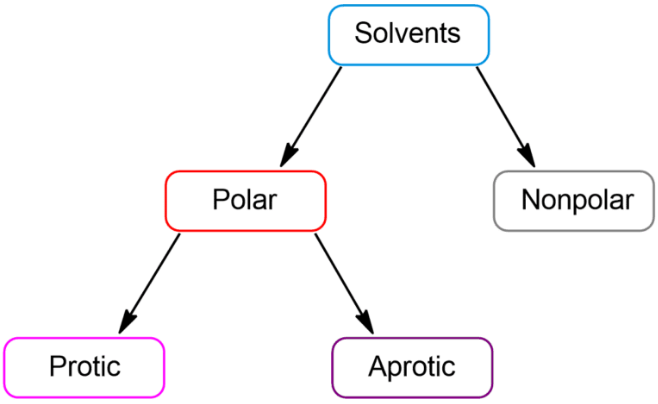
1. Solvent

- A solvent (as per the Latin solvō, "loosen, untie, solve") is a substance that dissolves a solute, resulting in a solution. A solvent is usually a liquid but can also be a solid, a gas, or a supercritical fluid. The quantity of solute that can dissolve in a specific volume of solvent varies with temperature.
- A solvent is a liquid that serves as the medium for a reaction. It can serve two major purposes:
  (i) (Non-participatory) to dissolve the reactants. Remember "like dissolves like"? Polar solvents are best for dissolving polar reactants (such as ions); nonpolar solvents are best for dissolving nonpolar reactants (such as hydrocarbons).
  (ii) Participatory: as a source of acid (proton), base (removing protons), or as a nucleophile (donating a lone pair of electrons). The only class of solvents for which this is something we generally need to worry about are polar protic solvents.
- Solvents are generally classified by the polarity, and considered either polar or non-polar, as indicated by the dielectric constant. However, as with many properties, the polarity is a continuous scale, and the correct question is not "is it polar or non-polar" but "how polar is it."
- Solvents can be classified into two categories: polar and non-polar.



1.2. "polar" and "non-polar" meaning

- ***Polar solvents*** have large dipole moments (aka "partial charges"); they contain bonds between atoms with very different electronegativities, such as oxygen and hydrogen.
- ***Non polar solvents*** contain bonds between atoms with similar electronegativities, such as carbon and hydrogen (think hydrocarbons, such as gasoline). Bonds between atoms with similar electronegativities will lack partial charges; it's this absence of charge which makes these molecules "non-polar".
- There are two direct ways of measuring polarity. One is through measuring a constant called "dielectric constant" or permitivity. The greater the dielectric constant, the greater the polarity (water = high, gasoline = low). A second comes from directly measuring the dipole moment.

1.3. Polar Solvents

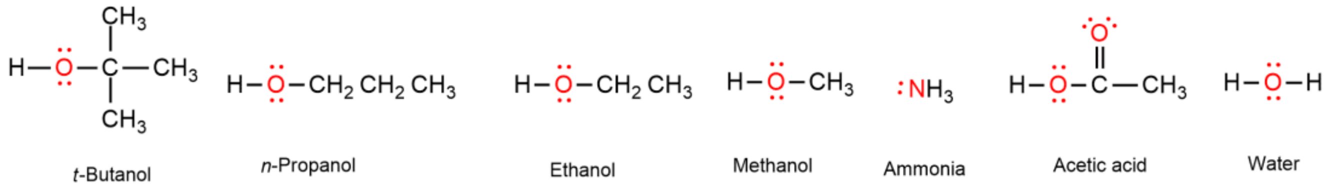
- **Polar solvents** contain bonds between atoms with very different electronegativities, such as oxygen and hydrogen, and have large dipole moments. Non-polar solvents contain bonds between atoms with similar electronegativities, such as carbon and hydrogen. These polar solvents can form hydrogen bonds with water to dissolve in water whereas non-polar solvents are not capable of strong hydrogen bonds.

- Polar solvents can be further divided into protic and aprotic.

1.3.1. Polar Protic Solvents

- Polar protic solvents are capable of hydrogen bonding because they contain at least one hydrogen atom connected directly to an electronegative atom (such as O-H or N-H bonds). They solvate cations and anions effectively. Polar protic solvents are water, ethanol, methanol, ammonia, acetic acid, and others.
- Polar protic solvents tend to have high dielectric constants and high dipole moments.
- Furthermore, since they possess O-H or N-H bonds, they can also participate in hydrogen bonding. These solvents can also serve as acids (sources of protons) and weak nucleophiles (forming bonds with strong electrophiles).

Polar Protic Solvents



Polar Protic Solvents		Dielectric Constant	Dipole Moment
$:NH_3$	Ammonia	~25	1.40 D
$H-O-C(CH_3)_2-CH_3$	*t*-Butanol	12	1.70 D
$H-O-CH_2CH_2CH_3$	*n*-Propanol	20	1.68 D
$H-O-CH_2CH_3$	Ethanol	25	1.69 D
$H-O-CH_3$	Methanol	33	1.70 D
$H-O-C(=O)-CH_3$	Acetic acid	6.2	1.74 D
$H-O-H$	Water	80	1.85 D

Common uses:

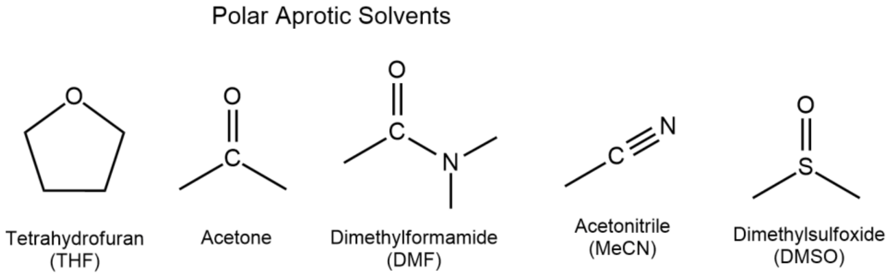
All: As the solvent for their conjugate bases

e.g. $NH_2^{\ominus}$/ NH_3 $EtO^{\ominus}$/ EtOH $HO^{\ominus}$/ H_2O *t*-Bu$O^{\ominus}$/ *t*-BuOH

1.3.2. Polar Aprotic Solvents

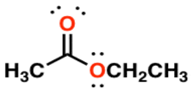
- Polar aprotic solvents contain no hydrogen atoms connected directly to an electronegative atom and they are not capable of hydrogen bonding. These are acetone, dimethyl sulfoxide, DMF (N,N-dimethylformamide), acetonitrile, HMF (hydroxymethylfurfural), crown ethers etc.
- An aprotic solvent is a solvent that has no O-H or N-H bonds.
- The "a" means "without", and "protic" refers to protons or hydrogen atoms.
- The specific meaning of aprotic is that the molecules have no H atoms on O or N.

- This means that the molecules cannot form H-bonds with themselves, but they may accept H-bonds from other molecules.
- For example, acetone does not have an O-H group, but it has a C=O group that can participate in H-bonding. So acetone is an aprotic solvent.



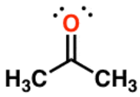
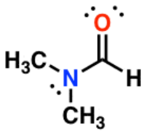
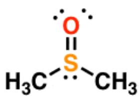
1.3.2.1. "Borderline" Polar Aprotic Solvents Have Small Dipole Moments and Low (<10) Dielectric Constants

- These solvents have moderately higher dielectric constants than the nonpolar solvents (between 5 and 20). Since they have intermediate polarity, they are good "general purpose" solvents for a wide range of reactions. They are "aprotic" because they lack O-H or N-H bonds. For our purposes they don't participate in reactions: they serve only as the medium.

"Borderline" Polar Aprotic Solvents		Dielectric Constant	Dipole Moment
CH_2Cl_2	Dichloromethane	9.1	1.60 D
	Tetrahydrofuran (THF)	7.5	1.75 D
	Ethyl acetate	6.0	1.78 D

1.3.2.3. *Polar Aprotic Solvents with Large (>10) Dielectric Constants*

These solvents all have large dielectric constants (>20) and large dipole moments, but they do not participate in hydrogen bonding (no O-H or N-H bonds). Their high polarity allows them to dissolve charged species such as various anions used as nucleophiles (e.g. CN^-, HO^-, etc.). The lack of hydrogen bonding in the solvent means that these nucleophiles are relatively "free" in solution, making them more reactive. For our purposes these solvents do not participate in reactions.

Polar Aprotic Solvents		Dielectric constant	Dipole Moment
	Acetone	21	2.88 D
	*N,N*-Dimethylformamide (DMF)	38	3.82 D
$H_3C{-}C{\equiv}N{:}$	Acetonitrile (MeCN)	37	3.92 D
	Dimethyl sulfoxide (DMSO)	47	3.96 D

1.3.3. Difference Between Protic and Aprotic Solvents

Basis of Comparison	Protic	Aprotic
Description	Protic solvents are capable of hydrogen bonding because they contain at least one hydrogen atom connected directly to an electronegative atom (such as O-H or N-H bonds).	Aprotic solvents contain no hydrogen atoms connected directly to an electronegative atom and they are not capable of hydrogen bonding.
Example	Water, alcohol, formic acid, hydrogen fluoride, Ethanol, methanol, ammonia, acetic acid etc	Acetone, dimethyl sulfoxide, DMF (N,N-dimethylformamide), acetonitrile, HMF (hydroxymethylfurfural), crown ethers
Hydrogen Bonding	They display hydrogen bonding.	They display hydrogen bonding.
Ability	They are often used to dissolve salts.	They can dissolve salt. Their ability to dissolve salts depends strongly on the nature of the salt.
Acidic Hydrogen	They have acidic hydrogen (although they may be very weak acids such as ethanol).	They do not have acidic hydrogen.
Effect on S_{N1} & S_N2	S_N1 reactions are significantly faster in polar Protic solvents than in polar Aprotic solvents.	S_N2 reactions are significantly faster in polar Aprotic solvents than in protic solvents.
Carbocation	S_N1 reaction works well for tertiary alkyl halide because the loss of the leaving group forms a tertiary carbonation which is the most stable form of carbocations. A polar protic solvent will stabilize this carbocation.	Polar Aprotic solvents work well for S_N2 reactions because they do not solvate nucleophiles. For example, if we have potassium fluoride and crown ether as a solvent, this ether will solvate potassium, not fluoride. Then, the fluoride will be free to participate in the reaction with a substrate.
Dielectric Constants & Polarity	They have high dielectric constants and high polarity.	They generally have intermediate dielectric constants and high dipole moments.
O-H &N-H Bonds	They are rich with O-H and N-H bonds.	They lack O-H and N-H bonds.
Application	All protic solvents are prone to proton reduction to yield hydrogen gas and are only used for reductive electrochemistry.	Aprotic solvents find applications in various industries such as oil and gas, paints and coatings, electronics, and pharmaceuticals.

1.3.4. Need to Know About Protic and Aprotic Solvent

1.3.4.1. About Protic Solvent

(i) Protic solvents are capable of hydrogen bonding because they contain at least one hydrogen atom connected directly to an electronegative atom (such as O-H or N-H bonds).

(ii) Examples of Protic solvents are water, alcohol, formic acid, hydrogen fluoride, Ethanol, methanol, ammonia, acetic acid etc.

(iii) Protic solvents display hydrogen bonding.

(iv) Protic solvents have an acidic hydrogen (although they may be very weak acids such as ethanol).

(v) Polar protic solvents are often used to dissolve salts.

(vi) S_N1 reactions are significantly faster in polar Protic solvents than in polar Aprotic solvents.

(vii) S_N1 reaction works well for tertiary alkyl halide because the loss of the leaving group forms a tertiary carbonation which is the most stable form of carbocations. A polar protic solvent will stabilize this carbocation.

(viii) Polar Protic solvents have high dielectric constants and high polarity.

(ix) Polar Protic solvents are rich with O-H and N-H bonds.

(x) All protic solvents are prone to proton reduction to yield hydrogen gas and are only used for reductive electrochemistry.

1.3.4.1. About Aprotic Solvent

(i) Aprotic solvents contain no hydrogen atoms connected directly to an electronegative atom and they are not capable of hydrogen bonding.

(ii) Examples of Aprotic solvents are acetone, dimethyl sulfoxide, DMF (N,N-dimethylformamide), acetonitrile, HMF (hydroxymethylfurfural), crown ethers etc.

(iii) Aprotic solvents are solvents that can accept hydrogen bonds.

(iv) Aprotic solvents do not have acidic hydrogen.

(v) Polar Aprotic solvents can dissolve salt. Their ability to dissolve salts depends strongly on the nature of the salt.

(vi) S_N2 reactions are significantly faster in polar Aprotic solvents than in protic solvents.

(vii) Polar Aprotic solvents work well for SN2 reactions because they do not solvate nucleophiles. For example, if we have potassium fluoride and crown ether as a solvent, this ether will solvate potassium, not fluoride. Then, the fluoride will be free to participate in the reaction with a substrate.

(viii) Aprotic solvents generally have intermediate dielectric constants and high dipole moments.

(ix) Aprotic solvents lack O-H and N-H bonds.

(x) Polar Aprotic solvents are generally incompatible with strong bases such as Grignard reagents or t-butyllithium. Aprotic solvents find applications in various industries such as oil and gas, paints and coatings, electronics, and pharmaceuticals.

1.4. Non-Polar Solvents

- These solvents have low dielectric constants (<5) and are not good solvents for charged species such as anions.
- Electric charge in the molecules of non-polar solvents is evenly distributed, therefore the molecules have low dielectric constant. Non-polar solvents are hydrophobic (immiscible with water). Non-polar solvents are lipophilic as they dissolve non-polar substances such as oils, fats, greases.