Solid Fat, Liquid Fat

Model 1. Triglycerides from different sources contains different types of fatty acids, and this gives them different physical properties, like *physical state* (solid, liquid or gas)

Table 10.1. Triglycerides from different food sources

Source	Fatty acids in triglycerides are…	Physical appearance
Animal triglycerides (e.g. butter, lard, tallow from cow, pig etc)	50% Saturated, 50% unsaturated (1-5% of the unsaturated is *trans*)	Solid (fat)
some Fish triglycerides (e.g. fish oil)	*Cis* unsaturated and polyunsaturated (contain *omega-3 fatty acids*)	Liquid (oil)
Plant triglycerides (e.g. peanut oil, olive oil, corn oil)	85% *Cis u*nsaturated and polyunsaturated, 15% saturated	Liquid (oil)

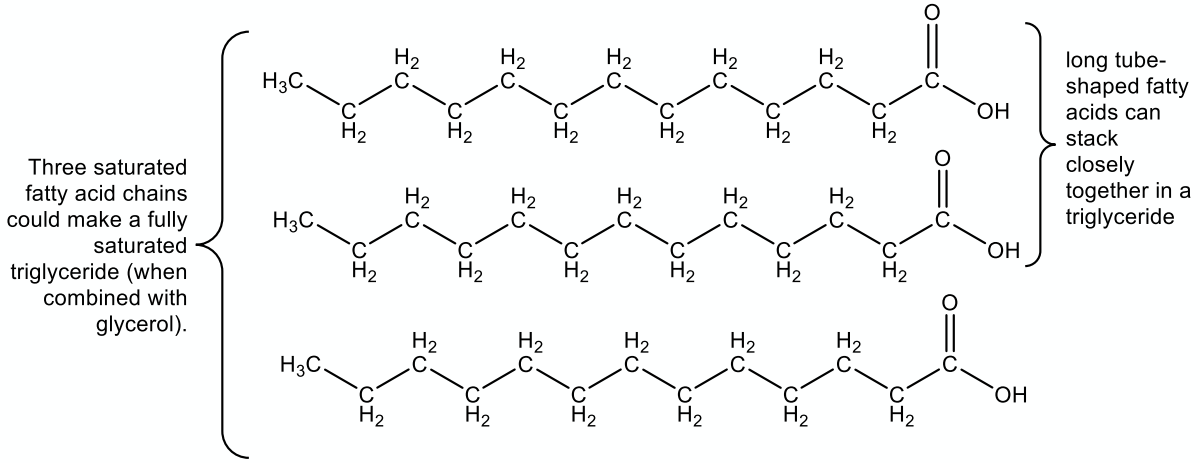
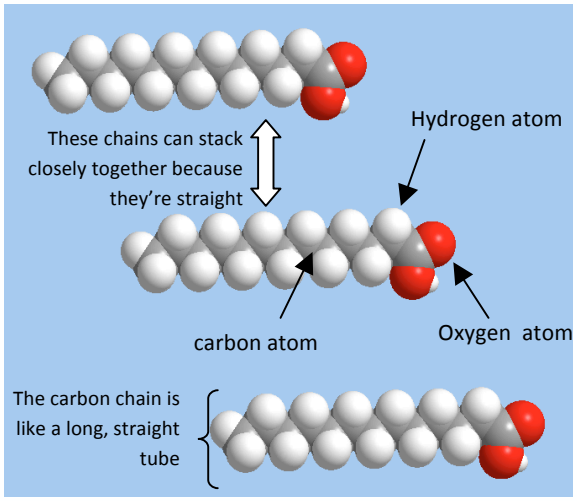


Figure 10.1. Saturated Fatty acids are long and straight and stack easily together



Three saturated fatty acid chains shown in a *space filling model*. This representation shows how much space the actual atoms would take up. The straight tube-like structure of the saturated fatty acid means it can stack closely with another saturated fatty acid in a triglyceride.

Figure 10.2. Saturated Fatty acids make long tubular 3-dimensional structures.

The weak, non-covalent forces that hold the carbon chains together are called *van der Waals forces*. *van der Waals forces* are very weak attractive interactions that occur between non-polar H-C bonds on neighboring molecules. Since they are so weak, the H-C bonds must be close together for the attraction to occur.

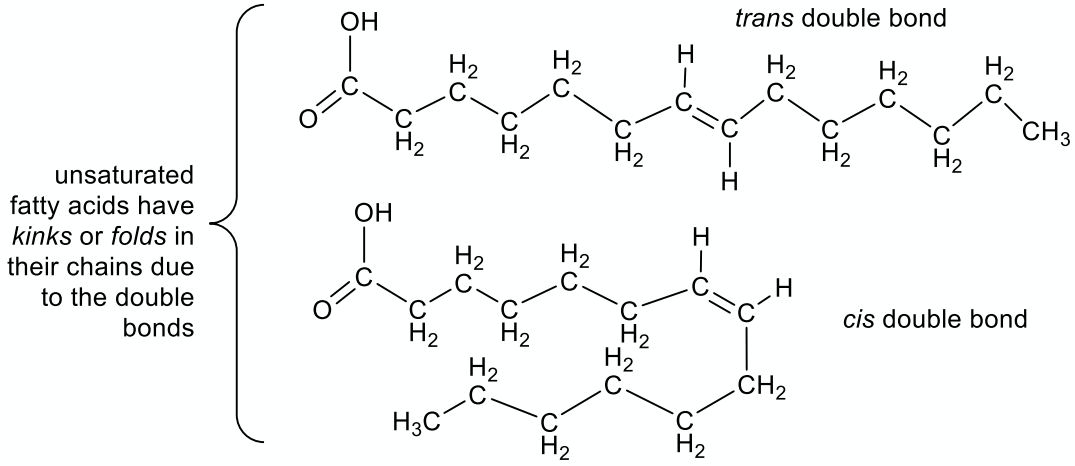
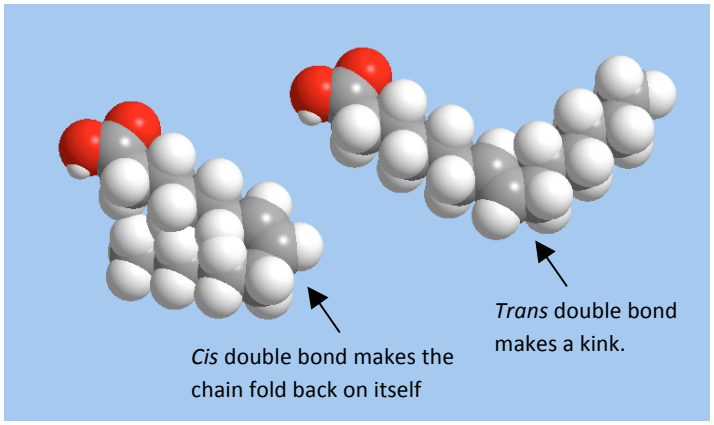


Figure 10.3. Unsaturated fats contain double bonds that put a bend in the chain



Because double bonds change the 3-dimensional shape of unsaturated fatty acids, they can no longer stack as closely together..

Figure 10.4. Unsaturated fats make kinked or folded 3-dimensional structures.

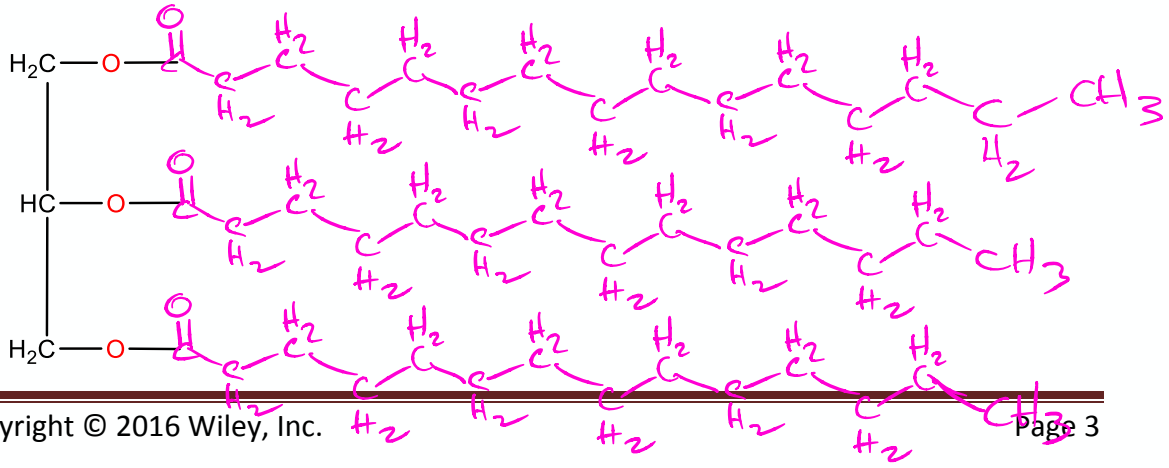
Especially, the *folded* 3-dimensional structure of the cis fatty acid means two chains cannot get close enough for good *van der Waals* contact. The *kinked* trans fatty acids don't form *van der Waals* contacts as well as saturated fatty acids, but they can get closer togther than cis fatty acids

Key Concept

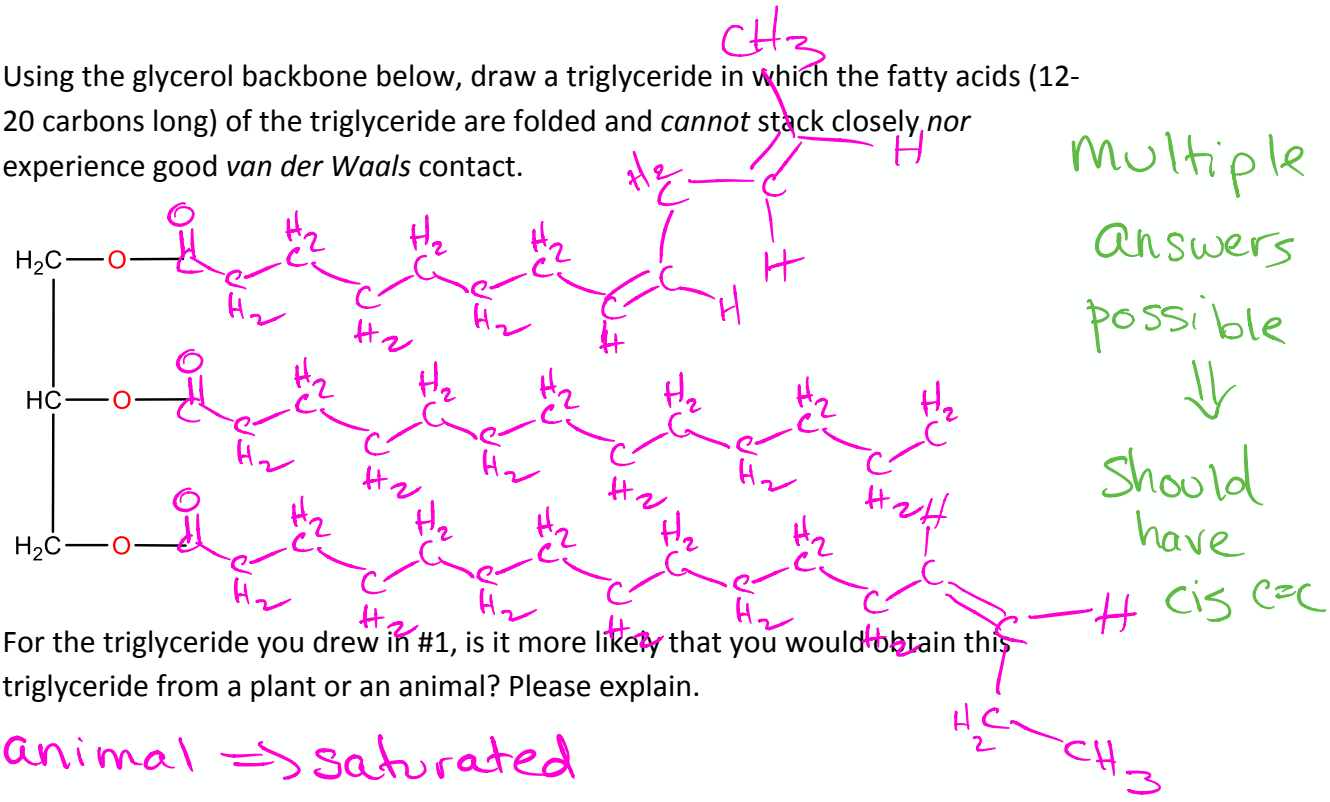
Solids are *solid* because of extensive intermolecular (between molecule) attraction. The large number of interactions holds the molecules tightly together in the solid phase. Liquids have fewer intermolecular attractions – and the molecules flow past each other more easily.

Questions

1. Using the glycerol backbone below, draw a triglyceride in which the fatty acids of the triglyceride are between 12 and 20 carbons long, can stack very closely together and experience good *van der Waals* contact.



2. Using the glycerol backbone below, draw a triglyceride in which the fatty acids (12-20 carbons long) of the triglyceride are folded and *cannot* stack closely *nor* experience good *van der Waals* contact.



multiple answers possible ⇓ Should have cis C=C

3. For the triglyceride you drew in #1, is it more likely that you would obtain this triglyceride from a plant or an animal? Please explain.

animal ⇒ saturated

4. For the triglyceride you drew in #2, is it more likely that you would obtain this triglyceride from a plant or an animal. Please explain.

plant ⇒ unsaturation + polyunsaturated

5. Rank the different types of fatty acids (saturated, trans monounsaturated and cis monounsaturated):
   a. Based on how well they can closely stack and form *van der Waals* contacts within and among triglycerides. Explain your ranking using the phrase *double bonds*.
   b. As solid, semisolid or liquid.

	saturated	trans-mono	cis-mono
a.	stack well	→	don't stack
b.	solid	semi-solid	liquid

6. How might *van der Waals* interactions between H-C bonds of neighboring non-polar triglycerides explain why some triglycerides are solids and some are liquids?

As the number of VDW interactions ↑, ↑ number of solids

7. How might you expect additional double bonds (2-3) to affect the "stackability" (and therefore the *van der Waals* contact) of polyunsaturated fatty acids within triglycerides.

↑ number of C=C ⇒ ↓ stackability

Cis fats are good for you!

Model 2. You've probably heard of vitamins as being *essential* to human health…so essential that we *must* get them from our diet, or we get very sick! Did you also know that some fats are also *essential* nutrients? In particular, the human body cannot make polyunsaturated fats (PUFAs) – so we *must* get them from our diet. Two of the most important fats for human health are linoleic acid and alpha linolenic acid – these "acids" are fatty acids that have been incorporated into plant *triglycerides*. Omega-6 fats are abundantly available in common plant oil such as vegetable oil and olive oil. Omega-3 fats are harder to come by…they are abundant in flaxseed oil, and also in fish oil!

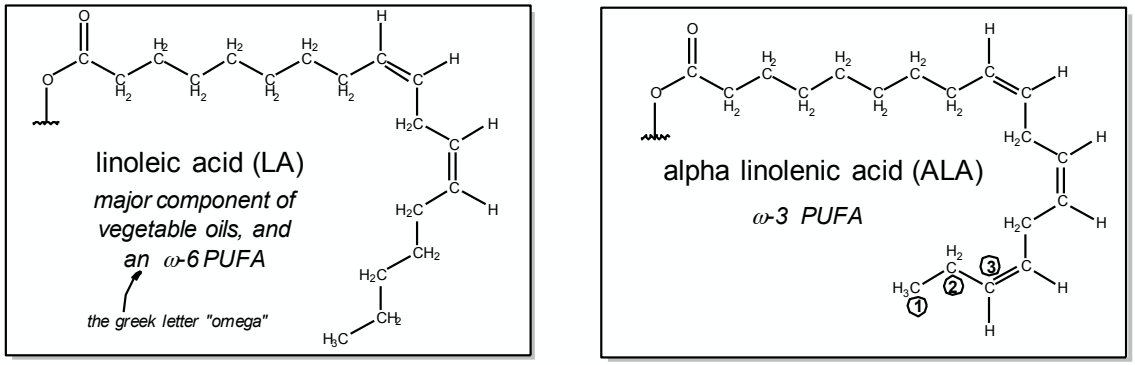
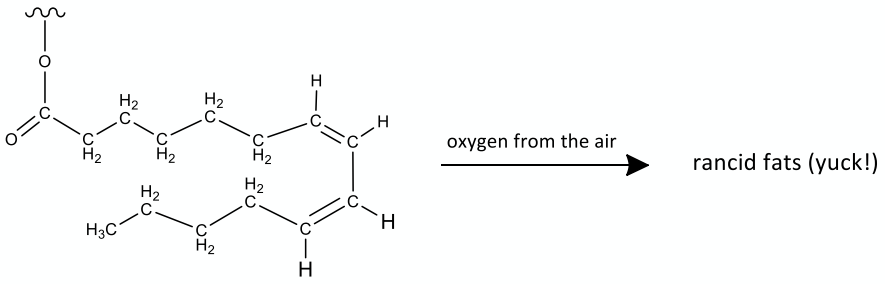


Figure 10.5. Two essential fats – the omega-6 fat Linolenic acid, and the omega-3 fat, alpha linolenic acid.



A fatty acid that is part of a plant triglyceride.
Plant triglycerides are comprised mostly of triglycerides made of cis polyunsaturated fatty acids.

Figure 10.6. Cis unsaturated bonds are prone to oxidation, which creates rancid fats.

PUFAs can only be made inside plants (only plants have the necessary enzymes to make these molecules), but animals (like fish!) can contain high concentrations of PUFAs if the animal's diet is made of PUFA containing plants. Since omega-3 fats are critical for our health *and* they are harder to get in our diets, food manufacturers are trying to add them to everything!

Another feature of naturally occurring polyunsaturated fats is their *stability* from a food production and shelf-life standpoint. Oils with *cis* double bonds are more likely to react with the oxygen in the air (undergoing oxidation) than those with either *trans* double bonds or all single bonds (i.e. saturated fats). Oxidation of fats breaks the long chains into shorter chains to yield stinky and unpleasant tasting products—this process turns the fat *rancid*.[1] In fact, PUFAs like the omega-3s are *so* unstable that they have short shelf lives and do not withstand the heat of cooking.

8. Why are omega-3 containing oils more unstable and prone to oxidation (from oxygen in the air) when compared to omega-6 oils?

Double bond closer to the edge and more exposed.

[1] Kimbrough, *ChemMatters,* 2007

9. Examine Figure 10.5. Considering that "omega" is the very end of the Greek alphabet. What might the name "omega-3" be referring to?

Double bond starts 3 carbons from the end.

10. Nuts (especially walnuts) are quick to become rancid if left out in the air at room temperature, (which is why you are supposed to store them dark and cold – like in the freezer). What about the triglyceride composition of nuts explains why they go rancid so easily?

↓
must have unsaturations

11. Eggland's Best Eggs claim to have 2x the amount of omega-3 fatty acids in their eggs compared to the "other" eggs in the grocery store. Based on what you know about the natural sources of omega-3 fatty acids, how can these farmers get more omega-3's into their eggs?

↳ Diet feed to chicken must be rich in ω-3 fatty acids

Making liquids fats….solid

Model 3. In 11011, the Procter and Gamble company first marketed Crisco - the first *solid* fat that came from plant derived triglycerides. In order to make the unsaturated plant oils into a solid fat, they needed to increase the amount of *van der Waals* contact between the carbon chains…they needed to take out the *folded* fatty acids and make them straight and stackable – the chemical process that makes this possible is called *hydrogenation*.

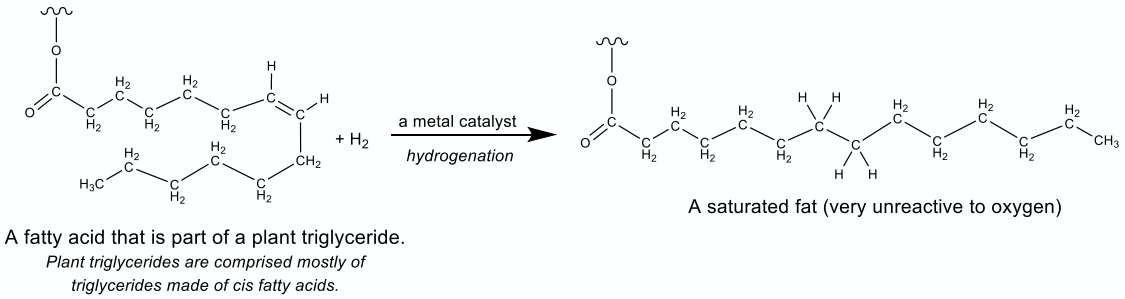


Figure 10.7. Hydrogenation of unsaturated fats makes saturated fat

Table 10.2 Example food products made by hydrogenation and partial hydrogenation

Product	Method	Oil source
Crisco (in 11011)	Hydrogenated and partially hydrogenated	Cottonseed oil: naturally 26% saturated, 18% monounsaturated and 50% polyunsaturated
Margarine (original)	Partially hydrogenated	Corn oil: naturally 13% saturated, 74% monounsaturated and 510% polyunsaturated

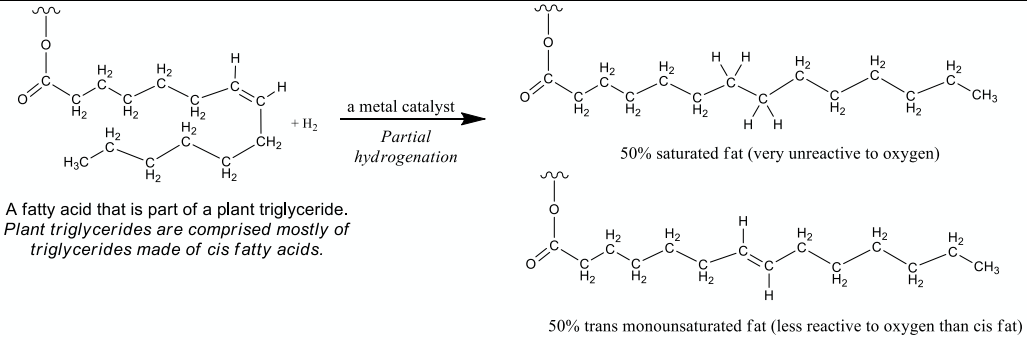


Figure 10.8. Partial Hydrogenation of unsaturated fats makes 50% saturated fat and 50% trans unsaturated fat.

The process of partial hydrogenation delivers less hydrogen to the sample of unsaturated fat. This makes less saturated fat, but another consequence is that the remaining unsaturated fatty acids undergo a chemical reaction that flips the orientation of the double bond – they go from *cis* to *trans*.

Until recently, partially hydrogenated fats were thought to be as healthy as the unsaturated fats they were made from. Indeed, as recently as the late 11080s, margarine was promoted as the healthy alternative to butter, and patients with heart disease or high cholesterol were put on diets that included margarine and other partially hydrogenated vegetable oils[2]. In 2006, the US government started requiring all manufacturers to list the amount of *trans* fats on the nutrition label.

Table 10.3. Health concerns or benefits associated with different triglycerides ("fats")

Saturated Fat	Saturated fats raise blood cholesterol which can contribute to the development of heart disease.[2] Therefore, saturated fats are acceptable in small amounts, but if your diet is too high in saturated fats, you are more likely to experience a variety of health problems, including obesity, high blood pressure, heart disease, and some types of cancers. This is why health care professionals advise us to eat a diet that is low in saturated fats[3].
Unsaturated Fat	Overall, unsaturated fats are healthier choices than saturated fats. Unsaturated fats are the primary component of plant based oils. But, as shown below, the latest studies indicate that the *type* of unsaturated fat you eat directly affects your health[2].
Trans unsaturated fats	*Trans* fats are rarely found in nature, and are present in foods most often as a result of *partial hydrogenation*, a chemical process. *Trans* fats also raise blood cholesterol (like saturated fats) which can contribute to the development of heart disease. This probably has to do with the fact that their "straighter" 3-dimensional structure resembles saturated fats more closely in comparison to *cis* fats[1].
Cis unsaturated fat	Triglycerides containing cis fatty acids are found naturally from plant sources and work to lower cholesterol. These "cis fats" include the omega-3 fatty acids. Omega-3 fatty acids made by plants; the best sources are walnuts and flaxseed (linseed oil). In fact the omega-3 fatty acids found in fish (the highest concentration in Atlantic salmon) originate from the tiny oceanic plants called phytoplankton the fish consume (so freshwater fish have negligible amounts of omega-3 fatty acids). Some omega-3's like linolenic acid are essential in the human diet for cardiovascular and immune function. Omega-3 fatty acids are also essential to the development and function of the brain and retina, and research indicates that an abundance in our diet helps ensure the health of central nervous system in infancy and throughout life[1].

12. Rank the types of fat (saturated, trans monounsaturated and cis monounsaturated) according to how quickly they will go *rancid*. Where does a fat that contains linolenic acid fit in this ranking? Why?

[2] McGee, H. On Food and Cooking, 2004.
[3] From "The Solid Facts about Trans Fats" by Doris R. Kimbrough, ChemMatters, Dec 2007

13. Explain how complete hydrogenation makes a plant oil behave like an animal fat.

Takes C=C and adds hydrogen atoms.
Fats become saturated
↳animal fat

14. Why do you think we are warned by health professionals to avoid diets high in saturated fat and foods that contain *trans* fat?

Increase chances of heart disease.

15. If you wanted to improve the health of your diet by removing *saturated fat* and replacing it with a better-for-you fat…what food could you remove from your diet and what should you replace it with?

Replace beef + poultry with fish + veg.

Putting it all together:

16. What type of fat is an omega-3 fatty acid? Saturated, monounsaturated or polyunsaturated? Is this consistent with the fact that omega-3's come from plant sources?

Polyunsaturated. Yes, plants can make polyunsaturated fats; animals can not.

17. Fat from beef and lamb is noticeably "harder" (i.e. more solid) than fat from poultry or pork. What can you conclude about the composition of triglycerides (fats) in beef and lamb vs. poultry and pork?

more saturated → less saturated.

18. Food manufacturers sell "spreadable" butter that is softer and easily spread, right out of the refrigerator. This "spreadable butter" is made of triglycerides with 41% saturated, 45% monounsaturated, and 14% polyunsaturated fatty acids. Stick butter (which is harder and not easily spread) is made of triglycerides with 68% saturated, 28% monounsaturated, and 4% polyunsaturated fatty acids. Explain the different physical properties of the two butters as a function of their fatty acid content (in this context, the fatty acids are *part* of triglycerides).[4]

Stick butter has higher amount saturated fats, which has more VDW interactions and makes the molecules stick together more.

19. Partial hydrogenation was attractive to food manufacturers because it increased product shelf life and reduced refrigeration requirements In effect, partial hydrogenation prevented the fats from going rancid. Why?

Oxidative rancidity occurs in the presence of C=C. Hydrogenation saturates the molecule (↓ number of C=C)

[4] Nutrition information publicly available from the USDA nutrient database (ndb.nal.usda.gov)