EngrD 2190 – Lecture 4

Concept: Process Design – Devising Chemical Reaction Cycles

Context: Producing CH_4 from CO_2 and thermal energy.
(exercise 2.30 – solution is posted)

Defining Questions:

Why 2 reaction steps for N_2H_4 synthesis by green chemistry?

$$2NH_3 + H_2O_2 \rightarrow N_2H_4 + 2H_2O \quad \text{(Lecture 2)}$$

Why 9 steps between landings in Olin Hall stairwalls?

Read Chapter 2, pp. 42-48.

Homework 1

Homework 1 due Friday 9/5:

Process Analysis: **2.7.**

Process Design: **2.24 and 2.25(part A only)**.

Read process design guidelines on p. 57.

See table of physical data on pp. 86-7.

For 2.24 and 2.25(A), you may assume perfect gas-solid separations; no solids in the gas stream and no gas in the solids stream.

Work in teams. Submit one solution set per team.

Submit *after* lecture or deliver to EngrD 2190 mailbox in a beige cabinet in the hallway across from 111 Olin Hall. ***Not to my mailbox.***

Homework is your chief means of assessing your command of the material.

Do not copy from other sources, such as graded homework and posted solutions from previous years.

Do not use past solutions to check your answers. Process analysis is part of process design. You should be developing methods of assessing your designs.

Homework 1

Homework 1 due Friday 9/5:

Process Analysis: **2.7.**

Process Design: **2.24 and 2.25(part A only).**

For process design exercises 2.24 and 2.25(A) append lists of ‘take-aways.’ ***What lessons did you learn from working these exercises?***

See lists of ‘take-aways’ appended to the TA powerpoint solutions presented in Calculation Sessions now posted at the EngrD 2190 website.

Professional Headshots - THURSDAY

Essential for your Handshake and LinkedIn Profiles.

Thursday, September 4, 5 - 7 p.m. in 128 & 245 Olin.

Schedule a sitting on this Google spreadsheet:

https://docs.google.com/spreadsheets/d/1rGtz49yTLEjjKZLiVfsTOh4YFqiArr_yjmFVIwr713Y/edit?usp=sharing

Hydrazine Synthesis (exercise 2.27, lecture 2)

Overall Reaction:

$$2NH_3 + H_2O_2 \rightarrow N_2H_4 + 2H_2O$$

Actual Process - Sequence of 2 Reactions:

$$H_2O_2 + 2CH_3C(O)CH_3 + 2NH_3 \rightarrow (CH_3)_2C{=}N\text{-}N{=}C(CH_3)_2 + 4H_2O$$

$$(CH_3)_2C{=}N\text{-}N{=}C(CH_3)_2 + 2H_2O \rightarrow N_2H_4 + 2CH_3C(O)CH_3$$

Hydrazine Synthesis (exercise 2.26)

Overall Reaction:

$$2NH_3 + Cl_2 + 2NaOH \rightarrow N_2H_4 + 2NaCl + 2H_2O$$

Actual Process - Sequence of 3 Reactions:

NaClO synthesis:

$$2NaOH + Cl_2 \rightarrow NaClO + NaCl + H_2O$$

Conversion of acetone to acetazine:

$$NaClO + 2CH_3C(O)CH_3 + 2NH_3 \rightarrow (CH_3)_2C{=}N\text{-}N{=}C(CH_3)_2 + NaCl + 3H_2O$$

Hydrolysis of acetazine:

$$(CH_3)_2C{=}N\text{-}N{=}C(CH_3)_2 + 2H_2O \rightarrow N_2H4 + 2CH_3C(O)CH_3$$

Hydrogen from Water and Thermal Energy

section 2.4.4 of Duncan & Reimer, pp. 36-39

Overall Reaction:

$$2H_2O \rightarrow 2H_2 + O_2$$

The Sulfur-Iodine cycle:

$$2H_2O + SO_2 + I_2 \rightarrow 2HI + H_2SO_4$$

$$2HI \rightarrow H_2 + I_2$$

$$H_2SO_4 \rightarrow H_2O + SO_3$$

$$SO_3 \rightarrow SO_2 + \tfrac{1}{2}O_2$$

Soda Ash Synthesis – The Solvay Process (exercise 2.16)

Overall Reaction:

$$CaCO_3 + 2NaCl \rightarrow Na_2CO_3 + CaCl_2$$

Actual Process - A Sequence of 5 Reactions:

Decomposition (1000°C):

$$CaCO_3 \rightarrow CaO + CO_2$$

Slaking:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Chlorination:

$$Ca(OH)_2 + 2NH_4Cl \rightarrow 2NH_4OH + CaCl_2$$

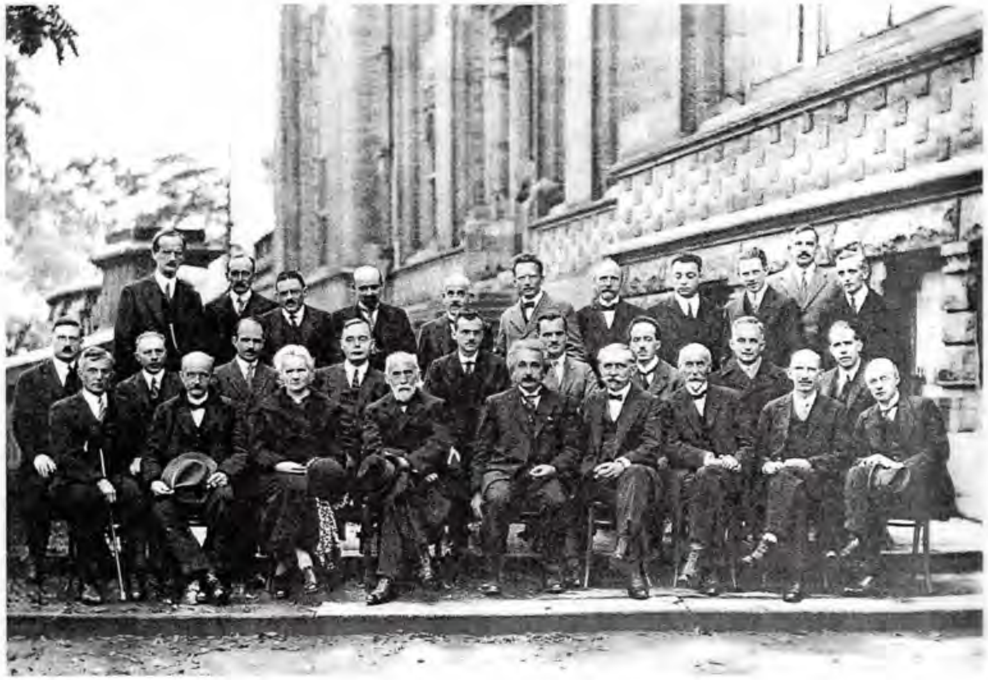
Carbonation:

$$NH_4OH + CO_2 + NaCl \rightarrow NH_4Cl + NaHCO_3$$

Calcination (300°C):

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

The 1927 Solvay Conference



In October 1927 leading scientists met at the Fifth International Congress on Physics and discussed quantum theory. These participants eventually accounted for 18 Nobel Prizes.

Front Row: Irving Langmuir, Max Planck, Marie Curie, Hendrick Lorentz, Albert Einstein, Paul Langevin, Charles Guye, Charles Wilson, Owen Richardson
Second Row: Peter Debye (Cornell Chemistry, after 1946), Martin Knudsen, William Bragg, Hendrik Kramers, Paul Dirac, Arthur Compton, Louis de Broglie, Max Born, Niels Bohr
Third Row: Auguste Piccard, E. Henriot, Paul Ehrenfest, Edouard Herzen, Théophile de Donder, Erwin Schrödinger, J. E. Verschaffelt, Wolfgang Pauli, Werner Heisenberg, Ralph Fowler, Leon Brillouin.

The conference was hosted by the Solvay Institute in Brussels, Belgium, which continues to provide a forum for the development of fundamental science. The Solvay Institute was founded by Ernest Solvay (1838-1922) who devised the Solvay process for producing soda ash (sodium carbonate, Na_2CO_3),a key reactant in the production of glass and paper. (See Duncan and Reimer, *Chemical Engineering Design and Analysis*, p. 44). However, Solvay made his fortune through a process he developed to produce ammonia. Solvay is generally described as a "scientist, philanthropist and industrialist" although his work would best be categorized as chemical engineering.

The top 25 thermochemical cycles for nuclear energy

NH2
Nuclear Hydrogen

Chp 2

Exercise 2.20

Cycle	Name	T/E*	T °C	Reaction	F†
1	Westinghouse [12]	T	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) +$ [illegible]	1/
		E	77	$SO_2(g) + 2H_2O(a) \rightarrow H_2$ [illegible]	
2	Ispra Mark 13 [13]	T	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) +$ [illegible]	
		E	77	$2HBr(a) \rightarrow Br_2(a) + H_2(g$ [illegible]	
		T	77	$Br_2(l) + SO_2(g) + 2H_2O(l) \rightarrow 2HBr(g) + H_2SO_4(a)$	1
3	UT-3 Univ. of Tokyo [8]	T	600	$2Br_2(g) + 2CaO \rightarrow 2CaBr_2 + O_2(g)$	1/
		T	600	$3FeBr_2 + 4H_2O \rightarrow Fe_3O_4 + 6HBr + H_2(g)$	1
		T	750	$CaBr_2 + H_2O \rightarrow CaO + 2HBr$	1
		T	300	$Fe_3O_4 + 8HBr \rightarrow Br_2 + 3FeBr_2 + 4H_2O$	1
4	Sulfur-Iodine [14]	T	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	1/
		T	450	$2HI \rightarrow I_2(g) + H_2(g)$	1
		T	120	$I_2 + SO_2(a) + 2H_2O \rightarrow 2HI(a) + H_2SO_4(a)$	1
5	Julich Center EOS [15]	T	800	$2Fe_3O_4 + 6FeSO_4 \rightarrow 6Fe_2O_3 + 6SO_2 + O_2(g)$	1/
		T	700	$3FeO + H_2O \rightarrow Fe_3O_4 + H_2(g)$	1
		T	200	$Fe_2O_3 + SO_2 \rightarrow FeO + FeSO_4$	6
6	Tokyo Inst. Tech. Ferrite [16]	T	1000	$2MnFe_2O_4 + 3Na_2CO_3 + H_2O \rightarrow 2Na_3MnFe_2O_6 + 3CO_2(g) + H_2(g)$	1
		T	600	$4Na_3MnFe_2O_6 + 6CO_2(g) \rightarrow 4MnFe_2O_4 + 6Na_2CO_3 + O_2(g)$	1/
7	Hallett Air Products 1965 [15]	T	800	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	1/
		E	25	$2HCl \rightarrow Cl_2(g) + H_2(g)$	1
8	Gaz de France [15]	T	725	$2K + 2KOH \rightarrow 2K_2O + H_2(g)$	1
		T	825	$2K_2O \rightarrow 2K + K_2O_2$	1
		T	125	$2K_2O_2 + 2H_2O \rightarrow 4KOH + O_2(g)$	1/
9	Nickel Ferrite [17]	T	800	$NiMnFe_4O_6 + 2H_2O \rightarrow NiMnFe_4O_8 + 2H_2(g)$	1
		T	800	$NiMnFe_4O_8 \rightarrow NiMnFe_4O_6 + O_2(g)$	1/
10	Aachen Univ Julich 1972 [15]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	1/
		T	170	$2CrCl_2 + 2HCl \rightarrow 2CrCl_3 + H_2(g)$	1
		T	800	$2CrCl_3 \rightarrow 2CrCl_2 + Cl_2(g)$	1
11	Ispra Mark 1C [13]	T	100	$2CuBr_2 + Ca(OH)_2 \rightarrow 2CuO + 2CaBr_2 + H_2O$	1
		T	900	$4CuO(s) \rightarrow 2Cu_2O(s) + O_2(g)$	1/
		T	730	$CaBr_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HBr$	2
		T	100	$Cu_2O + 4HBr \rightarrow 2CuBr_2 + H_2(g) + H_2O$	1
12	LASL- U [15]	T	25	$3CO_2 + U_3O_8 + H_2O \rightarrow 3UO_2CO_3 + H_2(g)$	1
		T	250	$3UO_2CO_3 \rightarrow 3CO_2(g) + 3UO_3$	1
		T	700	$6UO_3(s) \rightarrow 2U_3O_8(s) + O_2(g)$	1/
13	Ispra Mark 8 [13]	T	700	$3MnCl_2 + 4H_2O \rightarrow Mn_3O_4 + 6HCl + H_2(g)$	1
		T	900	$3MnO_2 \rightarrow Mn_3O_4 + O_2(g)$	1/
		T	100	$4HCl + Mn_3O_4 \rightarrow 2MnCl_2(a) + MnO_2 + 2H_2O$	3/
14	Ispra Mark 6 [13]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	1/
		T	170	$2CrCl_2 + 2HCl \rightarrow 2CrCl_3 + H_2(g)$	1
		T	700	$2CrCl_3 + 2FeCl_2 \rightarrow 2CrCl_2 + 2FeCl_3$	1
		T	420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	1

Cycle	Name	T/E*	T °C	Reaction	F†
15	Ispra Mark 4 [13]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	1/
		T	100	$2FeCl_2 + 2HCl + S \rightarrow 2FeCl_3 + H_2S$	1
		T	420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	1
		T	800	$H_2S \rightarrow S + H_2(g)$	1
16	Ispra Mark 3 [13]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	1/
		T	170	$2VOCl_2 + 2HCl \rightarrow 2VOCl_3 + H_2(g)$	1
		T	200	$2VOCl_3 \rightarrow Cl_2(g) + 2VOCl_2$	1
17	Ispra Mark 2 (1972) [13]	T	100	$Na_2O.MnO_2 + H_2O \rightarrow 2NaOH(a) + MnO_2$	2
		T	487	$4MnO2(s) \rightarrow 2Mn_2O_3(s) + O_2(g)$	1/
		T	800	$Mn_2O_3 + 4NaOH \rightarrow 2Na_2O.MnO_2 + H_2(g) + H_2O$	1
18	Ispra CO/Mn3O4 [18]	T	977	$6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2(g)$	1/
		T	700	$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$	1
		T	700	$CO(g) + 2Mn_3O_4 \rightarrow C + 3Mn_2O_3$	1
19	Ispra Mark 7B [13]	T	1000	$2Fe_2O_3 + 6Cl_2(g) \rightarrow 4FeCl_3 + 3O_2(g)$	3/
		T	420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	3/2
		T	650	$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2(g)$	1
		T	350	$4Fe_3O_4 + O_2(g) \rightarrow 6Fe_2O_3$	1/
		T	400	$4HCl + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O$	3/
20	Vanadium Chloride [19]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	1/
		T	25	$2HCl + 2VCl_2 \rightarrow 2VCl_3 + H_2(g)$	1
		T	700	$2VCl_3 \rightarrow VCl_4 + VCl_2$	2
		T	25	$2VCl_4 \rightarrow Cl_2(g) + 2VCl_3$	1
21	Mark 7A [13]	T	420	$2FeCl_3(l) \rightarrow Cl_2(g) + 2FeCl_2$	3/
		T	650	3FeCl + 4H O(g) → Fe O + 6HCl(g) + H (g)	1
		T	350	$4Fe_3O_4 + O_2(g) \rightarrow 6Fe_2O_3$	1/
		T	1000	$6Cl_2(g) + 2Fe_2O_3 \rightarrow 4FeCl_3(g) + 3O_2(g)$	1/
		T	120	$Fe_2O_3 + 6HCl(a) \rightarrow 2FeCl_3(a) + 3H_2O(l)$	1
22	GA Cycle 23 [20]	T	800	$H_2S(g) \rightarrow S(g) + H_2(g)$	1
		T	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	1/
		T	700	$3S + 2H_2O(g) \rightarrow 2H_2S(g) + SO_2(g)$	1/
		T	25	$3SO_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(a) + S$	1/
		T	25	$S(g) + O_2(g) \rightarrow SO_2(g)$	
23	US -Chlorine [15]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	1/
		T	200	$2CuCl + 2HCl \rightarrow 2CuCl_2 + H_2(g)$	1
		T	500	$2CuCl_2 \rightarrow 2CuCl + Cl_2(g)$	1
24	Ispra Mark 9 [13]	T	420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	3/
		T	150	$3Cl_2(g) + 2Fe_3O_4 + 12HCl \rightarrow 6FeCl_3 + 6H_2O + O_2(g)$	1/2
		T	650	$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2(g)$	1
25	Ispra Mark 6C [13]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	1/
		T	170	$2CrCl_2 + 2HCl \rightarrow 2CrCl_3 + H_2(g)$	1
		T	700	$2CrCl_3 + 2FeCl_2 \rightarrow 2CrCl_2 + 2FeCl_3$	1
		T	500	$2CuCl_2 \rightarrow 2CuCl + Cl_2(g)$	1
		T	300	$CuCl + FeCl_3 \rightarrow CuCl_2 + FeCl_2$	1

* T = thermochemical, E = electrochemical

† Multiplier for one mole of H_2O decomposed

Which chemical cycle is the best? Criteria?

GENERAL ATOMICS

Methane from CO_2 and Thermal Energy

heat + $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$ endothermic

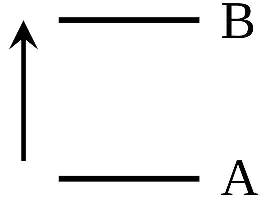
How much heat? Reaction temperature?

Thermodynamics: Given 2 chemical states,
the relative amounts at equilibrium are determined by
the difference in Gibbs energy and the temperature.

deductive,
verbal
statement

$A \leftrightarrow B$

energy



$$\Delta \overline{G}_{rxn} = \overline{G}_B - \overline{G}_A$$

inductive,
visual
example

$$\text{at equilibrium}: \frac{\text{amount of B}}{\text{amount of A}} = e^{-\Delta \overline{G}_{rxn}/RT}$$

eqn 2.4, p.37.

gas constant: $PV = nRT$
$R = 8.314$ J/(mol°C)

Methane from CO_2 and Thermal Energy

heat + $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$ endothermic

How much heat? $\dfrac{P_{CH_4} P_{O_2}^2}{P_{CO_2} P_{H_2O}^2} \propto e^{-\Delta \overline{G}_{rxn}/RT}$ like eqn (2.5), p. 37

$\Delta \overline{G}_{rxn} = \Delta \overline{H}_{rxn}^0 - T\Delta \overline{S}_{rxn}^0$ eqn (2.2), p. 37

large! $\Delta \overline{H}_{rxn}^0 = +802$ kJ/mol, $\Delta \overline{S}_{rxn}^0 = +0.0051$ J/(mol·K)

ΔS_{rxn} is small!
3 gas molecules →
3 gas molecules

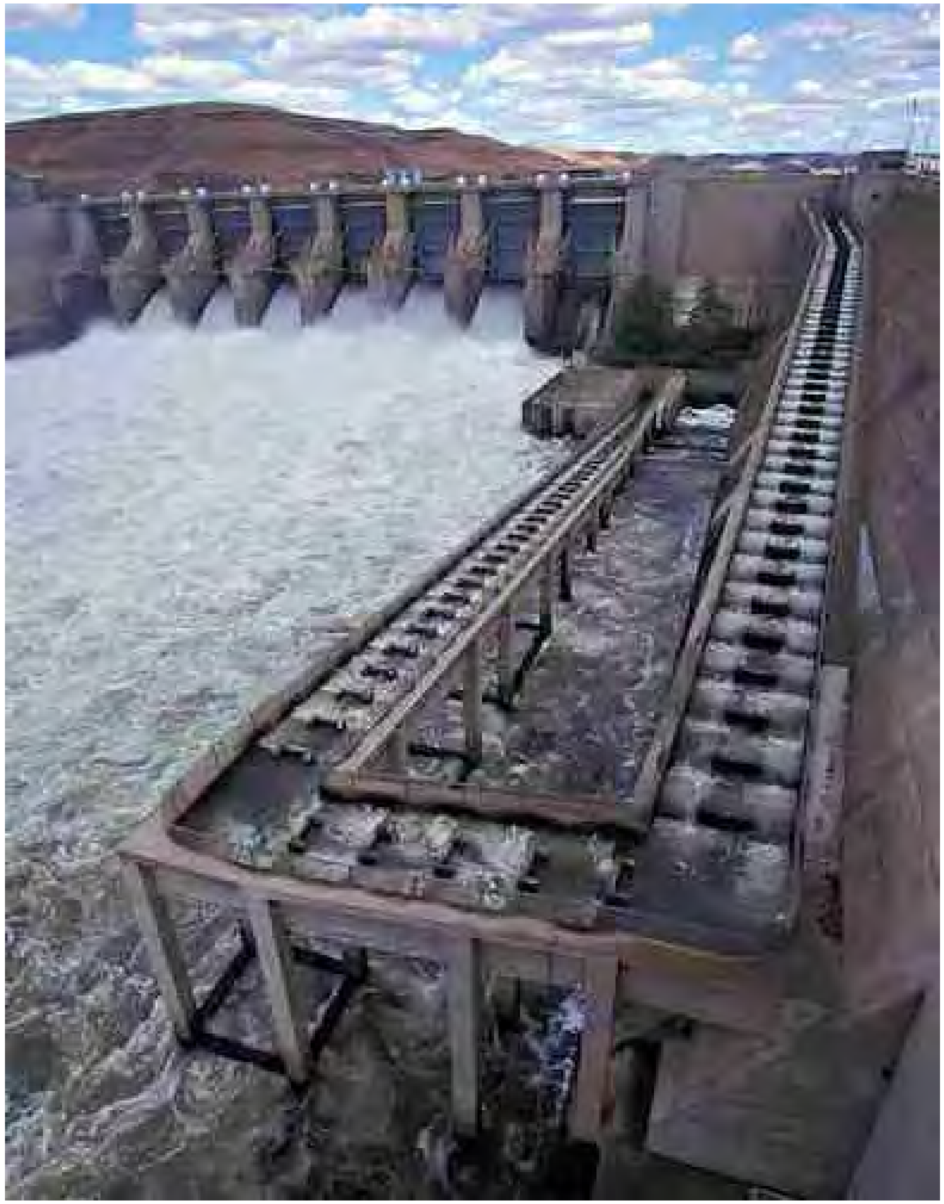
Like **Table 2.11.** CO_2 reacted at chemical equilibrium.

T (°C)	T (K)	$\Delta \overline{G}_{rxn}$ (kJ/mol)	fraction of CO_2 reacted
25	298	+802	10^{-141}
500	773	+798	10^{-54}
3,000	3,273	+786	10^{-11}
160,000	160,273	–21	0.5

Problem: Devise a reactor that operates at 160,000°C

Concept: Divide a large step into many small steps.

Example: Salmon migration past a large dam.



Methane from CO_2 and Thermal Energy

$$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$$

C and O are reduced.
Need to couple with an oxidation reaction.

What to oxidize?
Metals release energy when oxidized!

Proposal:
Couple the reduction of H_2O with the oxidation of Fe.

Also a good reducing agent!

Reaction 1: $3H_2O + 2Fe \rightarrow Fe_2O_3 + 3H_2$

Reaction 2: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Reaction 3: $2Fe_2O_3 \rightarrow 4Fe + 3O_2$

Do the three reactions form a cycle?

Is the net sum $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$?

Reaction 1: $\frac{4}{3}\times(3H_2O + 2Fe \rightarrow Fe_2O_3 + 3H_2)$

Reaction 2: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Reaction 3: $\frac{2}{3}\times(2Fe_2O_3 \rightarrow 4Fe + 3O_2)$

1. Start with reaction 2; it has the correct stoichiometric coefficient for CO_2.
2. Reaction 2 needs $4H_2$ $\Rightarrow$ Reaction 1 must produce $4H_2$.
3. Reaction 1 produces 4/3 Fe_2O_3 $\Rightarrow$ Reaction 3 must reduce 4/3 Fe_2O_3.

Net sum is $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$!

Are the reactor temperatures practical?

$$\text{Reaction 1:} \quad 3H_2O + 2Fe \rightarrow Fe_2O_3 + 3H_2$$

$$\text{Reaction 2:} \quad CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

$$\text{Reaction 3:} \quad 2Fe_2O_3 \rightarrow 4Fe + 3O_2$$

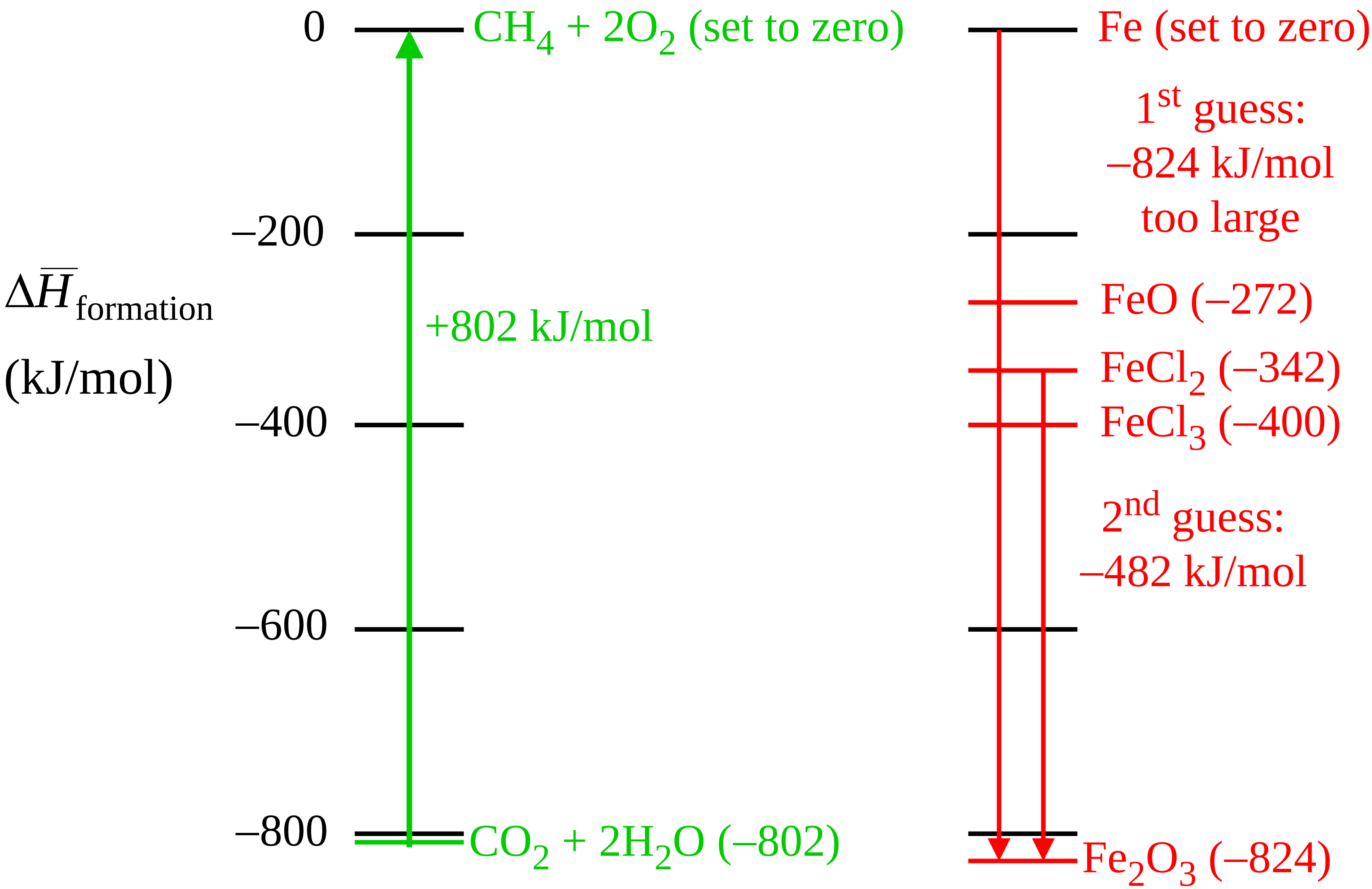
reaction	$\Delta\overline{H}^0_{rxn}$ kJ/mol	$\Delta\overline{S}^0_{rxn}$ kJ/(mol·K)	T_{rxn} ºC	$\Delta\overline{G}_{rxn}$ at T_{rxn} kJ/mol	% conversion
1	–99	–0.14	120	–45	99.998
2	–165	–0.17	200	–83	99.999999
3	+824	+0.28	~~3000~~	~~76~~	~~94.1~~
			2500	+62	6%

solid → solid + gas

Reaction favored by high temperature.

too low

Need a reducing agent less severe than Fe.



New Proposal: Couple the reduction of H_2O with the oxidation of $FeCl_2$.

Reaction 1: $4\times(3H_2O + 2FeCl_2 \rightarrow Fe_2O_3 + 4HCl + H_2)$

Reaction 2: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Reaction 3: $2\times(2Fe_2O_3 + 2Cl_2 + 8HCl \rightarrow 4FeCl_3 + 4H_2O + O_2)$

Reaction 4: $4\times(2FeCl_3 \rightarrow 2FeCl_2 + Cl_2)$

$$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$$

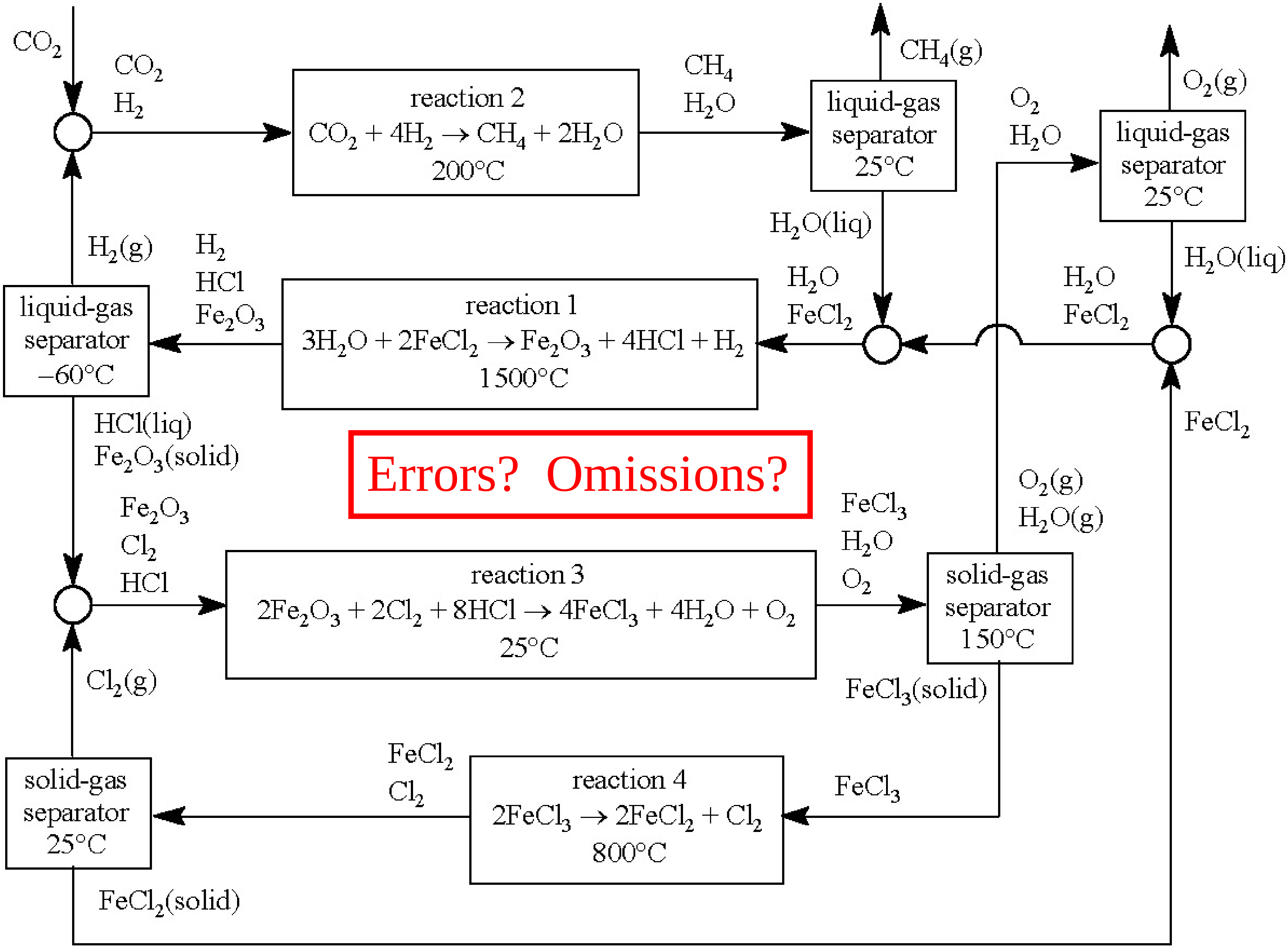
reaction	$\Delta\overline{H}^0_{rxn}$ kJ/mol	$\Delta\overline{S}^0_{rxn}$ kJ/(mol·K)	T_{rxn} °C	$\Delta\overline{G}_{rxn}$ at T_{rxn} kJ/mol	% conversion
1	+216	+0.16	1500	–74	99.3
2	–165	–0.17	200	–83	99.999
3	–354	–1.06	25	–38	99.9999
4	+115	+0.17	800	–72	99.97

practical temperatures!

All ~100.%
Assume all rxns go to completion.

Methane from CO_2 and Thermal Energy

overall reaction: $CO_2 + H_2O \rightarrow CH_4 + 2O_2$

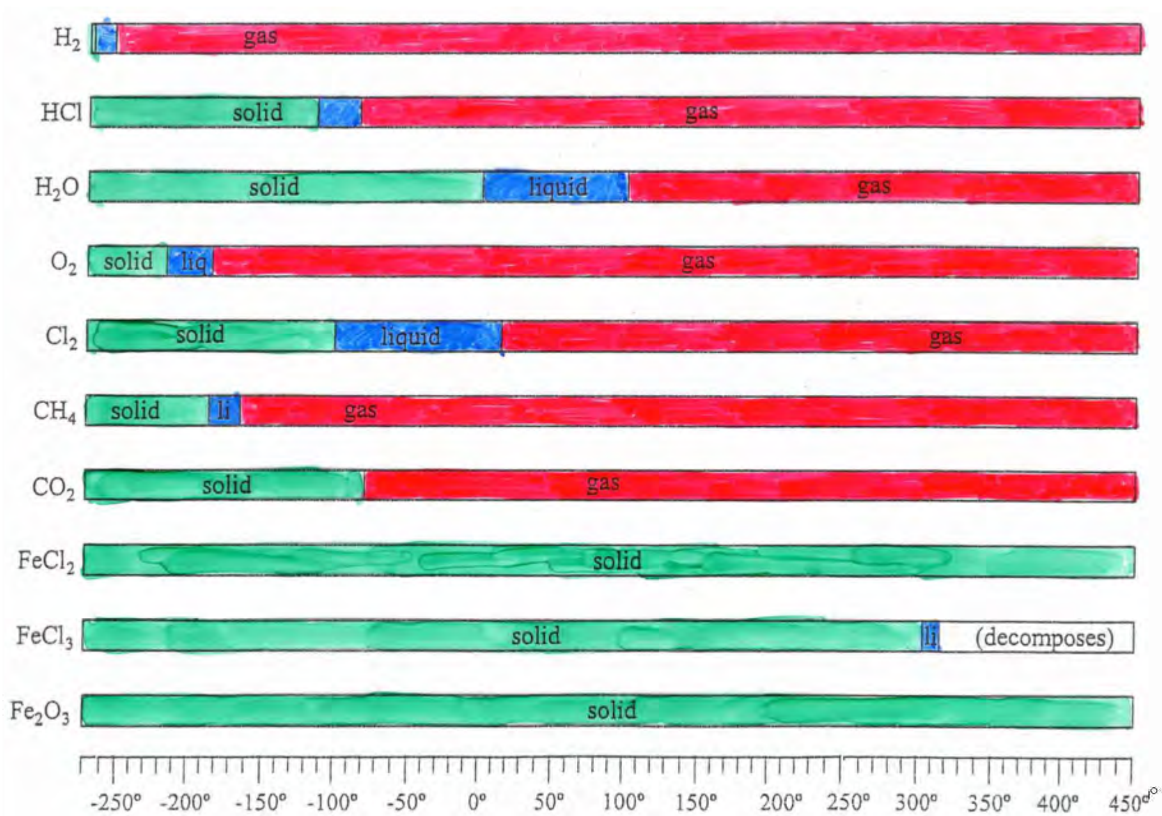


Physical Properties

	melting point (°C)	boiling point at 1 atm (°C)	solubility in water (g/L water at 25°C)
H_2	−259	−253	0.002
HCl	−114	−85	650
H_2O	0	100	∞
O_2	−218	−183	0.046
Cl_2	−102	−34	
CH_4	−182	−164	0.02
CO_2	−79*	−57**	1.5
$FeCl_2$	677	1023	7000
$FeCl_3$	306	315***	8000
Fe_2O_3	1566***		insoluble

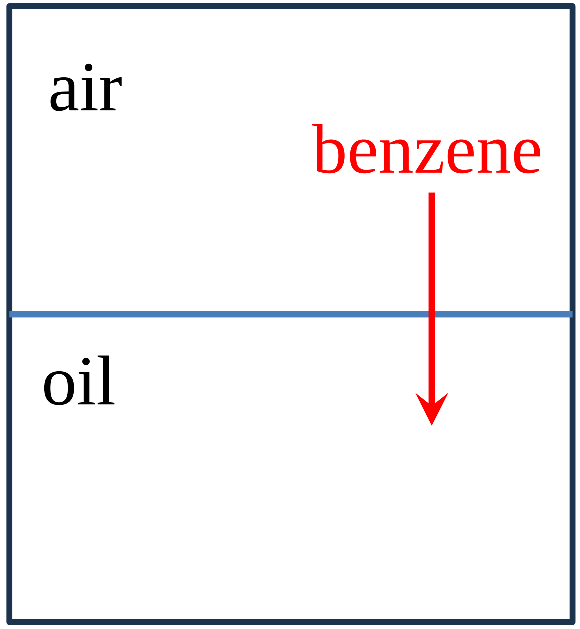
*sublimation point; solid to gas **at 5 atm ***decomposes

verbal



visual

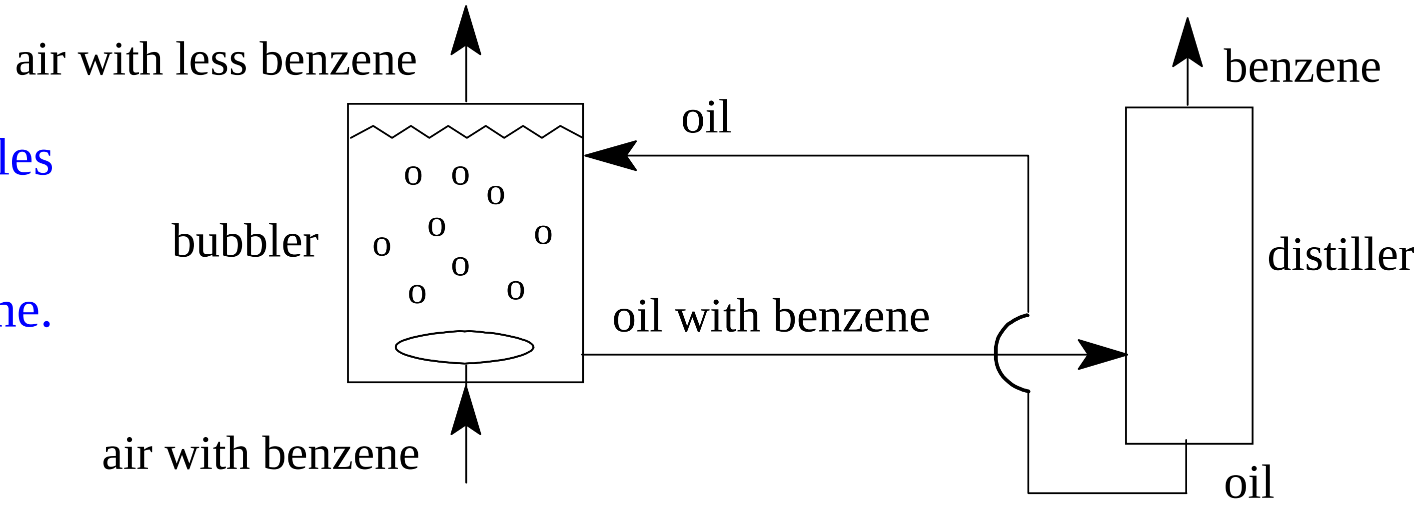
An Absorber – A Closed Unit



The oil phase absorbs benzene from the air phase.

An Absorber – An Open-Flow Unit

As air+benzene bubbles
rise through the oil,
the oil absorbs benzene.



Countercurrent flow: cleanest oil cleans the cleanest air.

Can design a unit to produce air with negligible benzene.

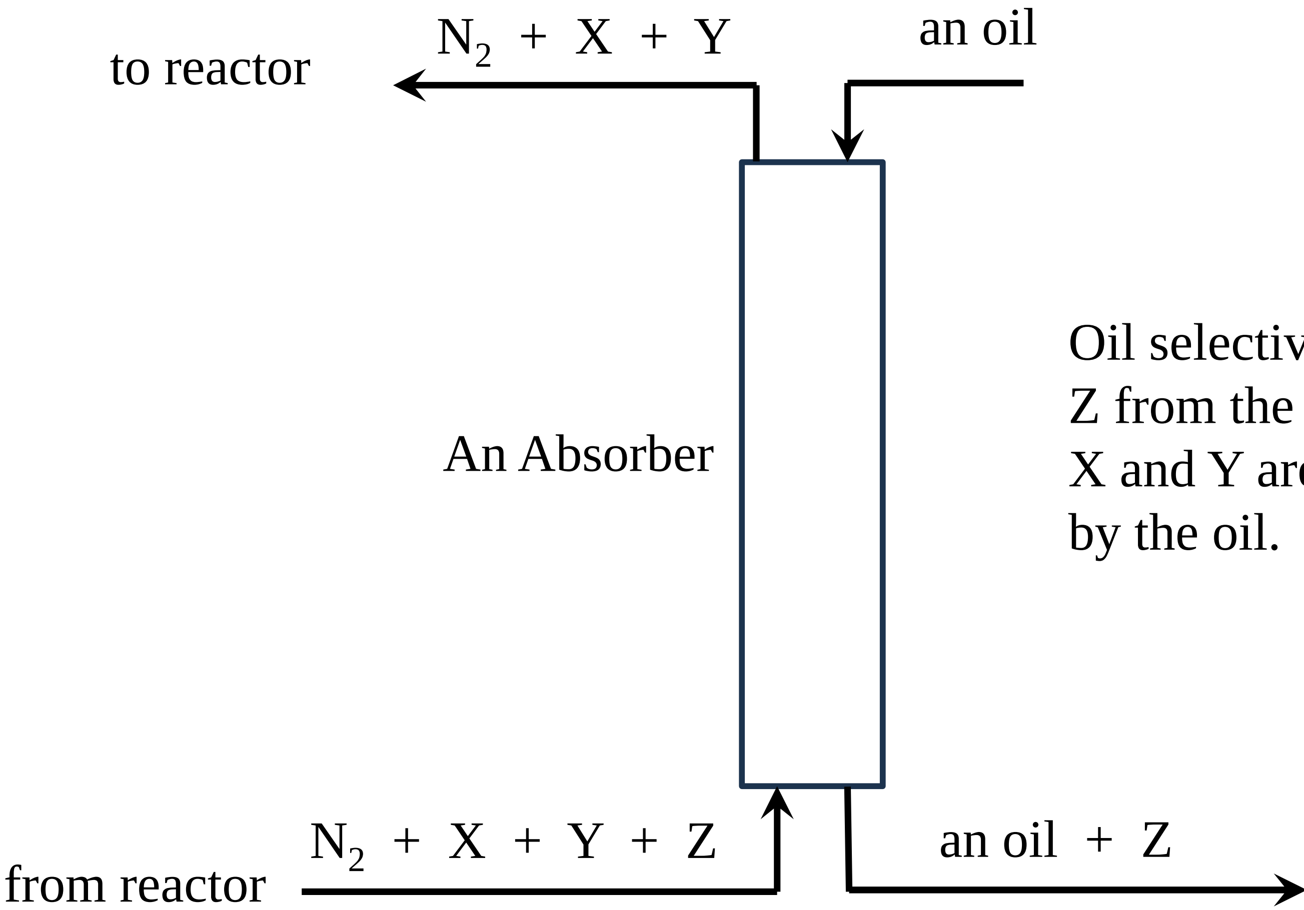
Selective Absorption for Separations

$$X + Y \rightarrow Z$$

Reaction is incomplete. Want to recycle reactants X and Y.

X, Y, and Z have similar boiling points.

Z is soluble in an oil. X and Y are not.



Oil selectively absorbs Z from the N_2 solvent. X and Y are not absorbed by the oil.