

Experiment II Overview: Preparation & Equilibration of Isomeric 2,3-Dimethylbutenes

H⁺ cat.
$$H^{+} \text{ cat.}$$

$$2$$

$$\Delta G^{\circ} = ?$$

$$\Delta H^{\circ} = ?$$

$$\Delta S^{\circ} = ?$$

$$\Delta S^{\circ} = ?$$

$$2,3-dimethyl-2-butene$$

$$"2-ene"$$

$$2,3-dimethyl-1-butene$$

$$"1-ene"$$

major activities in experiment II

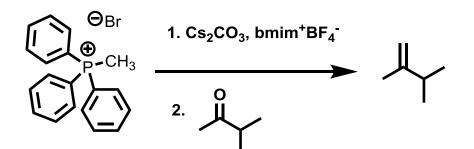
REPORT 2

REPORT 3

- synthesis of "2-ene" (major) / "1-ene" mixture by *Grignard* reaction followed by acid mediated *dehydration* (E1 elimination)
- synthesis of "1-ene" by Wittig olefination
- purification and isomer separation by distillation / fractional distillation
- equilibration of alkene isomers and analysis of alkene isomer distributions by gas chromatography (GC)
- determination of thermodynamic properties (ΔG° , ΔH° , ΔS°) by analyzing temperature dependence of equilibrium constant (K_{eq})

Recap of Week 5 and Summary of Tasks for Week 6 (see lab manual)

1-ene Synthesis



- + unreacted ketone (bp 92°C)
- + other volatile impurities

2-ene Synthesis

$$I-CH_{3} \xrightarrow{1. \text{ Mg, Et}_{2}O} \xrightarrow{OMgI} \xrightarrow{H_{3}O^{+}(aq)} \xrightarrow{OH} \xrightarrow{H^{+}, \text{ heat}} + \xrightarrow{\text{"alkoxide"}} \text{"alcohol"} \text{"alcohol"} \text{major minor}$$

bp 120-121°C

bp 73°C

bp 56°C

- + ether (bp 34.5°C)
- + other volatile imp.

Distillation

What is the boiling point of a *mixture* of liquids?

- > Temperature at which vapor pressure of solution = external pressure
- Vapor pressure of solution varies according to its <u>composition</u> and <u>vapor pressure of each pure compound</u> in the solution

Raoult's Law:

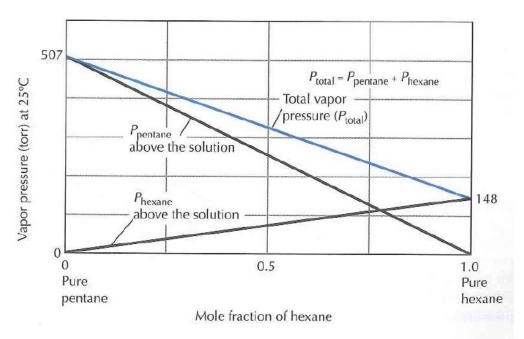
partial vapor pressure of gas in mixture (P_A) depends on its pure vapor pressure (P^o_A) and varies according to its mole fraction, χ_A

$$P_A = \chi_A * P_A^o$$

Dalton's Law:

total pressure of a gas mixture (P_{tot}) is the sum of the partial pressures of each gas

$$P_{total} = P_A + P_B + P_C + \dots$$



70 **Distillation** 65 Vapor 60 Temperature (°C) 55 50 45 FIGURE 12.4 Liquid Calculated 40 temperature-35.1 composition diagram for pentane/hexane 30 solutions at 1.0 atm 0.2 0.4 0.0 0.6 0.8 1.0 pressure. Mole fraction of hexane

Example: Liquid mixture of 75% hexane, 25% pentane (mol %).

What is boiling point of this mixture?

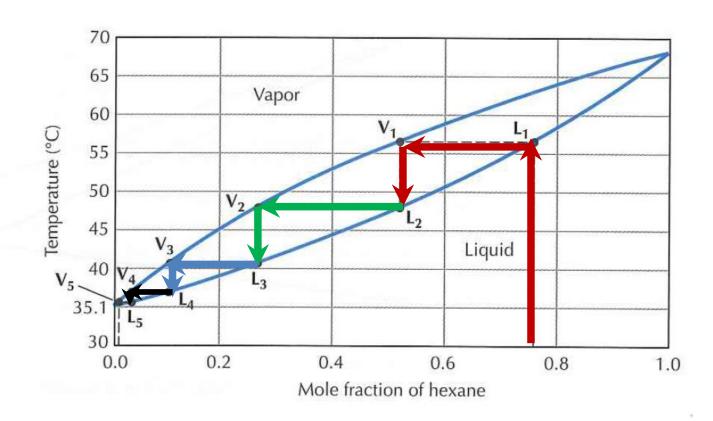
56°C

What is composition of vapor when the mixture begins to boil?

52% hexane, 48% pentane

Distillation

FIGURE 12.4
Calculated
temperaturecomposition diagram
for pentane/hexane
solutions at 1.0 atm
pressure.



Composition after 1 "cycle" of $\ell \rightleftharpoons g$ Composition after 2 "cycles" of $\ell \rightleftharpoons g$ Composition after 3 "cycles" of $\ell \rightleftharpoons g$ Composition after 4 "cycles" of $\ell \rightleftharpoons g$ Composition after 5 "cycles" of $\ell \rightleftharpoons g$ 52% hexane, 48% pentane
24% hexane, 76% pentane
11% hexane, 89% pentane
3% hexane, 97% pentane
~0.5% hexane, ~99.5% pentane

Separation Effectiveness & Efficiency

Theoretical Plate: The separation achievable in a single distillation step, i.e., one "cycle" of $\ell \rightleftharpoons g$; a measure of column effectiveness

How many theoretical plates do you need??

- > It depends on the compounds being separated
- It depends on the level of purity that is required if $\Delta bp = 100^{\circ}C$, then 1 plate will yield a fraction of 95% purity if $\Delta bp = 40^{\circ}C$, then 4 plates; if $\Delta bp = 10^{\circ}C$, then ~20 plates; if $\Delta bp = 2^{\circ}C$, then ~100 plates

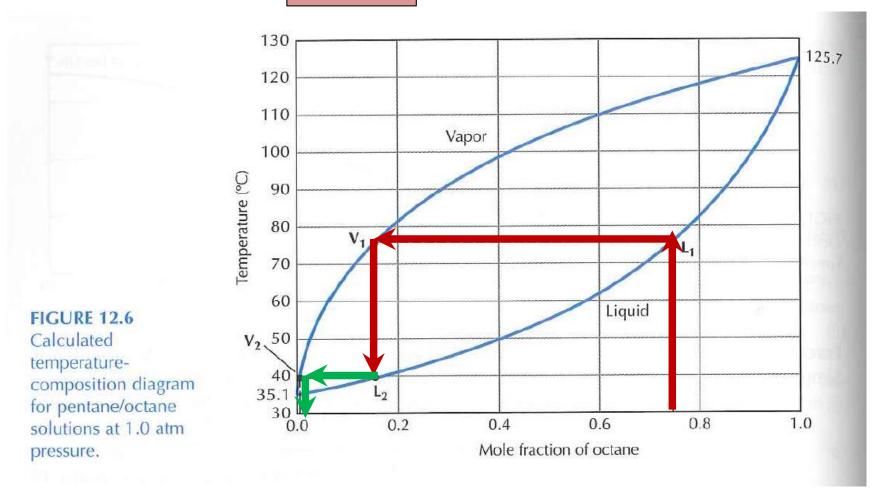
How do you increase the number of theoretical plates?

By using a column that has more surface area

Height Equivalent Theoretical Plate (HETP): a measure of column efficiency

Separation Effectiveness & Efficiency

How many theoretical plates are required to separate a mixture of 74% octane and 26% pentane (mol%)? 2 plates



Simple vs. Fractional Distillation

simple distillation

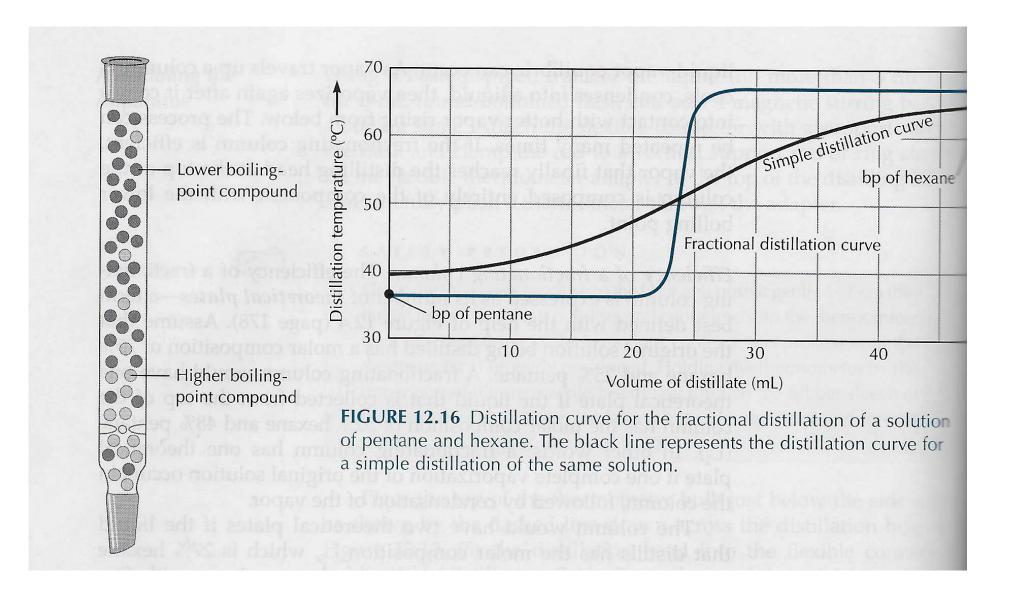
- typically only 1-3 TPs
- useful for components with large bp difference
- often used to remove low boiling solvents (e.g., ether)

fractional distillation

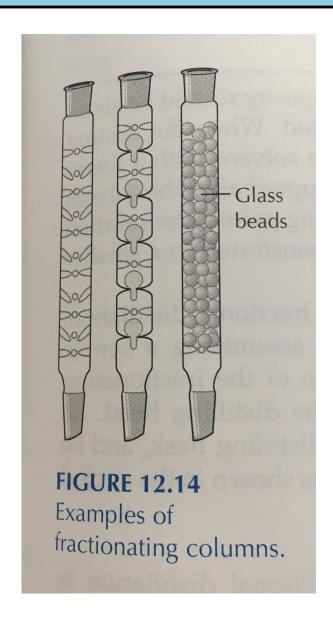
- involves >3 TPs
- a 'fractionating' column is used to maximize liquid/vapor equilibration (e.g., vigreux, glass bead packed etc.)
- distillate is collected in fractions (use 'cow' / fraction cutter)



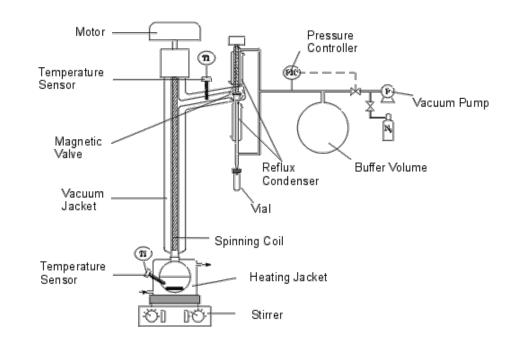
Simple vs. Fractional Distillation



Types of Fractionating Columns for Distillation

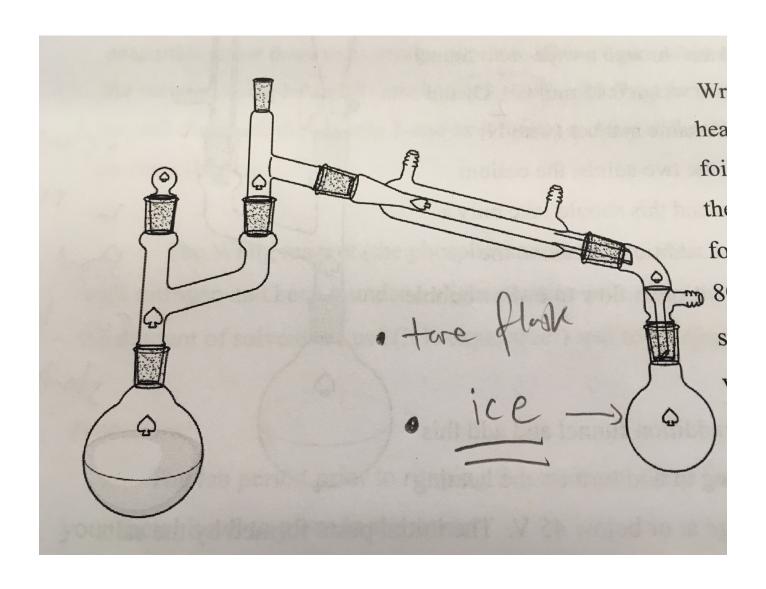


		Hold-up	
Column	HETP (cm.)	mL/plate	Comments
Vigreux (tube with	y of the jaction and terath	achieved. Similar	
indentations)	10	b mags big biopil	poor
Glass helices (tube filled	ill exist some system in	he colimna there w	good, but high
with 1/8" glass spirals)	3	0.8	hold up
Podbelniak (double spiral	(NR 13-13000 19 30 20 20 20 20 20 20 20 20 20 20 20 20 20	n de la constante de la consta	excellent, but
wire in tube)	Strand 1 poor	0.2	expensive
Me Library a market mapped at death	s.al sealing squares	medicular introduce	very good, but
oncentric tube	0.6	0.02	hard to use
		Bash Senda A	
inning band	2	0.02	good



Distillation Set-Ups for This Week

• Wittig: distill 1-ene away from ionic liquid and other contaminants, get mass & GC



Distillation Set-Ups for This Week

• Grignard: after work-up, distill off ether, then conduct dehydration/distillation of 2-ene

