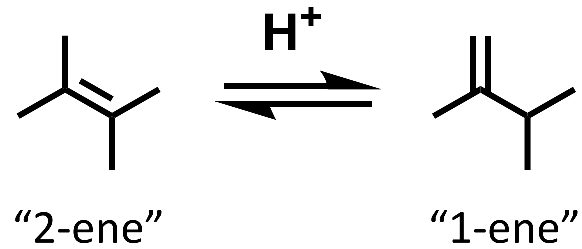
CH 361/CH 361H Lecture

Distillation &
Elimination Reaction

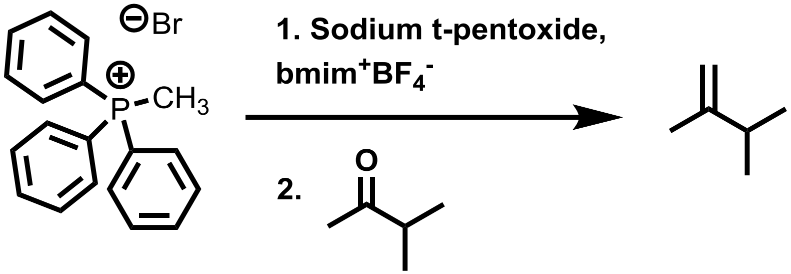
Nov. 1/2, 2016

Experiment II Overview



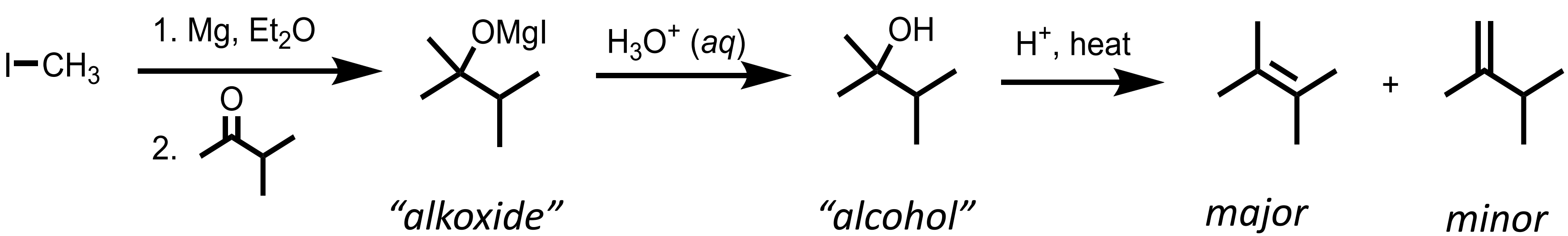
K_{eq} = ?
ΔG^o = ?
ΔH^o = ?
ΔS^o = ?

1-ene Synthesis



+ unreacted ketone (bp 92°C)
+ t-pentyl alcohol (bp 102°C)
+ other volatile impurities

2-ene Synthesis



bp 120-121°C

bp 73°C

bp 56°C

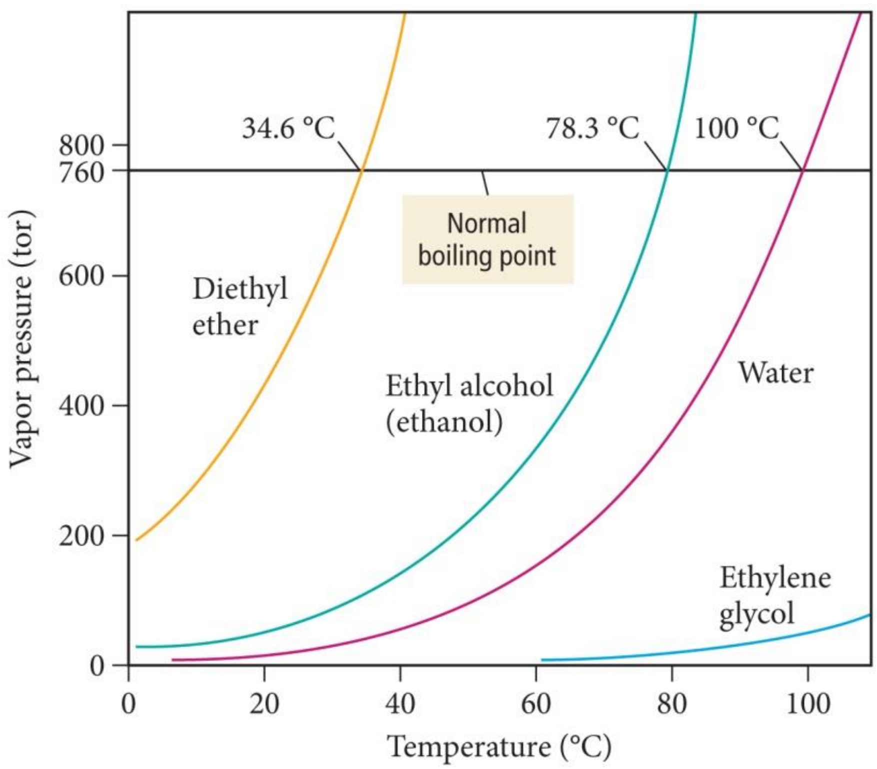
+ ether (bp 34.5°C)
+ other volatile imp.

Distillation

Distillation: separation technique that exploits differences in boiling points ("bp") between 2 or more compounds

Boiling Point: temperature at which vapor pressure of liquid = external pressure

Normal Boiling Point: temp. at which vapor pressure of liquid = 760 torr



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 *composition* and *vapor pressure of each pure compound* 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

$$P_A = \chi_A * P^o_A$$

Dalton's Law:
total pressure of a gas mixture (P_{tot}) is the sum of the partial pressures of each gas

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

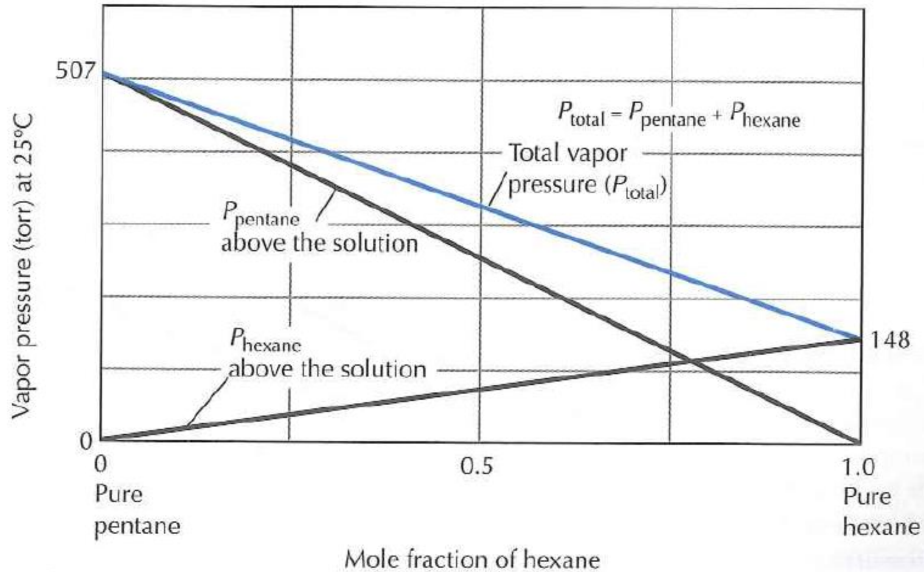


Figure from *"Laboratory Techniques in Organic Chemistry, 4th Edition"* by Mohrig, Alberg, Hofmeister, Schatz, Hammond

Distillation

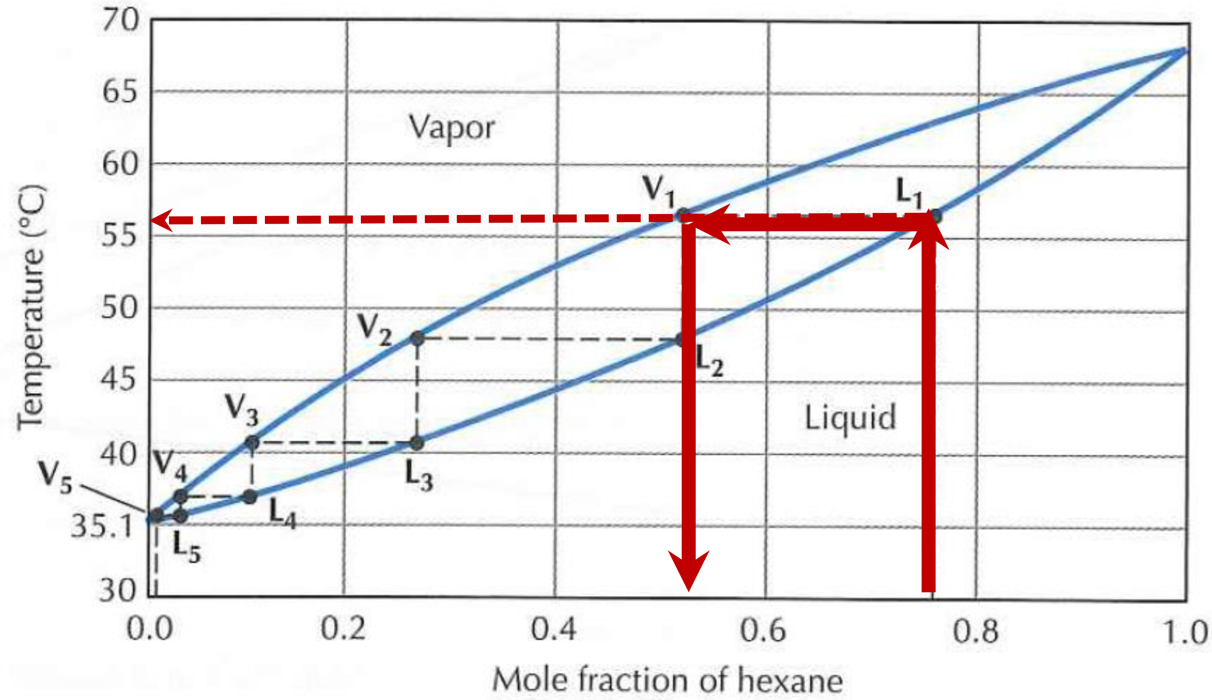


FIGURE 12.4 Calculated temperature-composition diagram for pentane/hexane solutions at 1.0 atm pressure.

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

Figure from *"Laboratory Techniques in Organic Chemistry, 4th Edition"*
by Mohrig, Alberg, Hofmeister, Schatz, Hammond

Distillation

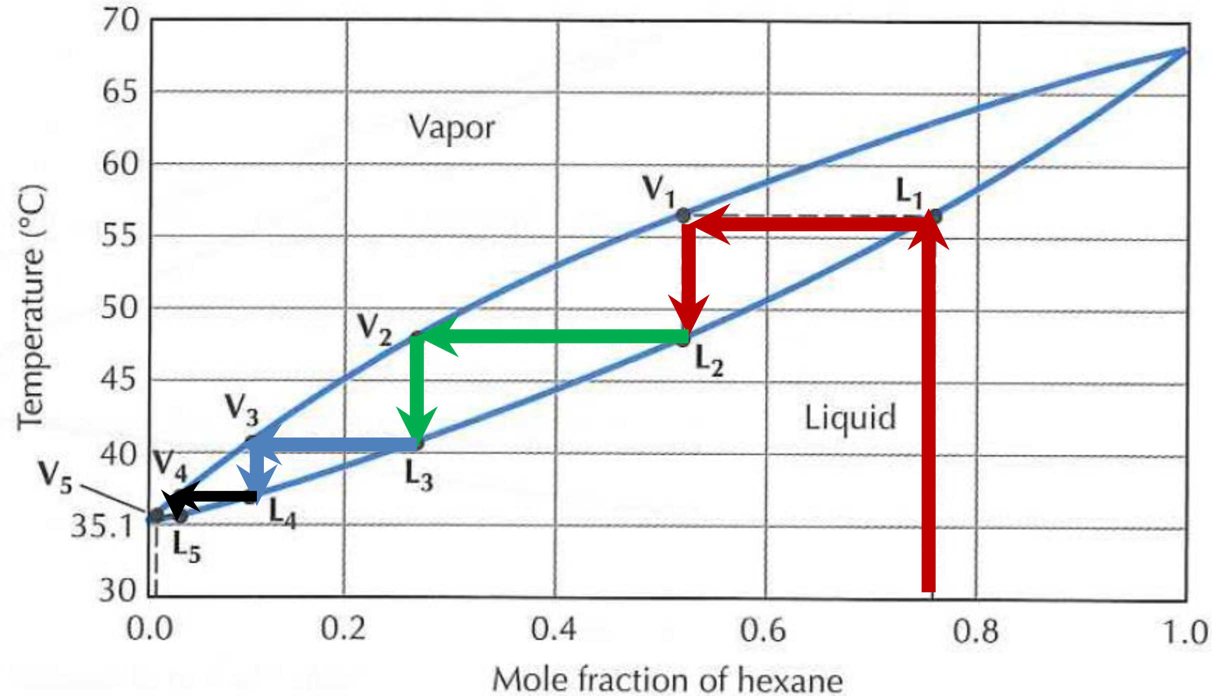


FIGURE 12.4
Calculated temperature-composition diagram for pentane/hexane solutions at 1.0 atm pressure.

Composition after 1 “cycle” of $\ell \rightleftharpoons g$ 52% hexane, 48% pentane

Composition after 2 “cycles” of $\ell \rightleftharpoons g$ 24% hexane, 76% pentane

Composition after 3 “cycles” of $\ell \rightleftharpoons g$ 11% hexane, 89% pentane

Composition after 4 “cycles” of $\ell \rightleftharpoons g$ 3% hexane, 97% pentane

Composition after 5 “cycles” of $\ell \rightleftharpoons g$ ~0.5% hexane, ~99.5% pentane

Figure from *“Laboratory Techniques in Organic Chemistry, 4th Edition”*
by Mohrig, Alberg, Hofmeister, Schatz, Hammond

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 Δbp = 100°C, then 1 plate will yield a fraction of 95% purity

if Δbp = 40°C, then 4 plates; if Δbp = 10°C, then ~20 plates;
if Δbp = 2°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

Photo credit: Wikipedia Commons

Separation Effectiveness & Efficiency

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

2 plates

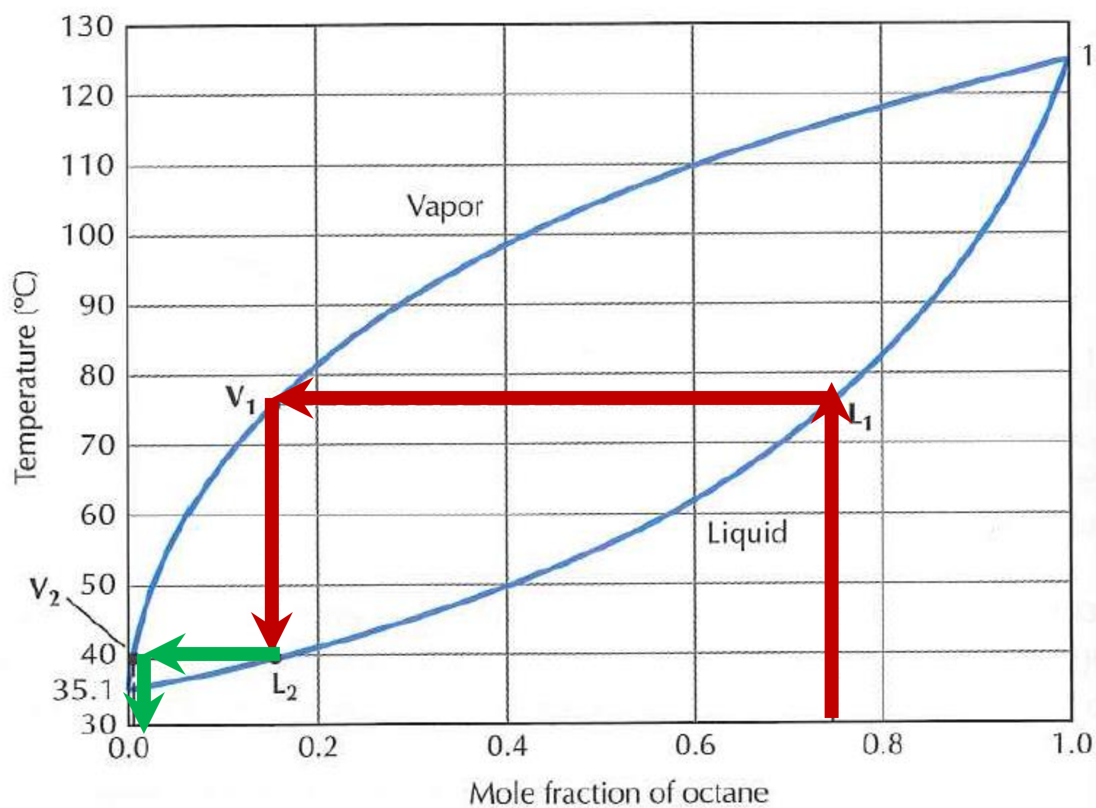


FIGURE 12.6 Calculated temperature-composition diagram for pentane/octane solutions at 1.0 atm pressure.

Figure from *"Laboratory Techniques in Organic Chemistry, 4th Edition"* by Mohrig, Alberg, Hofmeister, Schatz, Hammond

Simple vs. Fractional Distillation

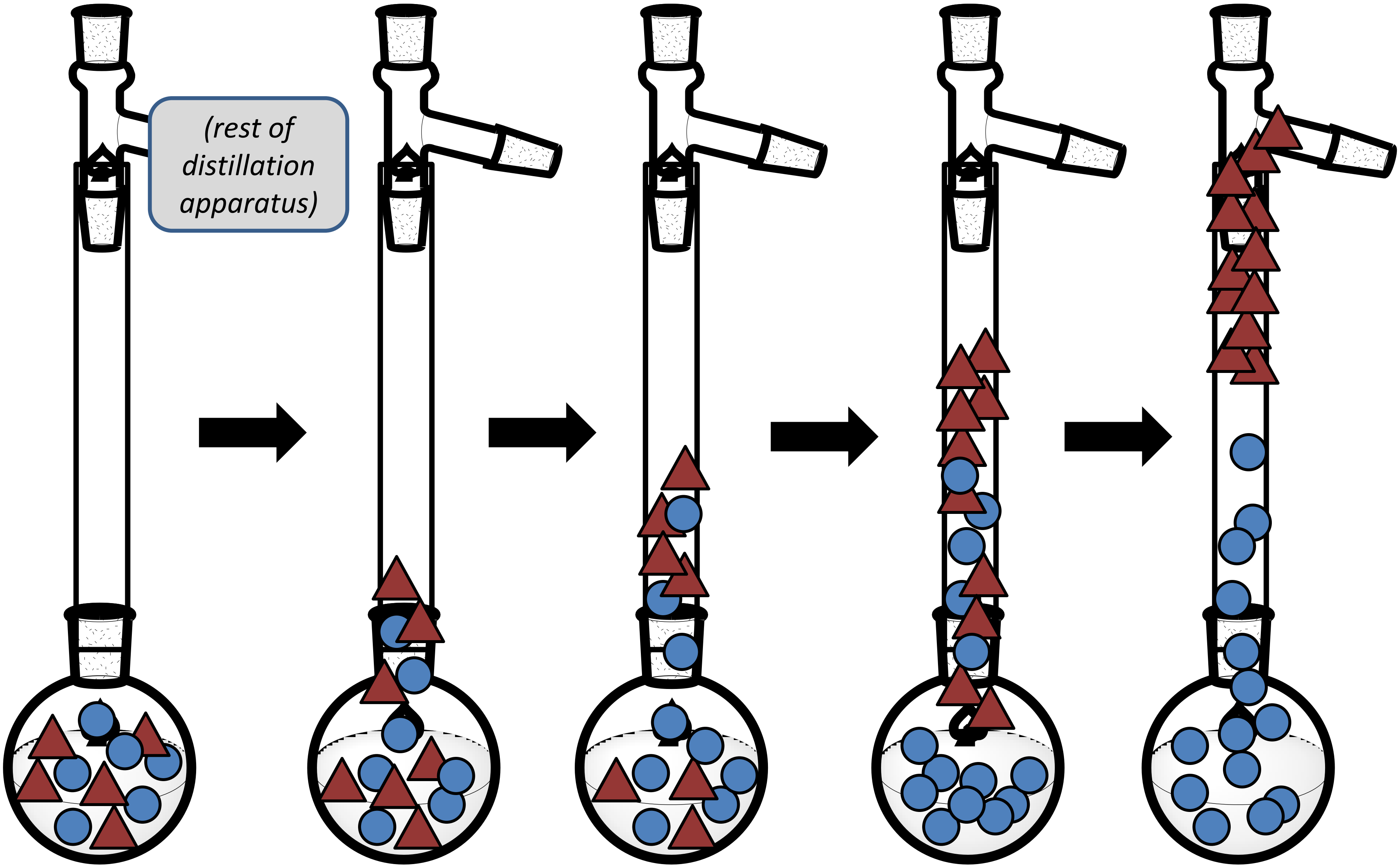
Simple distillation:

- Typically involves 1-3 theoretical plates
- Is used to separate compounds having large difference in bp
- Often used to remove low boiling solvents, e.g., ether

Fractional distillation:

- Involves > 3 theoretical plates
- A "fractionating" column is used (vigreux, glass bead packed, etc)
- Distillate is collected in fractions

Distillation Process



Practical Considerations

Setting up the distillation apparatus:

- Build from the bottom up
- Grease joints
- Position the thermometer correctly
- Insulation

Monitoring the distillation

How do you know when to collect a new fraction?

How do you know when the distillation is “done”?

Vacuum Distillation

Distillation can be performed under reduced pressure if bp > 200°C

- Reduced pressure reduces bp; distillation process is faster
- Also used to avoid possible decomposition of compound at high temps
- bp at reduced pressure is estimated using nomograph; actual bp must be recorded, along with actual pressure during collection of distillate

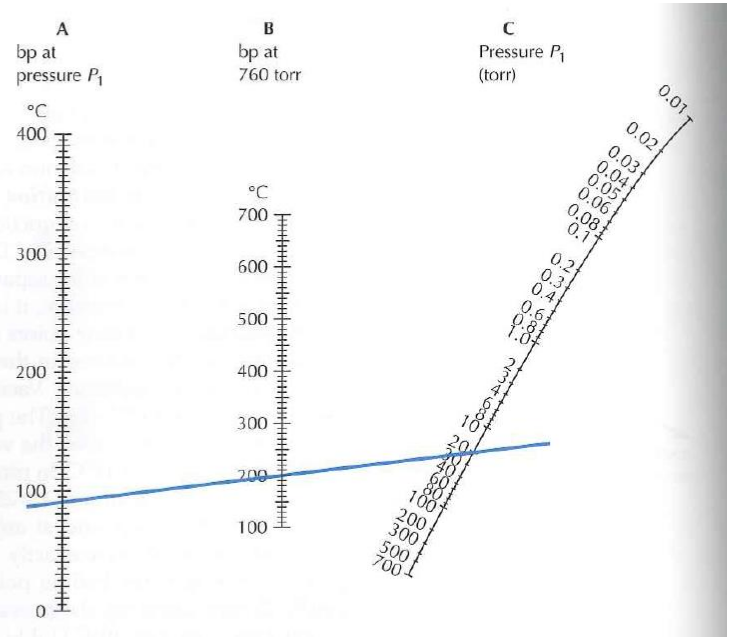


FIGURE 12.22
Nomograph for estimating boiling points at different pressures.

Figure from *"Laboratory Techniques in Organic Chemistry, 4th Edition"*
by Mohrig, Alberg, Hofmeister, Schatz, Hammond

Azeotropes

What is an azeotrope?

- a particular mole ratio of two (or more) compounds that will have the same composition in the vapor phase as the liquid phase

- Negative and positive azeotropes exist:

positive azeotrope has a bp that is ***lower*** than either of the two pure liquids

negative azeotrope has a bp that is ***higher*** than either of the two pure liquids; ex., water and HCl azeotrope bp 110^{o}C

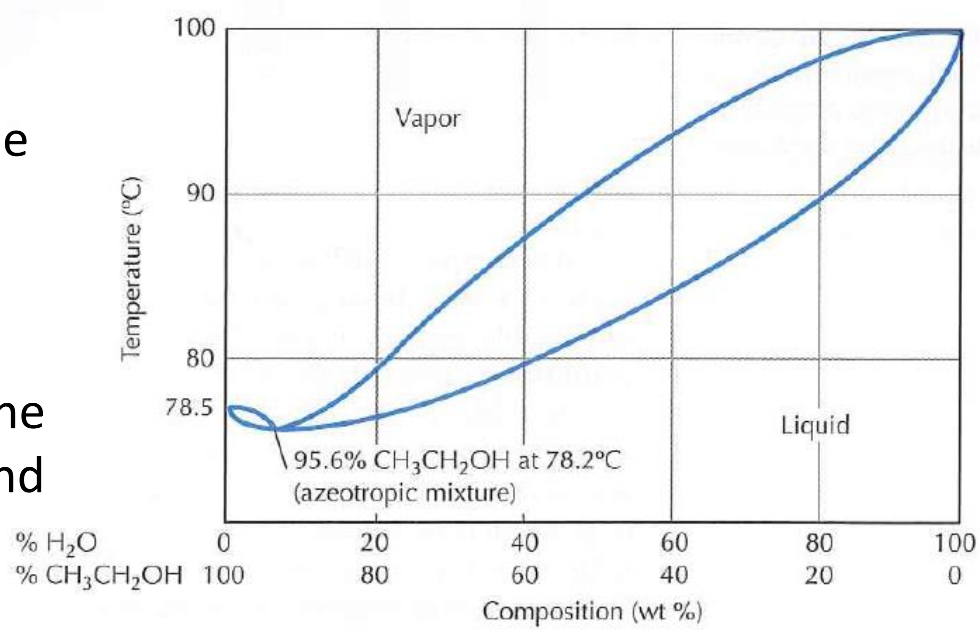


Figure from *"Laboratory Techniques in Organic Chemistry, 4th Edition"* by Mohrig, Alberg, Hofmeister, Schatz, Hammond

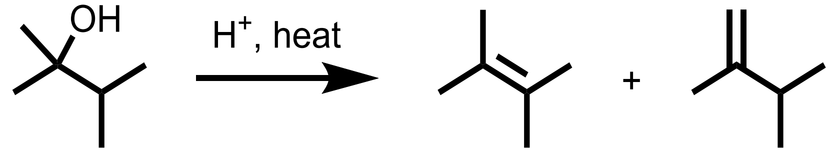
Azeotropes

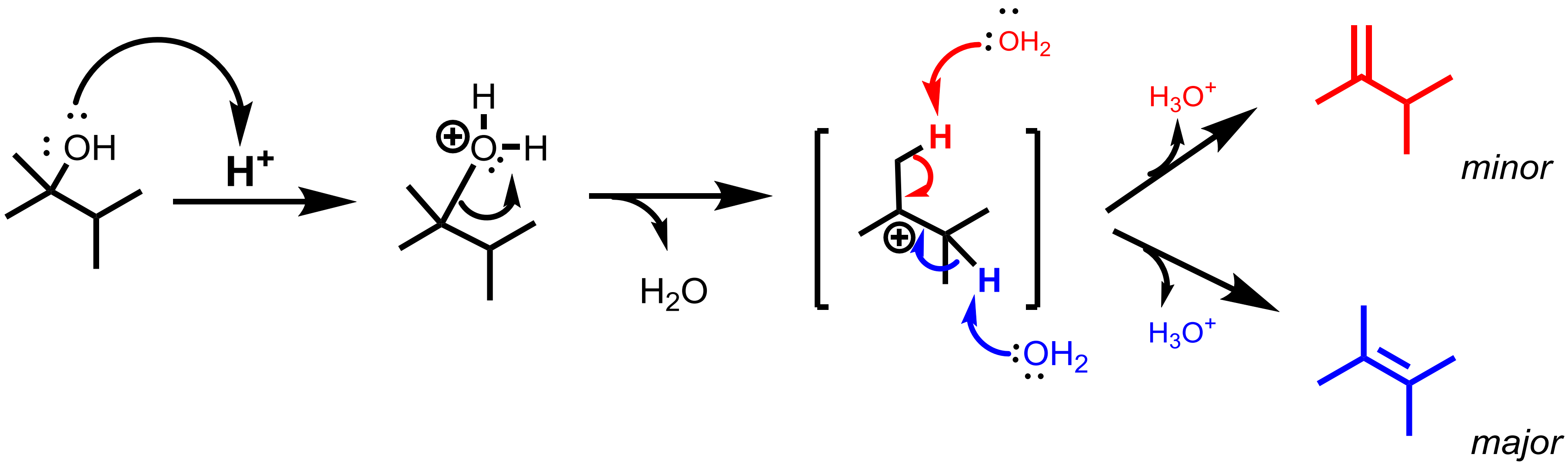
TABLE 12.2 Azeotropes formed by common solvents

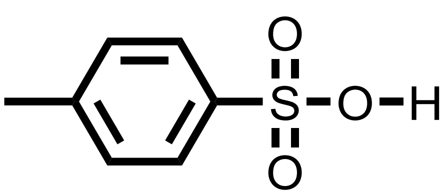
Component X (bp)	% by wt	Component Y (bp)	% by wt	Azeotrope bp
Water (100)	13.5	Toluene (110.7)	86.5	84.1
Water (100)	1.4	Pentane (36.1)	98.6	34.6
Methanol (64.7)	12.1	Acetone (56.1)	87.9	55.5
Methanol (64.7)	72.5	Toluene (110.7)	27.5	63.5
Ethanol (78.3)	68.0	Toluene (110.7)	32.0	76.7
Water (100)	1.3	Diethyl ether (34.5)	98.7	34.2

Table from *"Laboratory Techniques in Organic Chemistry, 4th Edition"*
by Mohrig, Alberg, Hofmeister, Schatz, Hammond

E1 Elimination Reaction







“H+” = tosic acid
(*p*-toluenesulfonic acid)