - 1) x_0$$

E: Equilibrium line

from chart or an equation.

Distillation Composition Profiles: Temperature profile will reflect composition)

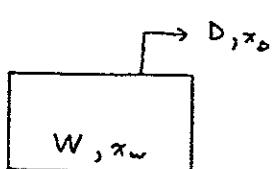


- R = reboiler LK = light key
- F = feed HK = heavy key
- C = condenser HNK = heavy non-key

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: $-x_d \frac{dW}{dt} = d(Wx_w) = W \frac{dx_w}{dt} + x_w \frac{dW}{dt}$
rearrange and integrate from initial to final:

$$\int_{w_0}^{w_f} \frac{dw}{w} = \int_{x_0}^{x_{w_f}} \frac{dx_w}{x_w - T_w} = \ln \frac{w_f}{w_0}$$

x_d is related to x_w by equilibrium — through a multistage tower above the reboiler.

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

Stripping and Absorption:

Definitions:

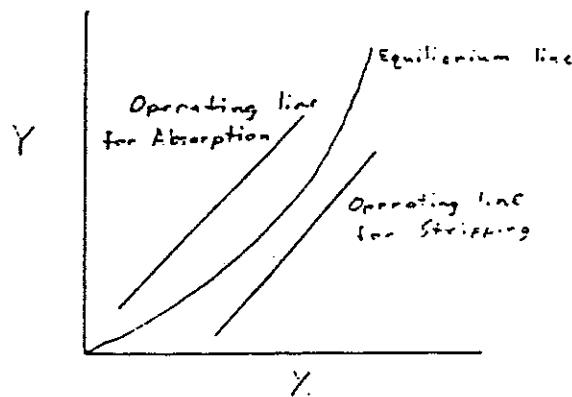
- Stripping is the separation of components from a liquid stream by vaporization into an insoluble gas stream.
- Absorption is the separation of components from a gas stream by absorbing into a nonvolatile liquid stream.
- The insoluble gas or nonvolatile liquid is the separating agent of the operation.

Constant Molar 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:

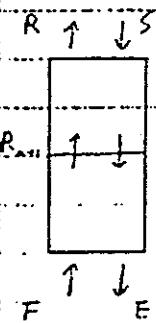
- Extraction is the separation of a solute from one liquid phase by transfer to a second liquid phase.
- Extraction may involve immiscible phases or partially miscible phases.

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 is constant.



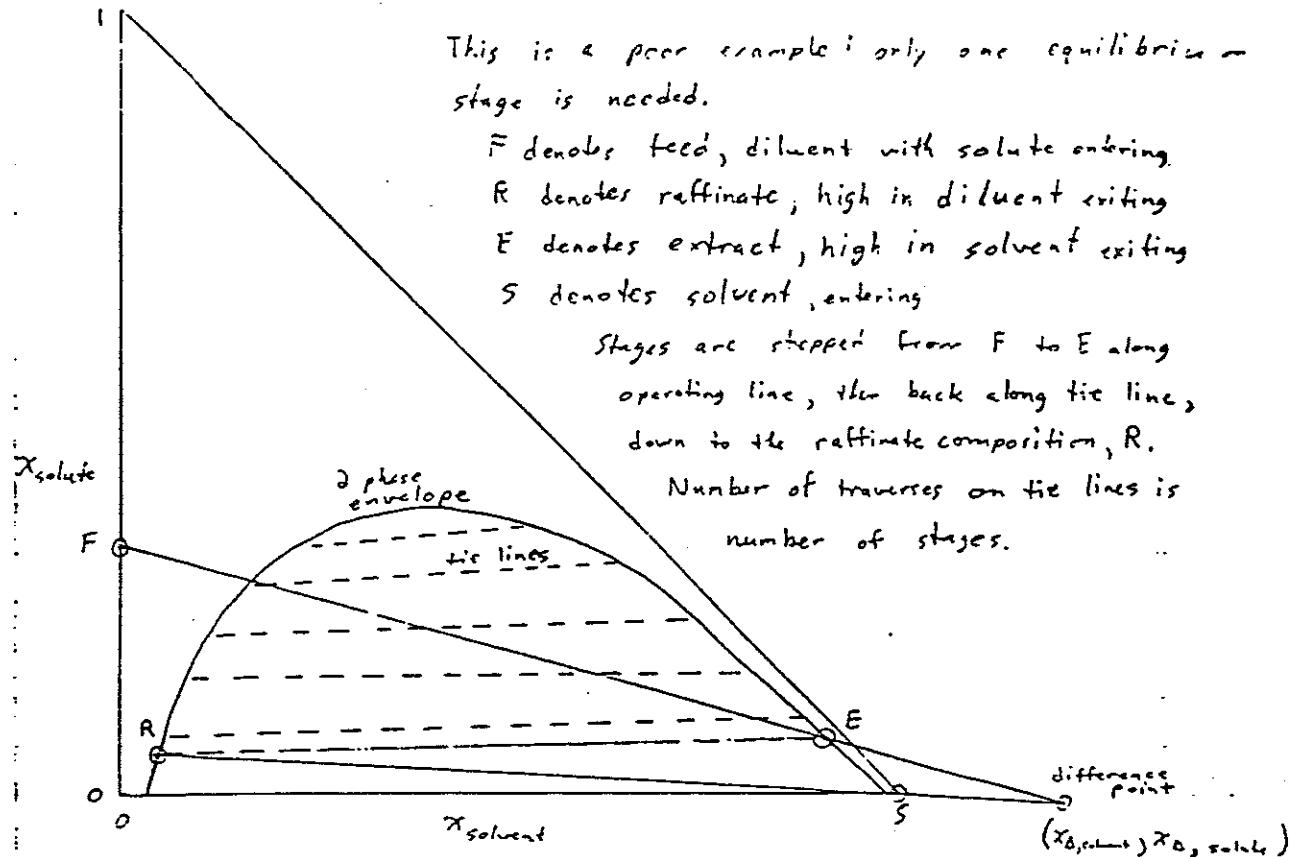
$$\text{Mass Balance: } F + S = E + R$$

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

$$\text{and } E_n x_n - R_{n+1} y_{n+1} = \Delta x_0 = \text{constant}$$

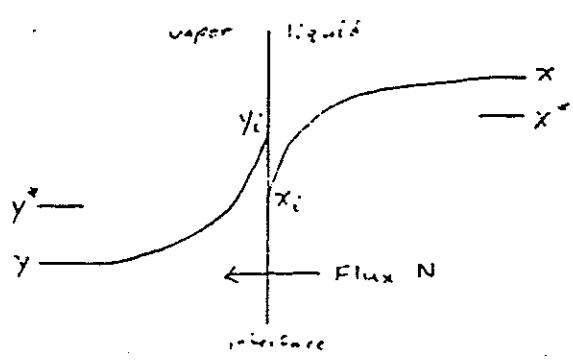
In a ternary system, x_0 for two components define a difference point. All operating lines in the column pass through this point.

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).



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, $h =$

$$h = \int_{y_i}^{y_{out}} \frac{d(y)}{(K_a S)(y - y^*)} = \int_{x_i}^{x_{out}} \frac{d(x)}{(K_x S)(x - x^*)}$$

with CMO:

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

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

$$HTU_G = \frac{G}{(K_a S)}, \quad HTU_L = \frac{L}{(K_x S)}$$

$$NTU_G = \int_{y_i}^{y_{out}} \frac{dy}{y^* - y}, \quad NTU_L = \int_{x_i}^{x_{out}} \frac{dx}{x^* - x}$$

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 (K_a) . 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 (K_a) .

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

12. Miscellaneous Distillation Information:

Some Distillation Design Correlations:

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

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

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

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

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

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

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

4) Kirk bridge equation - estimates optimum feed stage location:

$$\frac{N_R}{N} = \left[\left(\frac{z_{HK,F}}{z_{UK,F}} \right) \left(\frac{x_{LK,F}}{x_{UK,F}} \right)^2 \left(\frac{B}{D} \right) \right]^{0.306}$$

where N_R = # of stages in rectifying sectionand N_S = # of stages in stripping section

$$N = N_R + N_S$$

Crude Petroleum Composition:

	Volume %	BP (°C)	Products:
C ₁ - C ₄	1-2	< 30	Natural gas, LPG
C ₄ - C ₁₀	15-30	30-100	Petroleum Ether (C ₃ , C ₆), Ligroin (naphtha), straight-run gasoline
C ₁₀ - C ₁₅	5-20	100-300	Kerosene, heating oil
C ₁₅ - C ₂₅	10-40	300-400	Gas oil, diesel fuel, Lubricating oil waxes, asphalt
> C ₂₅	nonvolatile	> 400	Residual oil, paraffin wax, asphalt

Some Terms to Know:

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

Reflux : portion of (overhead) product returned to column

Reflux ratio : $R = \frac{L}{D}$, 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 bottom 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 separated.
- 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 molar percentages 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
- Easier service for corrosive materials
- Lower liquid holdup
- Lower pressure drops - good for vacuum operation
- Design of choice for diameters < 4 ft.

Feasibility Study

- 1) Raw Materials - availability / cost / quantity / quality.
- 2) Thermo/kinetics of Rns - equilibria, yields, ratios, opt conditions.
- 3) Facilities and Equipment - Now
- 4) Facilities and Equipment - to be purchased
- 5) Operation Cost and Investment Estimation.
- 6) Profits - probable and optimal - ROR.
- 7) Materials of Construction
- 8) Safety considerations - very important.
- 9) Markets (present + future, price range of product, size of market)
- 10) Competition
- 11) Properties of Products (value added?)
- 12) Sales and Servicing
- 13) Shipping Restrictions
- 14) Plant Location
- 15) Patent Situation.

Process Development

- occurs at pilot scale or semi-works basis.
- get design data - MIE B, TIP variations
Continuous vs. batch.

Preliminary Design Considerations.

- 1) Columns - # plates, diameter, materials, operating conditions.
- 2) Vessels - size (hold-up), packing or baffling, materials.
- 3) Reactors - catalyst? type / size, size, heat requirement, recycle and regeneration arrangements.
- 4) Heat Exchangers / Furnaces - heat duties, pressure drops, % vaporization.
- 5) Pumps / Compressors - type, power req'd, pressure drops, working pressures.
- 6) Instruments - function + controls, alarms.
- 7) Special Units - Mechanical separations, mixers, driers.
- 8) Utility Requirements.
- 9) Labor Requirements.
- 10) Estimate Economic Analysis.

Pumps - increase ME of fluid

- positive displacement - apply direct pressure to fluid < piston - reciprocating rollers - rotary.
 - centrifugal - use torque to generate rotation of impeller.
 - PD better for high μ fluids.
 - PD develop higher discharge pressures cheaper.
 - $Q \propto \text{PUMP speed}$.
- Control valve cannot be used - recycle part of fluid.

NPSH - Net Positive Suction Head.

- Within centrifugal pumps regions exist where $P < P_{inlet}$. If P_{inlet} is low $\min P < P_v$, so vapor forms on impellers \rightarrow cavitation.
- Cavitation - lowers pump head and efficiency
- leads to pitting of impeller blades.
- NPSH corresponds to diff betw P_{inlet} and P_v .

$$NPSH = \frac{P_{in} - P_v}{\rho} (144 \frac{\text{ft}}{\text{g}}); \quad NPSH [\text{ft}] ; \quad \rho [\text{lbm ft}^{-3}] ; \quad g_c = 32.2 \frac{\text{lbf s}^2}{\text{lbm ft}}$$

Pump Calculations

- Perform ME balance (Bernoulli Eqn) around system of interest.

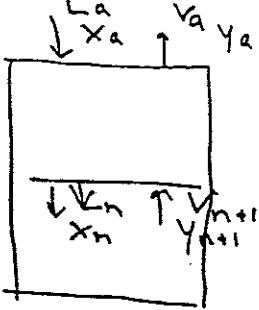
$$\frac{\alpha_2 V_2^2}{2} - \frac{\alpha_1 V_1^2}{2} + g \Delta h + \frac{\Delta P}{\rho} + \hat{W} + \hat{E}_v = 0 ; \quad \hat{E}_v = \frac{4D}{D} f \frac{V^2}{2} + \sum e_i \frac{V_i^2}{2}$$

Affinity Laws: $\frac{Q_2}{Q_1} = \frac{S_2}{S_1} ; \quad \frac{H_2}{H_1} = \frac{S_2^2}{S_1^2} ; \quad \frac{NPSH_2}{NPSH_1} = \frac{S_2^2}{S_1^2} ; \quad \frac{HP_2}{HP_1} = \frac{S_2^3}{S_1^3}$

Characteristic Curves.

For system of interest know: required head, power requirement, and NPSH. Then choose pump which meets these criteria from characteristic curve.

General McCabe Thiele Diagrams.



$$L_n x_n + V_{n+1} = V_n y_n + L_n x_n$$

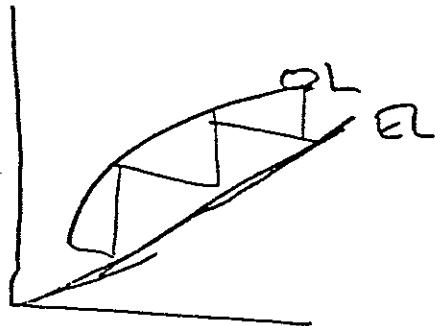
$$V_{n+1} = \frac{L_n}{V_{n+1}} x_n + \frac{V_n y_n - L_n x_n}{V_{n+1}}$$

$$L = L_a(1-x_a) \quad V = V_a(1-x_a)$$

$$V_{n+1} = \frac{\left(\frac{x_n}{1-x_n}\right)L + \left(\frac{y_n}{1-y_n}\right)V - \left(\frac{x_n}{1-x_n}\right)L}{V + \left(\frac{x_n}{1-x_n}\right)L + \left(\frac{y_n}{1-y_n}\right)V - \left(\frac{x_n}{1-x_n}\right)L}$$

Operating Line Expression.

Absorber



Stripping / Extraction
EL above OL.

Kremser Eqn < both EL / OL straight >

$$\begin{aligned} Y_n &= \frac{L}{V} Y_n + \frac{V y_A - L x_A}{V} \\ &= \frac{L}{V_m} Y_n + \frac{V y_A - L x_A}{V} ; \quad \frac{L}{V_m} = A \end{aligned}$$

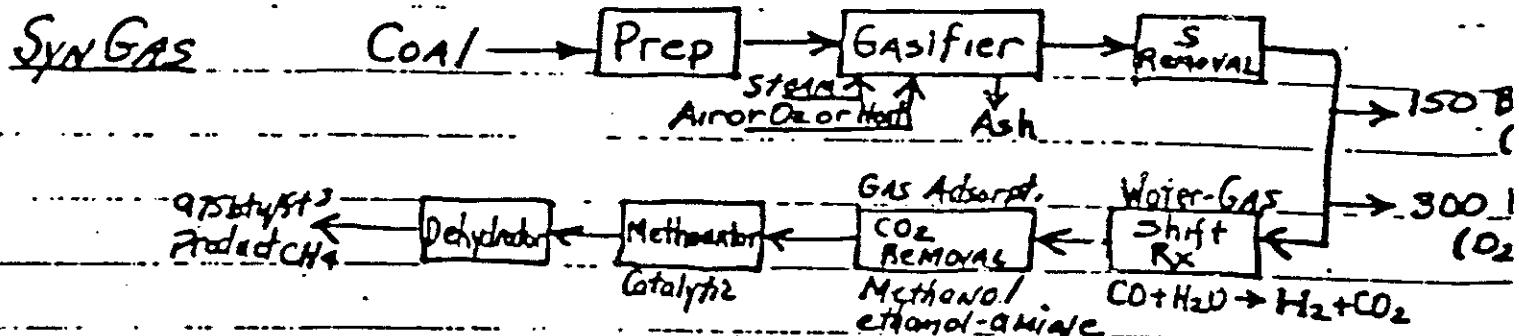
$$\begin{aligned} Y_{n+1} &= A Y_n + y_A - A x_A \\ &= A Y_n + y_A - A y_A^* \quad \Rightarrow \quad A^N = \frac{Y_B - Y_B^*}{Y_A - Y_A^*} \Rightarrow N = \frac{\ln \left(\frac{Y_B - Y_B^*}{Y_A - Y_A^*} \right)}{\ln A} \end{aligned}$$

L phase Equations

$$N = \frac{\ln \left(\frac{x_n - x_A^*}{x_B - x_B^*} \right)}{\ln S}$$

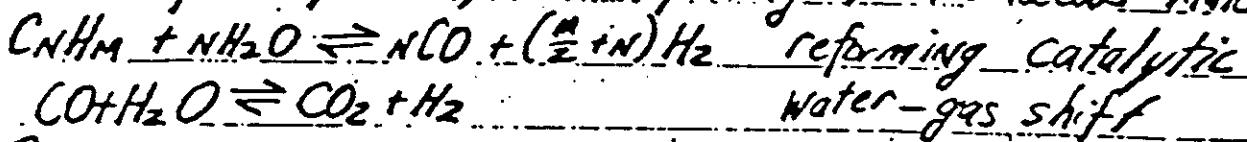
$$S = 1/A$$

PURIFICATION - PROCESS



CO₂ - Flue Gas, Fermentation, Lime-kiln (Absorption) (Scrubbing)

H₂ - Electrolysis of H₂O, Steam Reforming of Carbonaceous Materials



Purification - CO water-gas shift, scrubbing, catalytic methanation, CO₂-H₂S Solvent Scrubbing, Absorption, Cryogenic

O₂/N₂ - liquefaction and rectification of air

2 columns, Lower Column - High Pressure (Condenser N₂)
Upper - Low Pressure (Reboiler - O₂)

Acetylene - Pyrolytic Cracking of Natural Gas $2\text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + 3\text{H}_2$

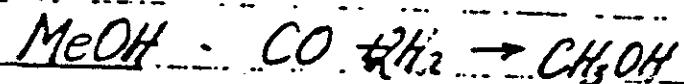
SO₂ - Burn S or by roasting of Metal Sulfides

CO - Cryogenic purification of Synthesis gas with H₂ as by product

N₂O - NH₄NO₃ → N₂O + 2H₂O^{exo}, caustic purification for Nitric Acid dichromate for Nitric oxide

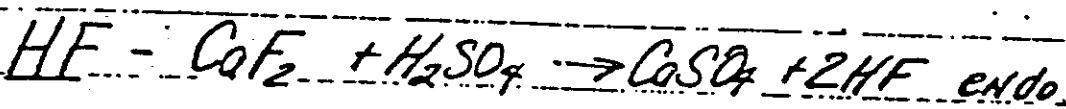
PRELIM - PROCESS

Formaldehyde = H_2CO catalytic oxidation of MeOH



EtOH = hydration of ethylene

Acetic Acid = oxidation of acetaldehyde, fermentation



Mass Transfer

driving force is a concentration or activity difference

Distillation

- separate by vaporization (volatility difference)

- Examples

Alcohols and water

Liquid air \Rightarrow N₂, O₂, Ar

Crude \Rightarrow gas, kerosene, fuel oil

Gas Absorption

soluble vapor absorbed by a liquid from an inert gas

example: washing of ammonia from ammonia/air by water

Desorption or Stripping

solute is transferred from the solvent liquid to the gas phase

Humidification

pure liquid removed from an inert by condensation

example: water vapor from air on a cold surface

Drying

liquid (H₂O) is separated by a hot, dry gas \Rightarrow coupled to humidification of gas

Liquid Extraction

- 2 component mixture treated with solvent that preferentially dissolves one

Leaching (Solid Extraction)

- soluble material dissolved from an inert solid with a liquid solvent

Crystallization

- obtain good quality crystals of good purity by leaving impurities in melt or solution

Equilibrium Stage Operation Basics

- Mass balances - Ben p. 25

Enthalpy balances: $L_n H_{Ln} + V_n H_{Vn} = L_{n-1} H_{Ln-1} + V_{n-1} H_{Vn-1}$

Operating and Equilibrium Lines

written from mass balances: $y = \frac{Lx}{V} + \frac{Dx_0}{V}$

- if L, V are const, we have constant molal overflow and the operating line is straight

- equilibrium lines come from data

- to transfer a component from $L \rightarrow V$, the op line must be below the eq line

$$\Delta F = Y_e - Y_{n+1}$$

- to transfer from the $V \rightarrow L$ (as in gas absorption), the op line must be above the eq line

$$\Delta F = Y_{n+1} - Y_e$$

McCabe-Thiele Method

- may be used to determine the number of ideal stages in any cascade (gas absorption, rectification, leaching, or extraction)

Flash Distillation

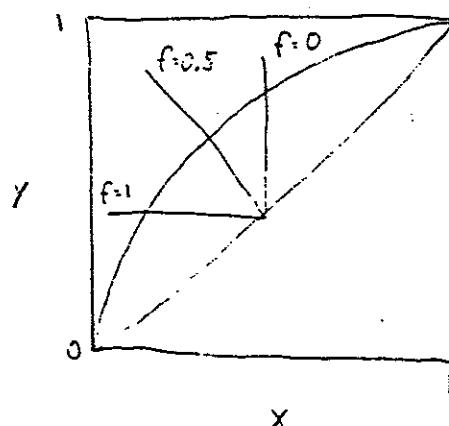
- single stage partial vaporization without reflux

- Material balance: $X_F = f y_0 + (1-f) X_B$ f = mol fraction of feed vaporized
for feed line $y = \frac{X_F}{f} - \frac{(1-f)x}{f}$

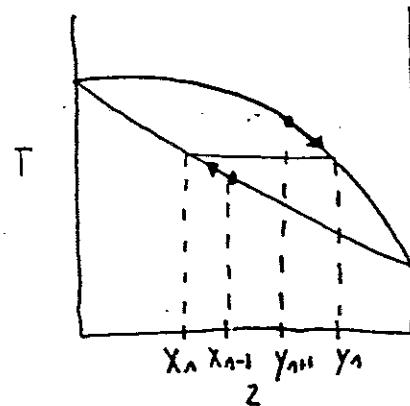
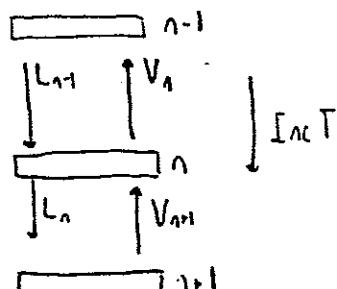
- intersection w/ equilibrium line occurs at $X = X_B$ and $y = y_0$

- use to recover water from seawater by simply reducing pressure into unit (flash vaporize)

- use to separate components that boil at widely different temperatures



Savy's rectifying column showing Distillation



Column Balances

$$L = L + D$$

$$Z_F = L X_0 + D X_B$$

$$V = L + D$$

$$\bar{L} = \bar{V} + D$$

Operating Lines

$$\text{Rectifying: } y = \frac{Lx}{V} + \frac{Dx_0}{V}$$

$$\text{Stripping: } y = \frac{\bar{L}x}{\bar{V}} - \frac{Dx_B}{\bar{V}}$$

$$\text{Feed Line: } q = \text{liquid fraction} = 1-f$$

$$V_y = Lx + D x_0$$

$$\bar{V}_y = \bar{L}x - D x_B$$

$$\text{Subtracting, } y(V - \bar{V}) = x(L - \bar{L}) + D x_0 + D x_B$$

$$D x_0 + D x_B = F Z_F$$

$$y(V - \bar{V}) = x(L - \bar{L}) + F Z_F$$

$$\bar{L} = L + qF \quad V = \bar{V} + (1-q)F$$

$$y(1-q)F = x(-qF) + F Z_F$$

$$y = \frac{-qx}{1-q} + \frac{Z_F}{1-q}$$

q

$$q = \text{liquid fraction} = 1-f$$

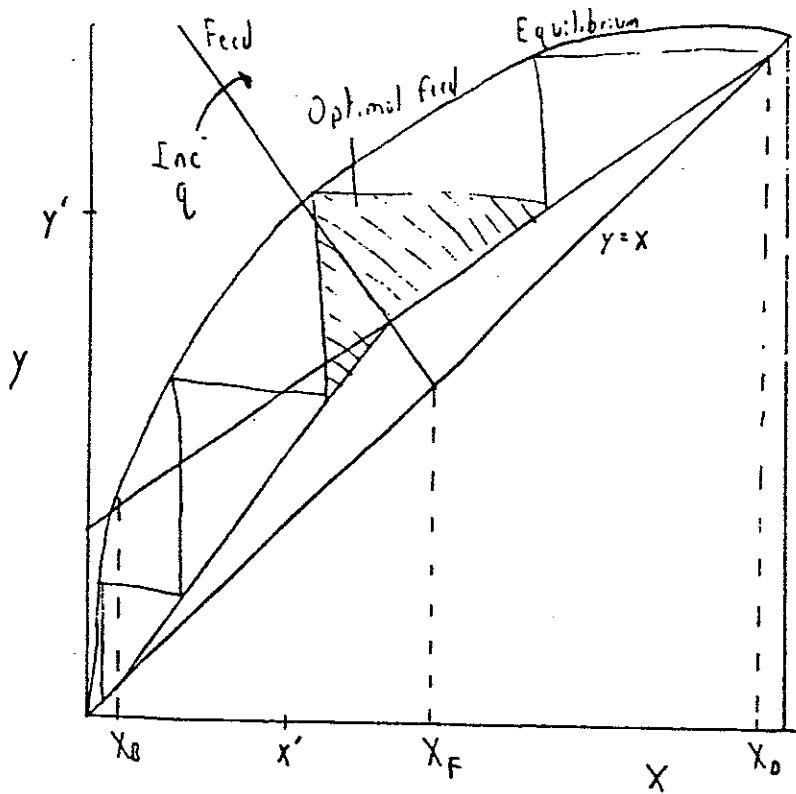
for subcooled liquid,

$$q = 1 + \frac{c_{PL}(T_{BP} - T_F)}{\Delta H_{VAP}}$$

for superheated vapor,

$$q = -\frac{c_{PV}(T_{DP} - T_F)}{\Delta H_{VAP}}$$

M McCabe-Thiele Diagram



Feed Line

$$y = \frac{Z_F}{1-q} - \frac{qX}{1-q}$$

Rectifying Op Line

$$y = \frac{Lx}{V} + \frac{DX_0}{V}$$

Stripping Op Line

$$y = \frac{\bar{L}x}{\bar{V}} - \frac{\bar{D}X_B}{\bar{V}}$$

Equilibrium

$$\text{data or } y = k_x x = \frac{\alpha x}{1+(\alpha-1)x}$$

$$\alpha = p_1 s / p_2 s$$

How does a Murphree efficiency change the diagram?

Draw in an effective equilibrium curve.

2. How do you find the minimum number of ideal stages?

Use the $y=x$ line as your operating line.

3. How do you find $R_{min}(L/D_{min})$?

Find x', y' where the feed line intersects the equilibrium line.

$$R_{min} = \frac{x_0 - y'}{y' - x'}$$

4. $q \Rightarrow$ for a subcooled liquid that condenses 0.15 mol vapor at the feed plate, $q = \text{mol feed}$

5. Partial condenser and partial reboiler count as a stage.

6. Separation factor: $\alpha = \frac{p_1 s}{p_2 s}$

Positive Suction Head (NPSH)

head from Bernoulli: ϵ_{gh} must be greater than the NPSH to avoid cavitation at the pump

$$NPSH = \frac{g_c}{g} \left(\frac{P_{SURF} - P_{VAPOR}}{\rho} - \text{friction in line} \right) - (\text{pump height above reservoir})$$

$$NPSH = \frac{g_c}{g} \left(\frac{P_{SURF} - P_{ATM}}{\rho} - F \right) - L$$

Cavitation

If the suction pressure is only slightly greater than the vapor pressure, liquid may vaporize and cause severe erosion

If the suction pressure is less than the vapor pressure, there will be vaporization in the line and no liquid can be drawn to the pump

Positive Displacement Pumps

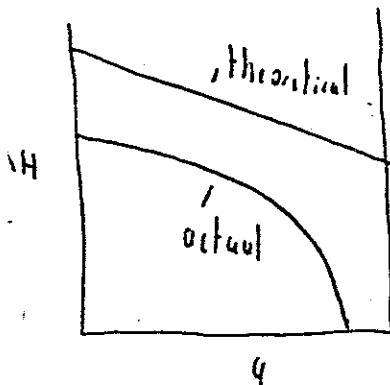
Volume of liquid is trapped in a chamber and emptied at a higher pressure

1. Reciprocating - Chamber is a stationary cylinder with a piston
2. Rotary - Chamber moves from inlet to discharge

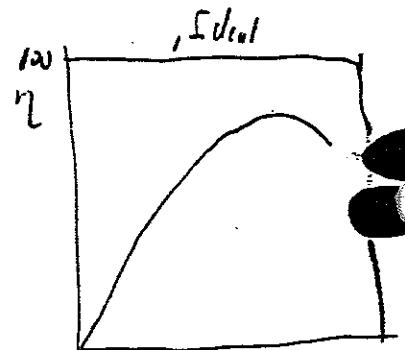
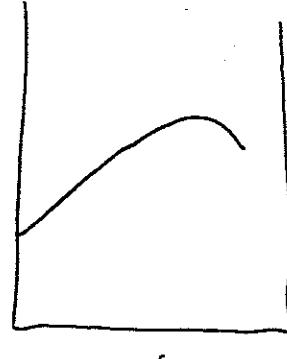
Centrifugal Pumps

Mechanical energy is increased by centrifugal action (such as by a high speed rotary impeller)

Characteristic Curves



Difference due to circulation Power



How do you construct a T-x-y diagram?

1. Bubble curve

Ideal $\Rightarrow y_i P = X_i P_i^{\text{SAT}} \quad P_i^{\text{SAT}} = f(T)$

Essentially all liquid, so $X_i = Z_i$

At $T_B, \sum y_i = 1$

- Solve for T where $\sum \frac{X_i P_i^{\text{SAT}}}{P} = 1$

After T is found, we can find y_i .

2. Dew curve

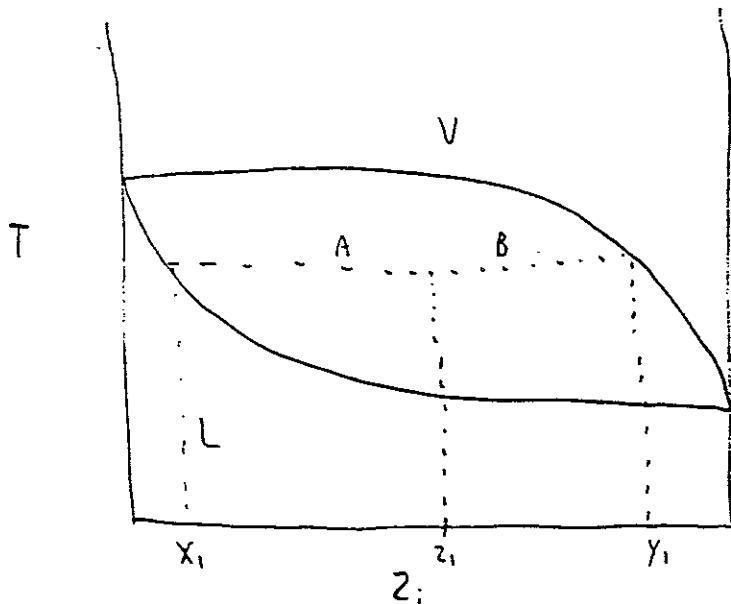
Ideal $\Rightarrow y_i P = X_i P_i^{\text{SAT}}$

Essentially all vapor $\Rightarrow y_i = Z_i$

At $T_D, \sum X_i = 1$

Find T where $\sum \frac{y_i P}{P_{\text{SAT}}} = 1$

After T is found, can find X_i .



Remember tie lines

Vapor: comp = y_i
vapor fraction = $\frac{A}{A+B}$

Liquid: comp = x_i
liquid fraction = $\frac{B}{A+B}$

Separation Heuristics - Order of Importance.

- 1 Remove corrosive/hazardous components
- 2 Avoid T/P extremes
- 3 Favor Ordinary Distillation, if $\alpha < 1.05 \rightarrow$ MSA.
- 4 Perform easiest split first. - decreasing order of α_{AB}
- 5 If α_{AB} const - decreasing order of mol fractions.
- 6 If neither α_{AB} , x very late 1 by 1 m overhead product.
- 7 When blended products favored - produce directly w/ min blending
- 8 Take valuable components off top as bottom accumulates.

- 1 - H_2SO_4
- 2 - O_2
- 3 - N_2
- 4 - Ethylene
5. NH_3
- 6 Line, C_6O
- 7 $NaOH$
- 8 Cl_2
- 9 H_3PO_4
10. Propylene.