

Saponification Values

Kevin M. Dunn

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Saponification Values

- What they are
- Why they are what they are
- How to measure them for yourself

Acknowledgements

- Stephen English
- Kevin Thompson
- Brad Benedetti
- Alex Garcia
- William Slack

SAP's: What They Are

- 144 g NaOH per 1000 g of palm oil
- 144 g NaOH per kg of palm oil
- 144 mg NaOH per g of palm oil
- 144 parts NaOH per thousand parts of palm oil (144 ppt)
- 14.4 parts NaOH per hundred parts of palm oil (14.4%)
- 0.144 g NaOH per g of palm oil

SAP's: In Other Units

- 144 oz NaOH per 1000 oz of palm oil
- 144 lb NaOH per 1000 lb of palm oil
- 144 ton NaOH per 1000 ton of palm oil
- 0.144 oz NaOH per oz of palm oil
- 0.144 lb NaOH per lb of palm oil
- 0.144 ton NaOH per ton of palm oil

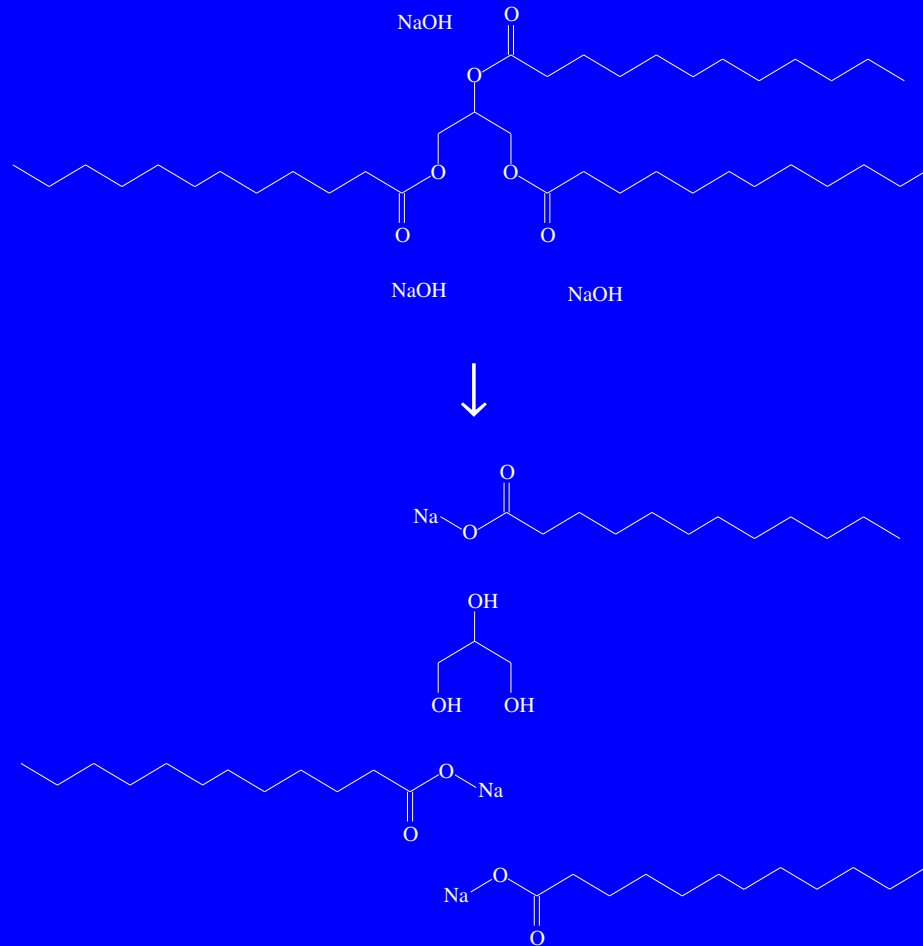
SAP's In Practice

$$\begin{aligned} ? \text{ oz NaOH} &= 120 \text{ oz } \cancel{\text{Palm Oil}} \left(\frac{144 \text{ oz NaOH}}{1000 \text{ oz } \cancel{\text{Palm Oil}}} \right) \\ &= 17.3 \text{ oz NaOH} \end{aligned}$$

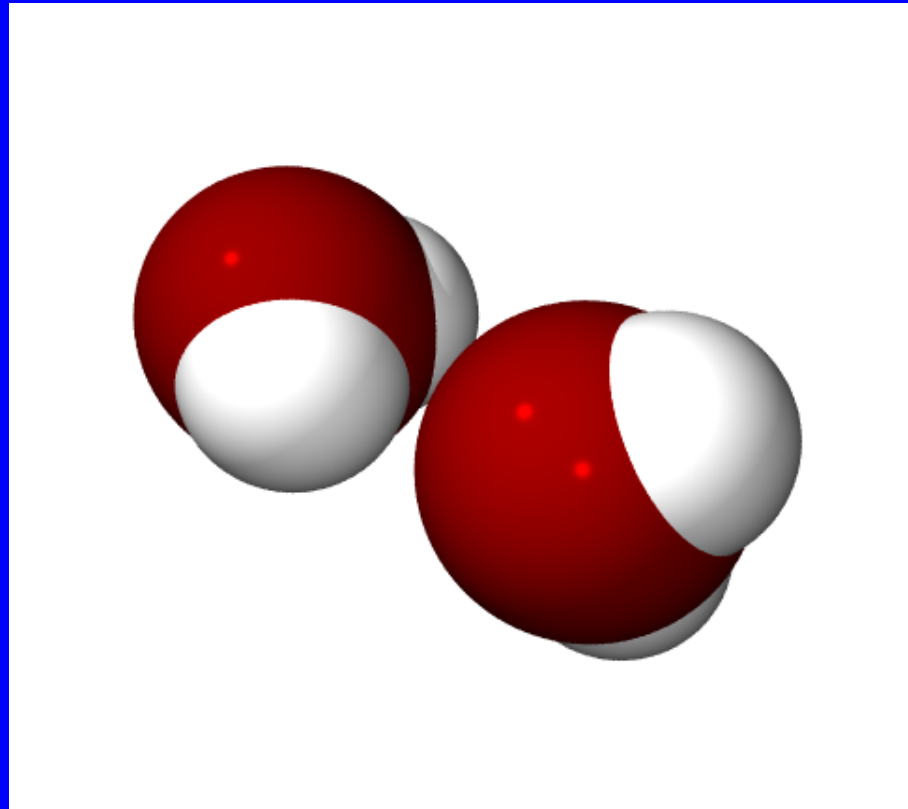
$$\begin{aligned} ? \text{ oz NaOH} &= 30 \text{ oz } \cancel{\text{Coconut Oil}} \left(\frac{191 \text{ oz NaOH}}{1000 \text{ oz } \cancel{\text{Coconut Oil}}} \right) \\ &= 5.7 \text{ oz NaOH} \end{aligned}$$

- You need (17.3 + 5.7) or 23.0 oz of NaOH
- At 5% discount you need 21.9 oz of NaOH

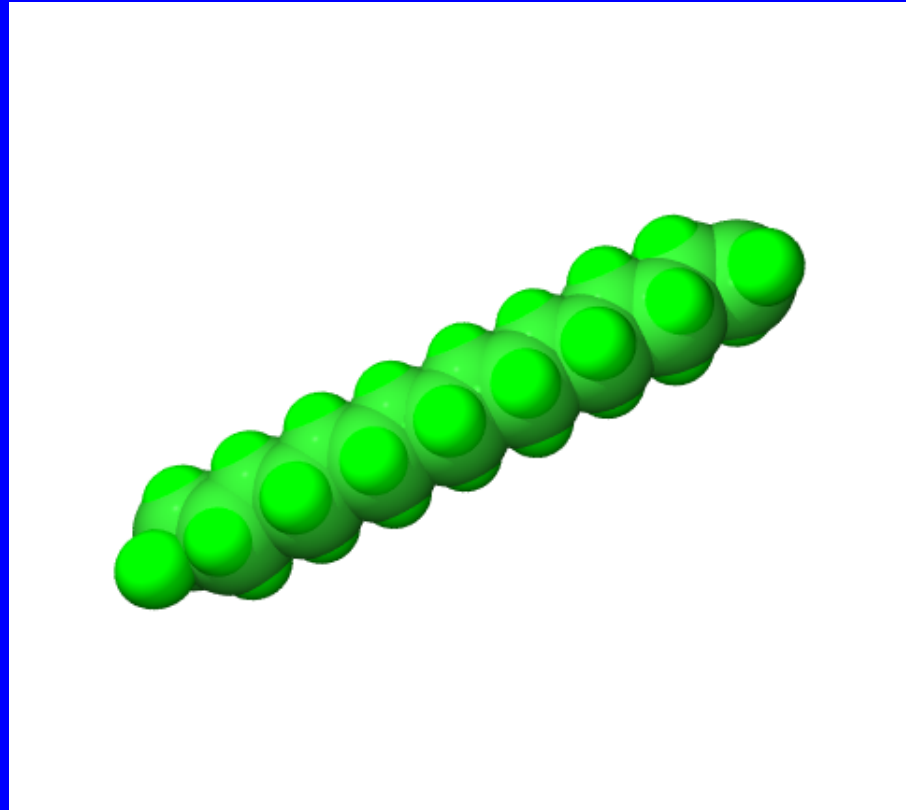
The Fundamental Equation


















Water



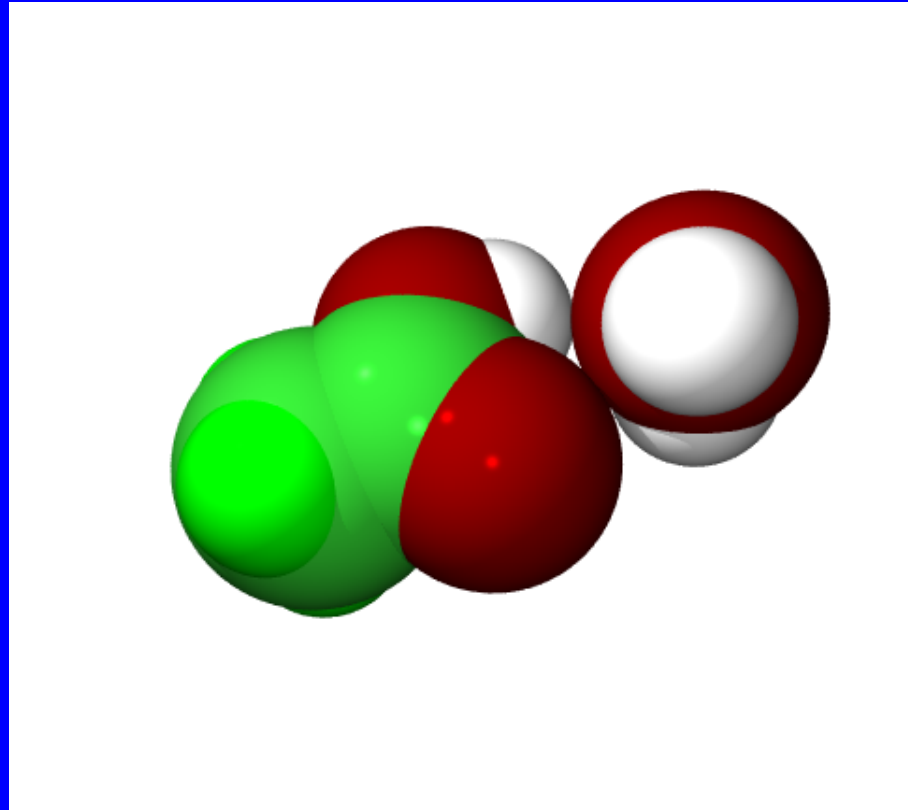
Hexadecane



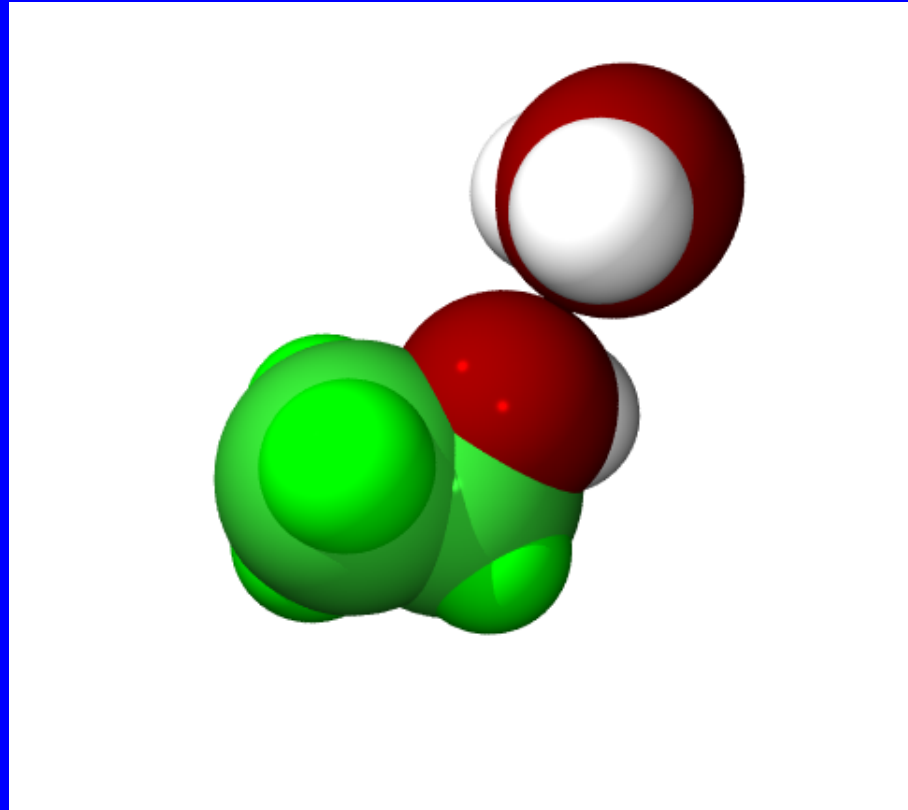
Alkanes

ethane	C_2H_6	
propane	C_3H_8	
butane	C_4H_{10}	
pentane	C_5H_{12}	
hexane	C_6H_{14}	
heptane	C_7H_{16}	
octane	C_8H_{18}	
nonane	C_9H_{20}	
decane	$C_{10}H_{22}$	
undecane	$C_{11}H_{24}$	
dodecane	$C_{12}H_{26}$	
tridecane	$C_{13}H_{28}$	
tetradecane	$C_{14}H_{30}$	
pentadecane	$C_{15}H_{32}$	
hexadecane	$C_{16}H_{34}$	

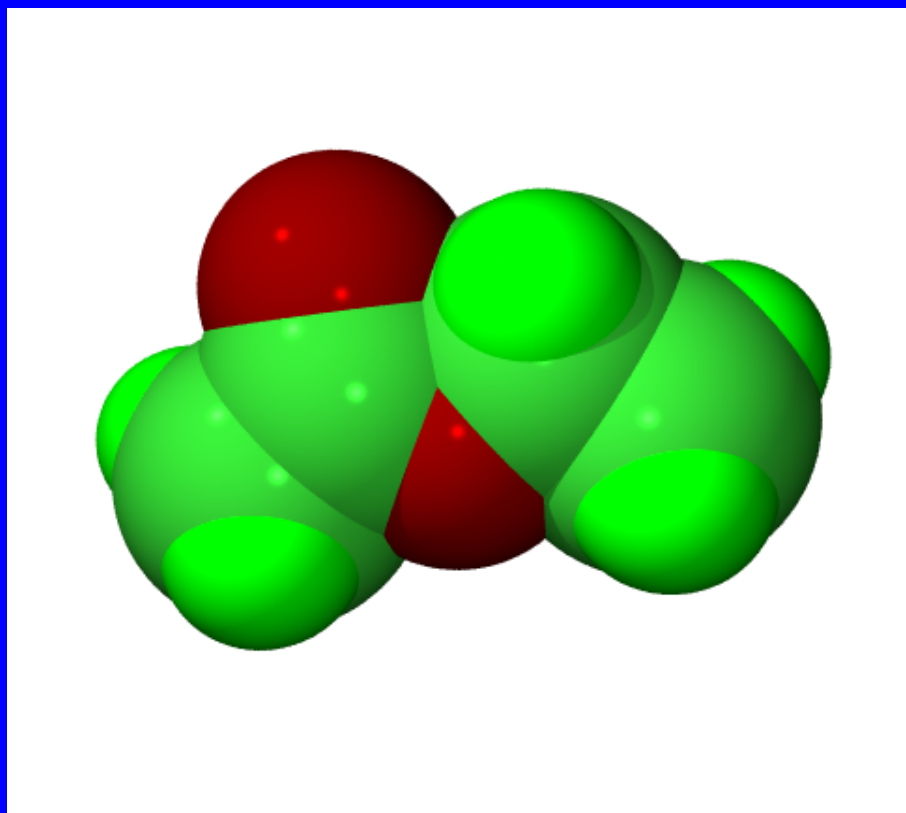
Acids



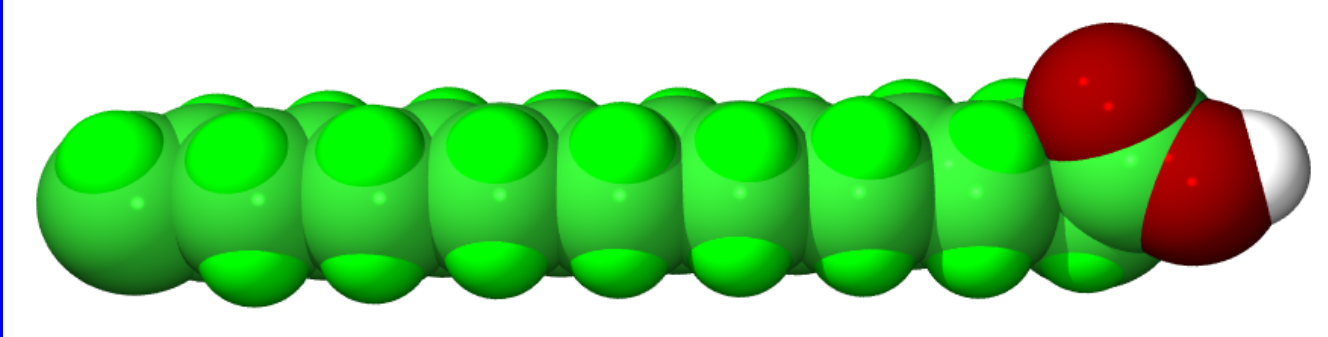
Alcohols



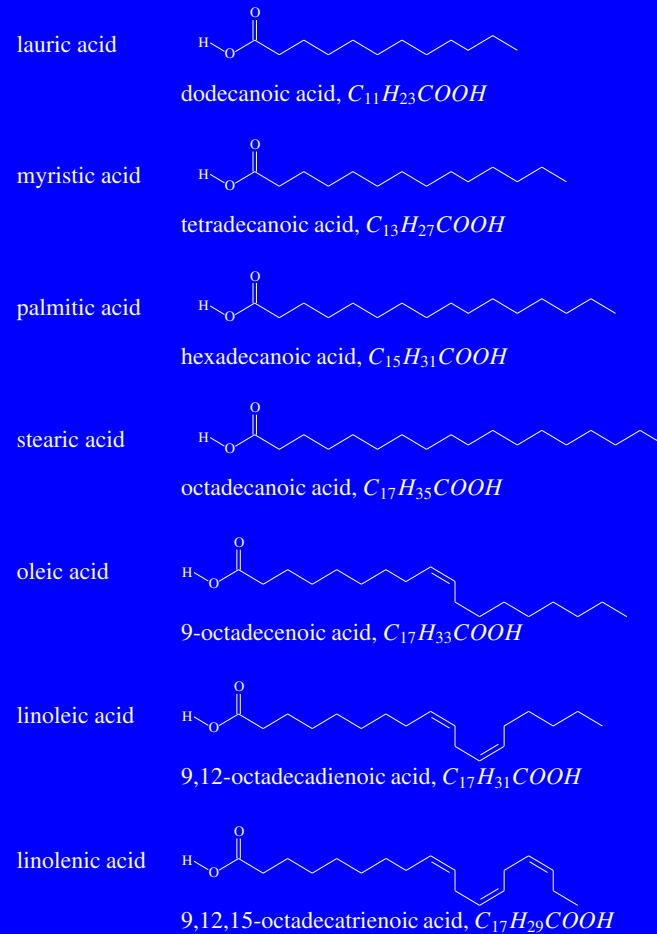
Esters



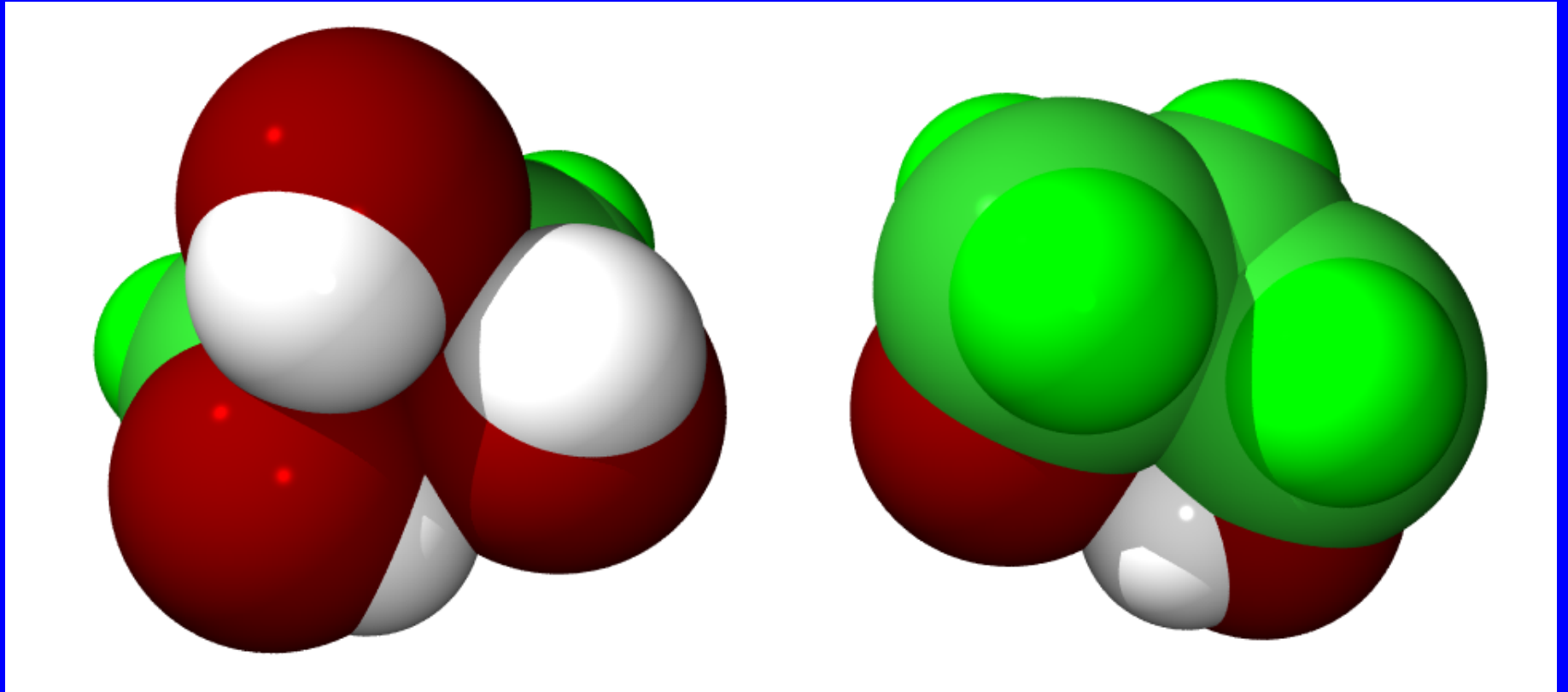
Stearic Acid



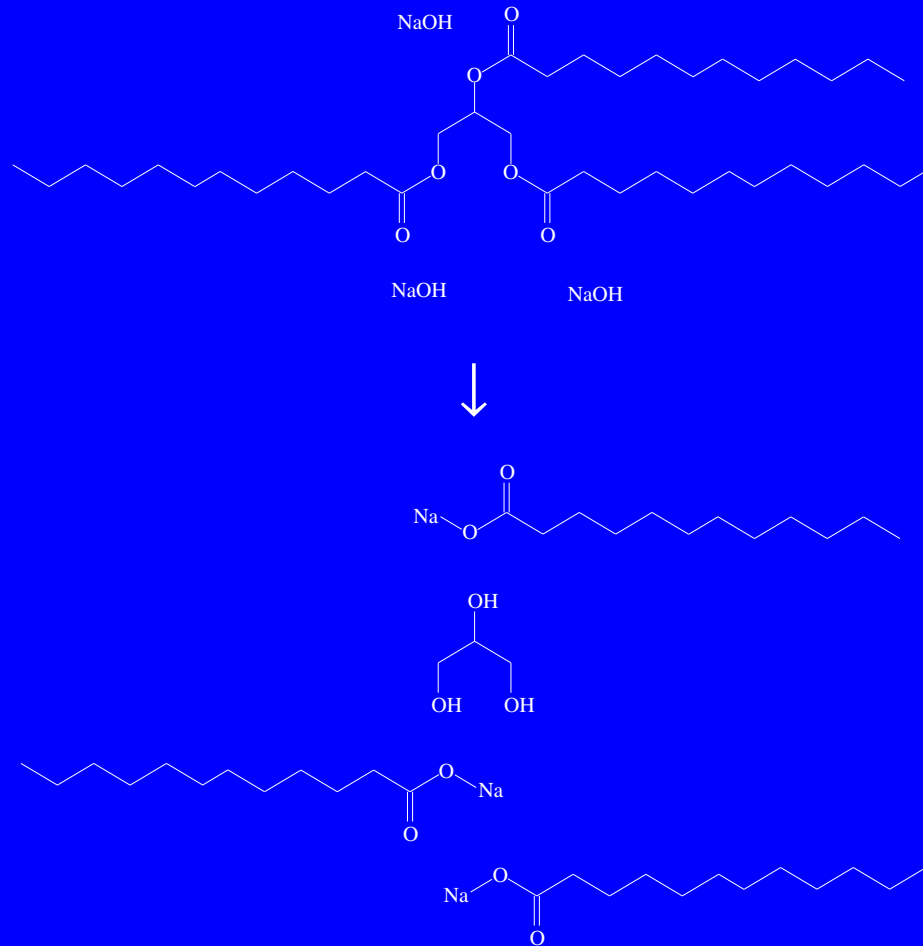
Fatty Acids



Glycerol



The Fundamental Reaction



SAP's: Why They Are What They Are

- How many eggs to make a 3-egg omelet?
- How many dozens of eggs to make a dozen 3-egg omelets?
- How many gross of eggs to make a gross of 3-egg omelets?
- How many moles of eggs to make a mole of 3-egg omelets?

Lyes and More Lyes

- How many NaOH to react with one fat?
- How many dozens of NaOH to react with a dozen fat?
- How many gross of NaOH to react with a gross of fat?
- How many moles of NaOH to react with a mole of fat?

Atomic Weights

- 1 gram of hydrogen = 1 mole
- 12 gram of carbon = 1 mole
- 16 gram of oxygen = 1 mole
- 23 gram of sodium = 1 mole
- 39 gram of potassium = 1 mole

Formula Weights

- 40 grams of NaOH = 1 mole (23 + 16 + 1)
- 56 grams of KOH = 1 mole (39 + 16 + 1)
- 638 grams of C₃₉H₇₄O₆ (glyceryl trilaurate) = 1 mole
- 806 grams of C₅₁H₉₈O₆ (glyceryl tripalmitate) = 1 mole
- 890 grams of C₅₇H₁₁₀O₆ (glyceryl tristearate) = 1 mole

Stoichiometry

$$\begin{aligned} ? \text{ g NaOH} &= 1000 \text{ g fat} \left(\frac{1 \text{ mol fat}}{890 \text{ g fat}} \right) \left(\frac{3 \text{ mol NaOH}}{1 \text{ mol fat}} \right) \left(\frac{40 \text{ g NaOH}}{1 \text{ mol NaOH}} \right) \\ &= 135 \text{ g NaOH} \end{aligned}$$

$$\begin{aligned} ? \text{ g KOH} &= 1000 \text{ g fat} \left(\frac{1 \text{ mol fat}}{890 \text{ g fat}} \right) \left(\frac{3 \text{ mol KOH}}{1 \text{ mol fat}} \right) \left(\frac{56 \text{ g KOH}}{1 \text{ mol KOH}} \right) \\ &= 189 \text{ g KOH} \end{aligned}$$

SAP's

Fat	g NaOH/kg fat	g KOH/kg fat
glyceryl trilaurate	188	263
coconut oil	191	268
glyceryl tripalmitate	149	208
palm oil	142	199
glyceryl tristearate	135	189
tallow	140	196

Why Measure SAP Values?

- The SAP of an oil will vary from supplier to supplier
 - Different ratios of fatty acids
 - Different quantities of unsaponifiables
 - Seasonal variation

Why Measure SAP Values?

- The purity of NaOH and KOH will vary from supplier to supplier
 - Different moisture content
 - Sodium and potassium carbonate
 - Hygroscopic nature
- Quality Assurance
- Oils with unknown or uncertain SAP's

SAP's by Brute Force

- Suppose Palm Oil has an SAP between 140 and 146: make 9 batches of soap
 - 139, 140, 141, 142, 143, 144, 145, 146, 147 g NaOH / kg oil
- Test each cured soap for excess alkali
- About half of these soaps will be too alkaline for use

Making Little Soaps for Analysis

- Precise weighing of small quantities
- Battery acid and phenolphthalein
- KOH and alcohol instead of NaOH and water
- 20 g of oil or fat
- Oven curing of sample soaps

The Balance



The Jennings JScale JS-50x can weigh up to 50 g to within 0.01 g. The auto-off feature can be disabled. It uses AAA batteries. It costs about \$50.

Weighing Synthetically



Weighing Analytically



Battery Acid



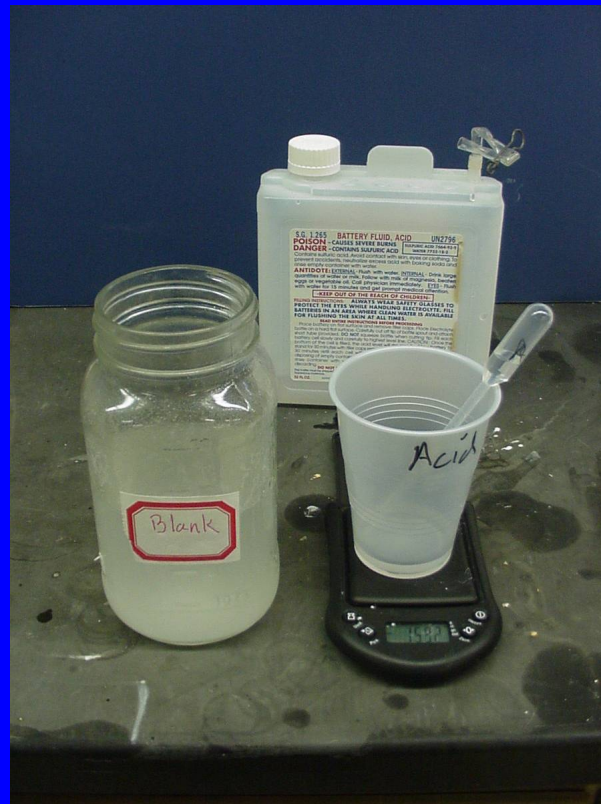
Standardizing the Battery Acid

- Half-fill a one-quart glass jar with distilled water
- Analytically weigh 10.XX g of NaOH or KOH into the jar
- Add 3 drops of 1% phenolphthalein indicator
- Analytically weigh battery acid into jar until endpoint
- Record the weight of acid required to neutralize 10.XX g of base

Start of Titration



The Endpoint



Standardized Battery Acid

- In this case it took 33.52 g of acid to titrate 9.96 g of NaOH
- In this case it took 22.74 g of acid to titrate 10.07 g of KOH

6% Alcoholic KOH



Making Liquid Soap

- Synthetically weigh 100.00 g of alcoholic KOH into a one-quart glass jar
- Analytically weigh 20.XX g of melted oil into the jar
- Screw lid onto jar--lid should have small hole in it
- Shake the solution until thoroughly mixed
- Cure in oven for one hour at 160°F

The Soap Oven



Soap Curing in the Oven



Titration the Blank

- Synthetically weigh 100.00 g of alcoholic KOH into a one-quart glass jar
- Add distilled water until jar is half full
- Add 3 drops of 1% phenolphthalein indicator
- Analytically weigh battery acid into jar until endpoint
- In this case it took 16.68 g of acid to titrate 100.00 of KOH solution

Titrating the Soap

- Remove cured liquid soap from oven
- Add distilled water until jar is half full
- Add 3 drops of 1% phenolphthalein indicator
- Analytically weigh battery acid into jar until endpoint
- In this case it took 7.02 g of acid to titrate soap

The Important Measurements

- 33.52 g acid = 9.96 g NaOH
- 22.74 g acid = 10.07 g KOH
- 20.00 g of palm oil to make soap
- 16.68 g acid = blank
- 7.02 g acid = soap

The SAP Calculation

$$\begin{aligned} ? \text{ g NaOH} &= 1000 \text{ g Fat} \left(\frac{16.68 - 7.02 \text{ g Acid}}{20.00 \text{ g Fat}} \right) \left(\frac{9.96 \text{ g NaOH}}{33.52 \text{ g Acid}} \right) \\ &= 144 \text{ g NaOH} \end{aligned}$$

$$\begin{aligned} ? \text{ g KOH} &= 1000 \text{ g Fat} \left(\frac{16.68 - 7.02 \text{ g Acid}}{20.00 \text{ g Fat}} \right) \left(\frac{10.07 \text{ g KOH}}{22.74 \text{ g Acid}} \right) \\ &= 214 \text{ g KOH} \end{aligned}$$

Palm Oil SAP's

Fat	g NaOH/kg fat	g KOH/kg fat
Hurst (1907)	144	202
Gadd (1913)	144	202
Thomssen and Kemp (1937)	140-146	196-205
Levitt (1951)	143-146	200-205
Cavitch (1997)	142	199
McDaniel (2000)	142	199
Dunn and English (2006)	144	214

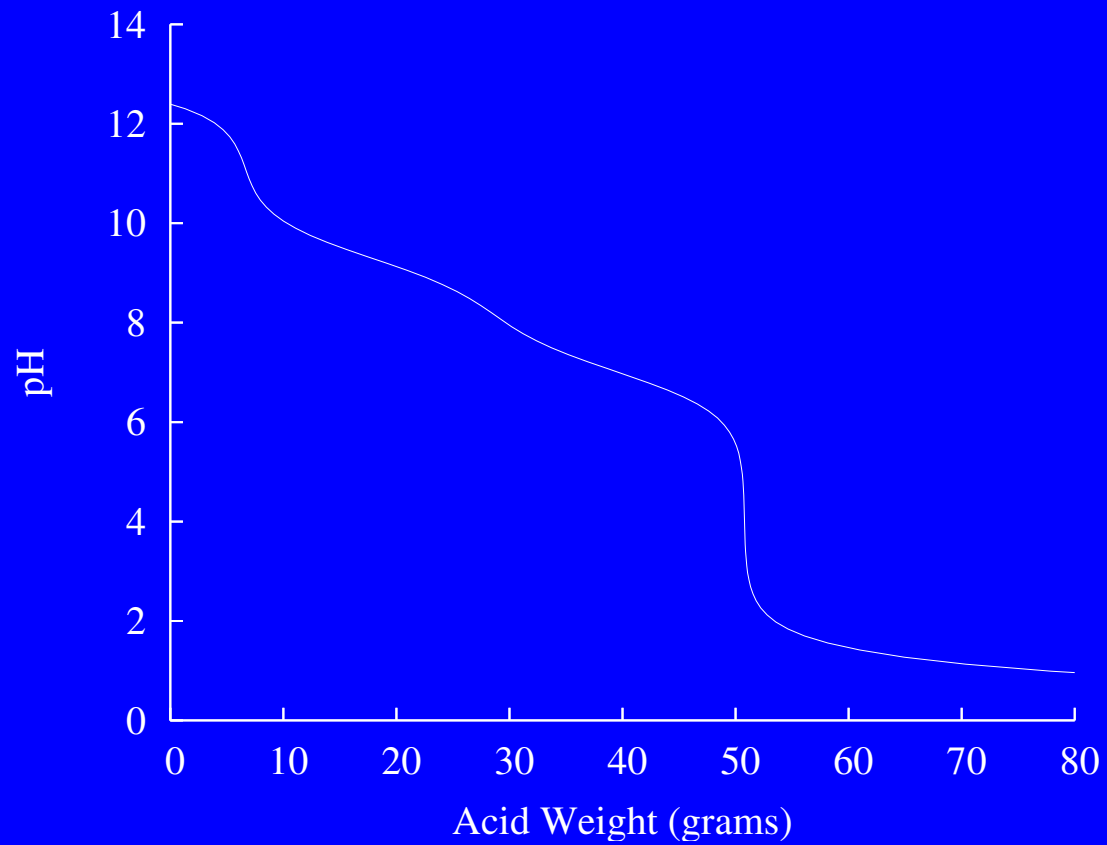
Is It Worth the Trouble

- About 2 hours, start to finish
- Save time by testing several oils at once
 - Several soaps can oven-cure simultaneously
 - The same blank can be used for several soaps
- Good SAP needed when lye discount is small

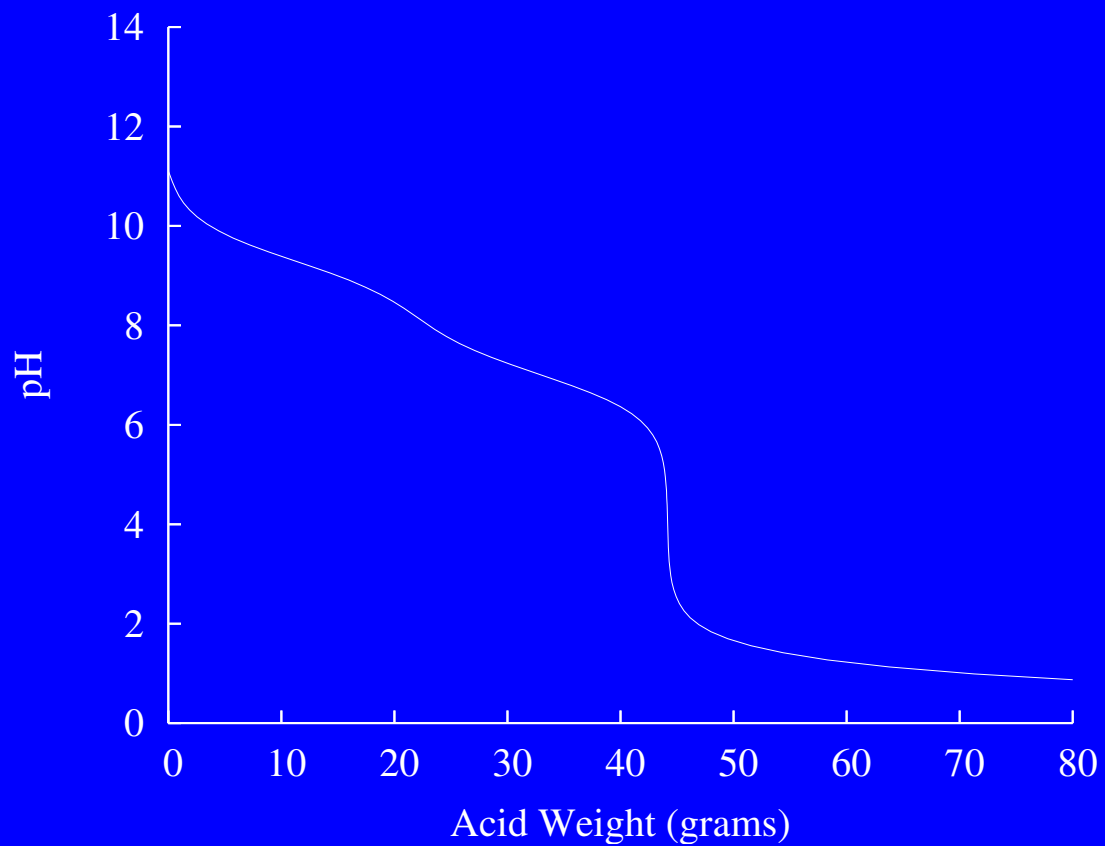
Lye Discount

- Why do we discount lye?

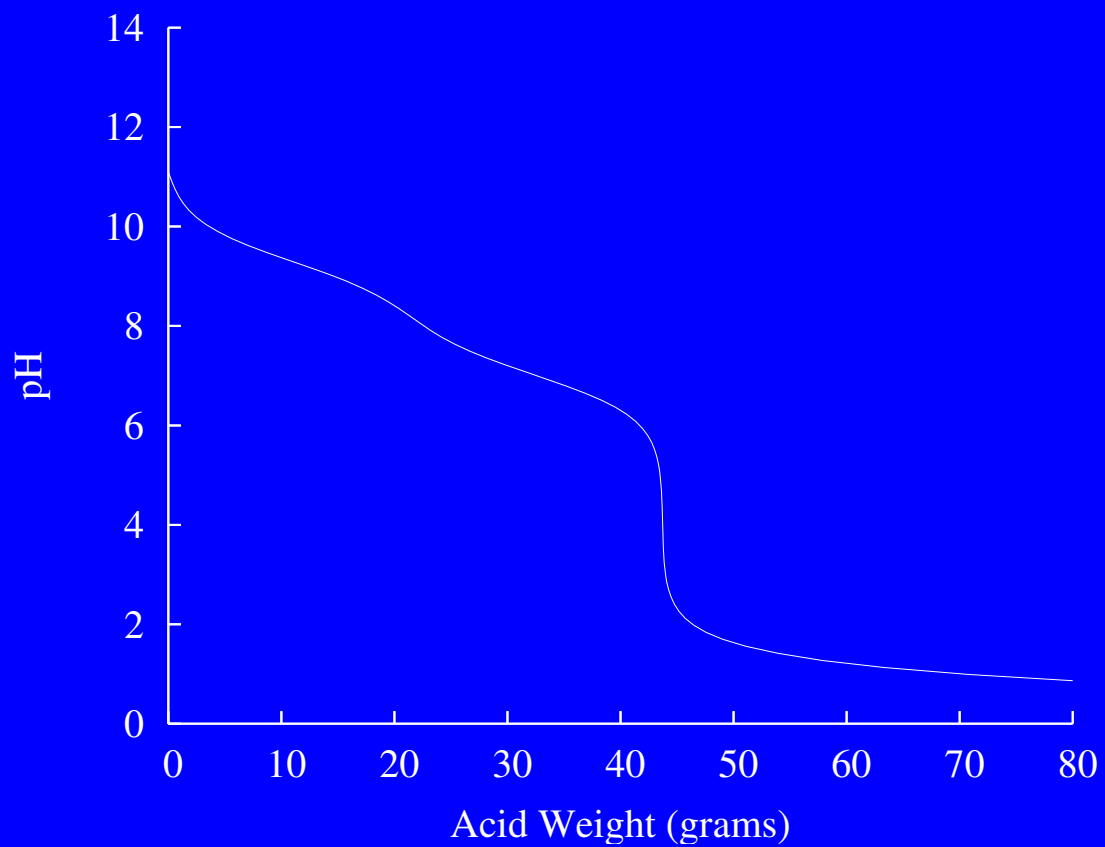
2% Lye Excess



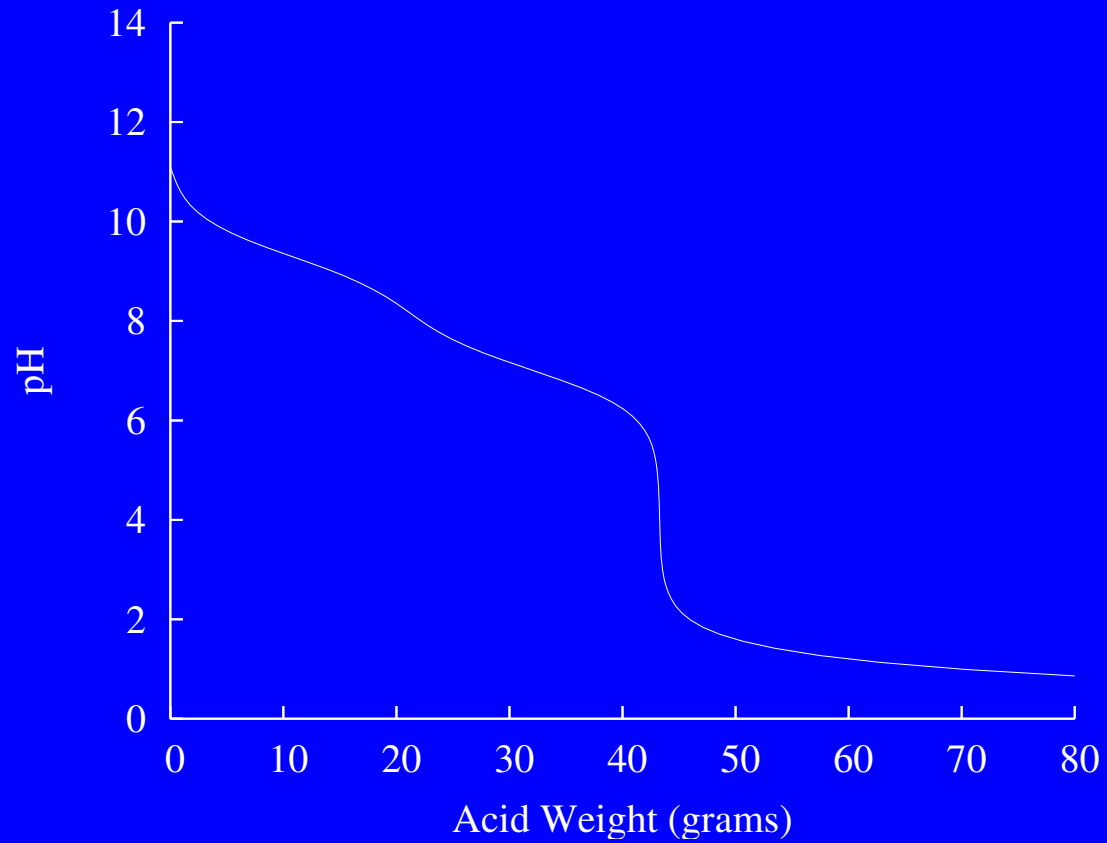
0% Lye Excess



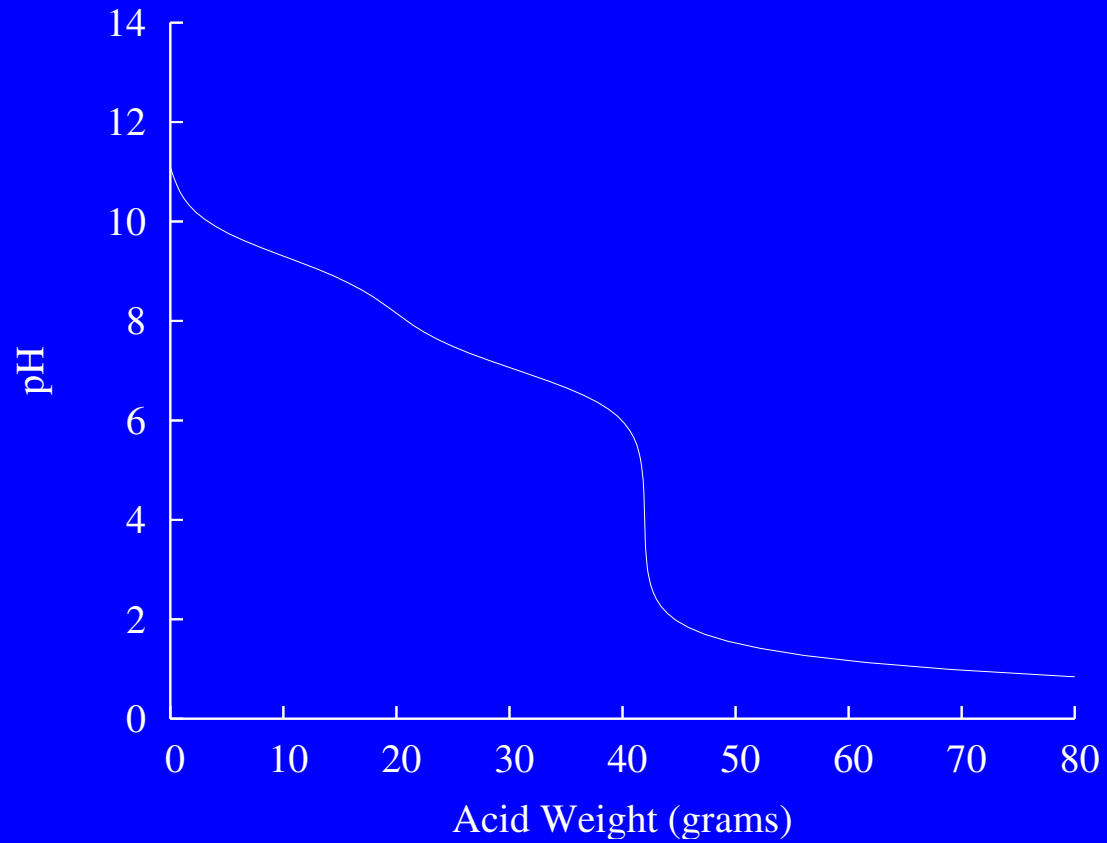
1% Lye Discount



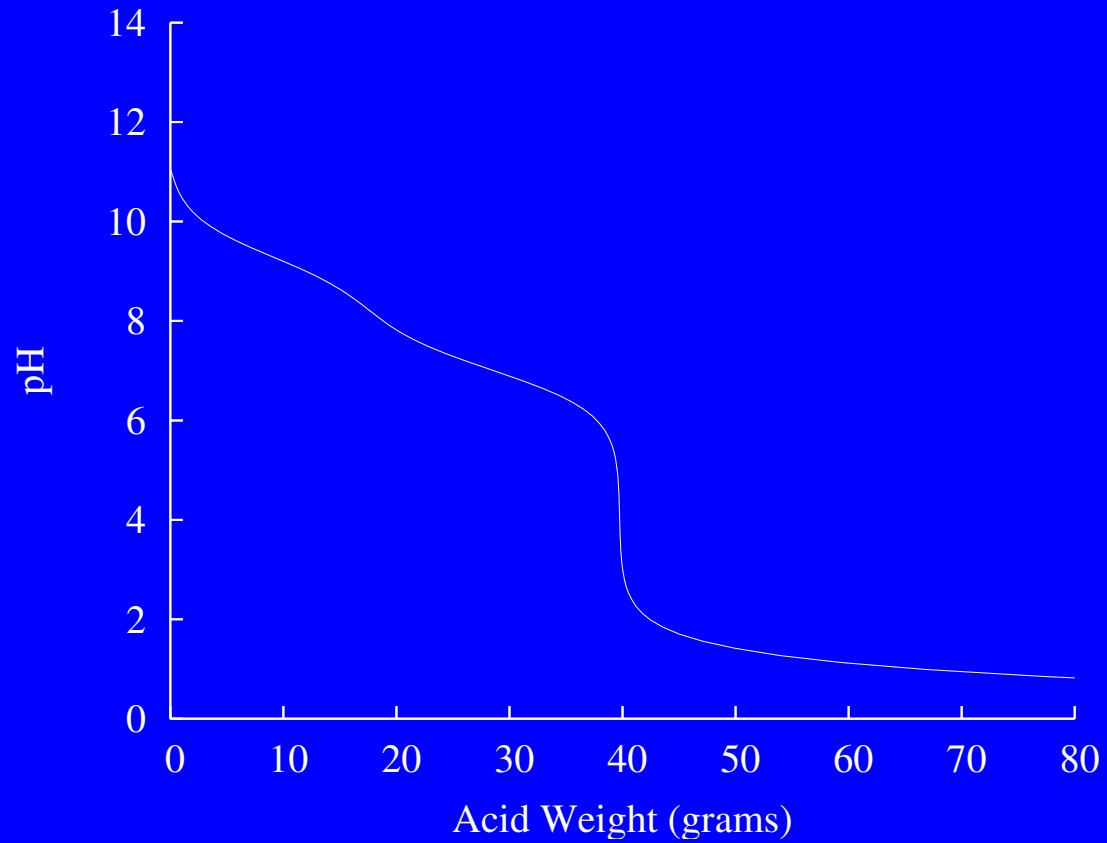
2% Lye Discount



5% Lye Discount



10% Lye Discount



DOS Update

- 8 additives were tested at 3 different concentrations
- Treated olive oil soaps were aged at 50°C for 1800 hours
- Shelf life was determined by measuring color of soaps over time
- When color density reached twice its initial value, soap was deemed to have expired
- Ineffective additives: Vitamin E, BHA, Sodium Citrate, Carnosic Acid

Effective Additives

- 0.03% EDTA
- 0.07% BHT
- 0.12% Rosemarinic Acid

- When buying ROE, maximize Rosemarinic Acid content if possible
- EDTA was very effective even at very small concentrations

Metal Contamination

- EDTA seems to work by sequestering metals
- Calcium and Iron reduce shelf life
- Copper has no effect on shelf life
- Use distilled water if your tap water is high in Calcium or Iron
- Calcium and Iron may be present in oils or lyes

EDTA Safety

“Final Report on the Safety Assessment of EDTA, Calcium Disodium EDTA, Diammonium EDTA, Dipotassium EDTA, Disodium EDTA, TEA-ADTA, Tetrasodium EDTA, Tripotassium EDTA, Trisodium EDTA, HEDTA, and Trisodium HEDTA” International Journal of Toxicology, 21, pp. 95-142, 2002

- Cosmetic Ingredient Review Expert Panel
- Oral toxicity in test animals was minimal
- Dermal toxicity and irritation was minimal
- Conclusion: EDTA is safe for use in cosmetics

Why Talk of Cancer?

- Very small amounts of Nitrilotriacetate can be found in EDTA
- Nitrilotriacetate is a potential oral carcinogen in rats at large doses
- Nitrilotriacetate is absorbed in the gut of the rat but not the human
- Nitrilotriacetate is absorbed in the gut of the rat but not the human
- Ask for MSDS when you purchase EDTA, look for nitrilotriacetate

Conclusions

- You can measure SAP with a \$50 scale
- Excessive lye discount is not necessary
- You can eliminate DOS
- A chemistry book for soapmakers?
- (cavemanchemistry.com)

Questions

Saponification Values

Kevin M. Dunn, Hampden-Sydney College

HSMG 2006

- (<http://cavemanchemistry.com>)
- (<http://oldwillknott.com>) Jennings JScale JS-50x
- (<http://cynmar.com>) Transfer pipettes, phenolphthalein
- (<http://boyercorporation.com>) NaOH, KOH
- Auto Parts Store: battery acid
- Walmart, etc.: Denatured alcohol

Equations

- 33.52 g acid = 9.96 g NaOH
- 20.00 g of palm oil to make soap
- 16.68 g acid = blank (100.00 g of 6% alcohol)
- 7.02 g acid = soap

$$\begin{aligned} ? \text{ g NaOH} &= 1000 \text{ g Fat} \left(\frac{16.68 - 7.02 \text{ g Acid}}{20.00 \text{ g Fat}} \right) \left(\frac{9.96 \text{ g NaOH}}{33.52 \text{ g Acid}} \right) \\ &= 144 \text{ g NaOH} \end{aligned}$$

Preventing DOS

- Use 0.03% EDTA (0.3 g / kg oil) add to lye
- Or 0.07% BHT (0.7 g / kg oil) add to lye
- Or 0.12% Rosemarinic Acid (1.2 g ROE / kg oil) add to oil
- When buying ROE, maximize Rosemarinic Acid content if possible
- Ask for MSDS when you purchase EDTA, avoid nitrilotriacetate impurity
- Avoid Calcium and Iron in water used for soapmaking

EDTA Safety

“Final Report on the Safety Assessment of EDTA, Calcium Disodium EDTA, Diammonium EDTA, Dipotassium EDTA, Disodium EDTA, TEA-ADTA, Tetrasodium EDTA, Tripotassium EDTA, Trisodium EDTA, HEDTA, and Trisodium HEDTA” International Journal of Toxicology, 21, pp. 95-142, 2002

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