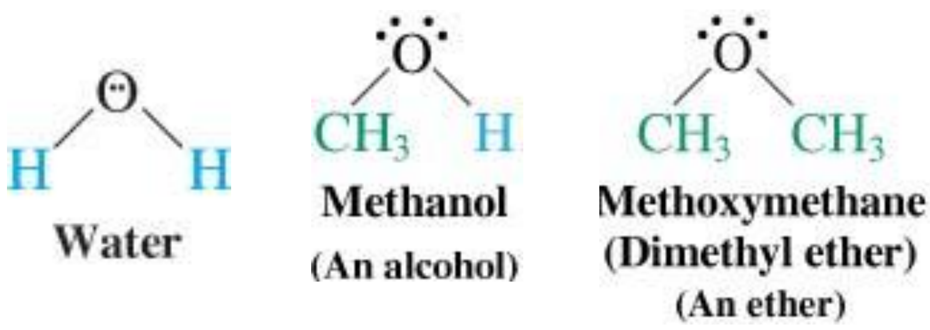
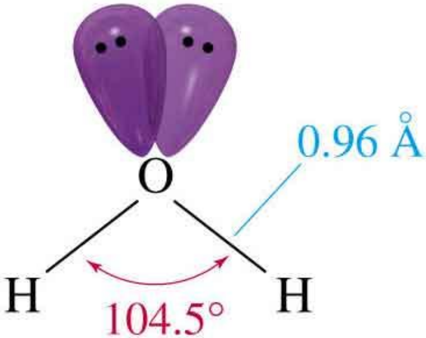
Alcohols

Structure of Alcohols

- Alcohols can be thought of as a derivative of water in which a hydrogen atom has been replaced by an alkyl group.
- Replacement of the 2nd hydrogen on the water molecule leads to an ether.

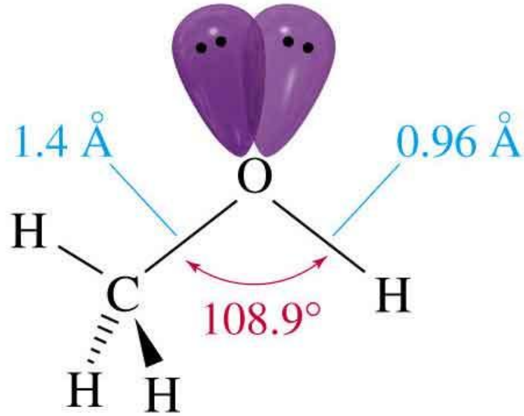


Structure of Alcohols

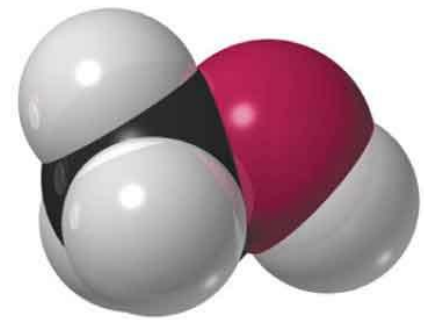


water


water



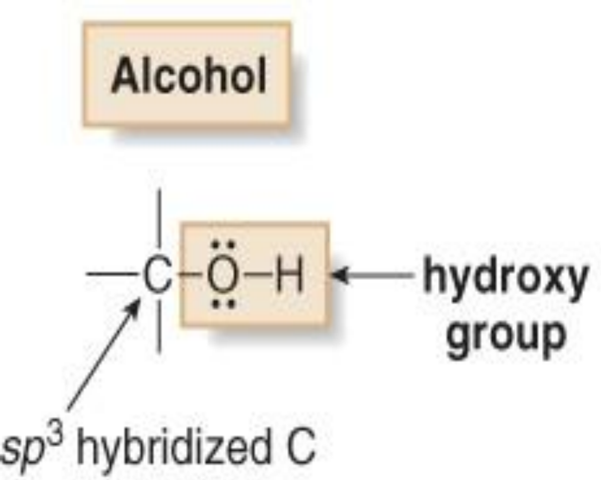
methyl alcohol

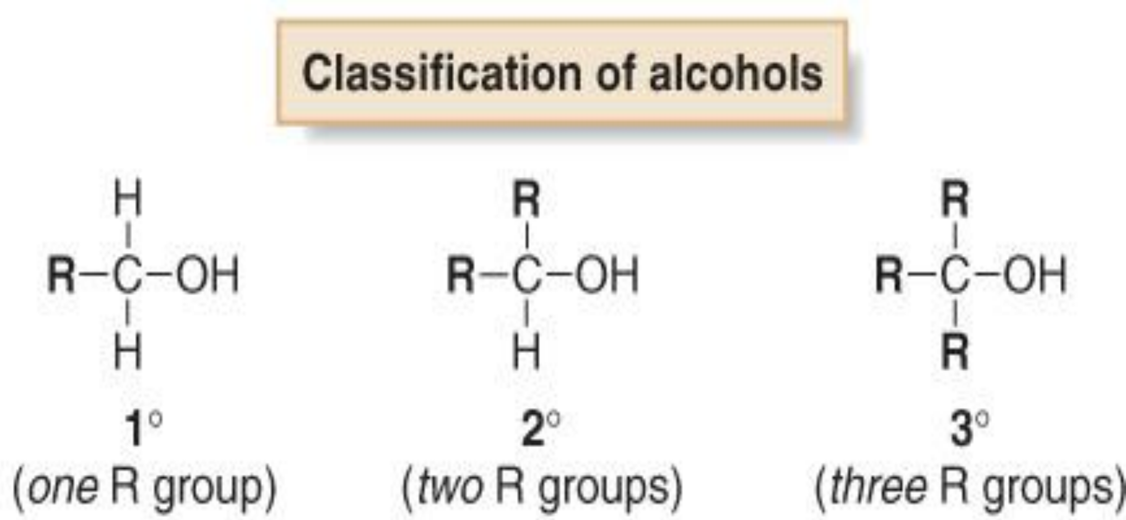

methyl alcohol

- Hydroxyl (OH) functional group
- Oxygen is *sp*^{3} hybridized.

Classification

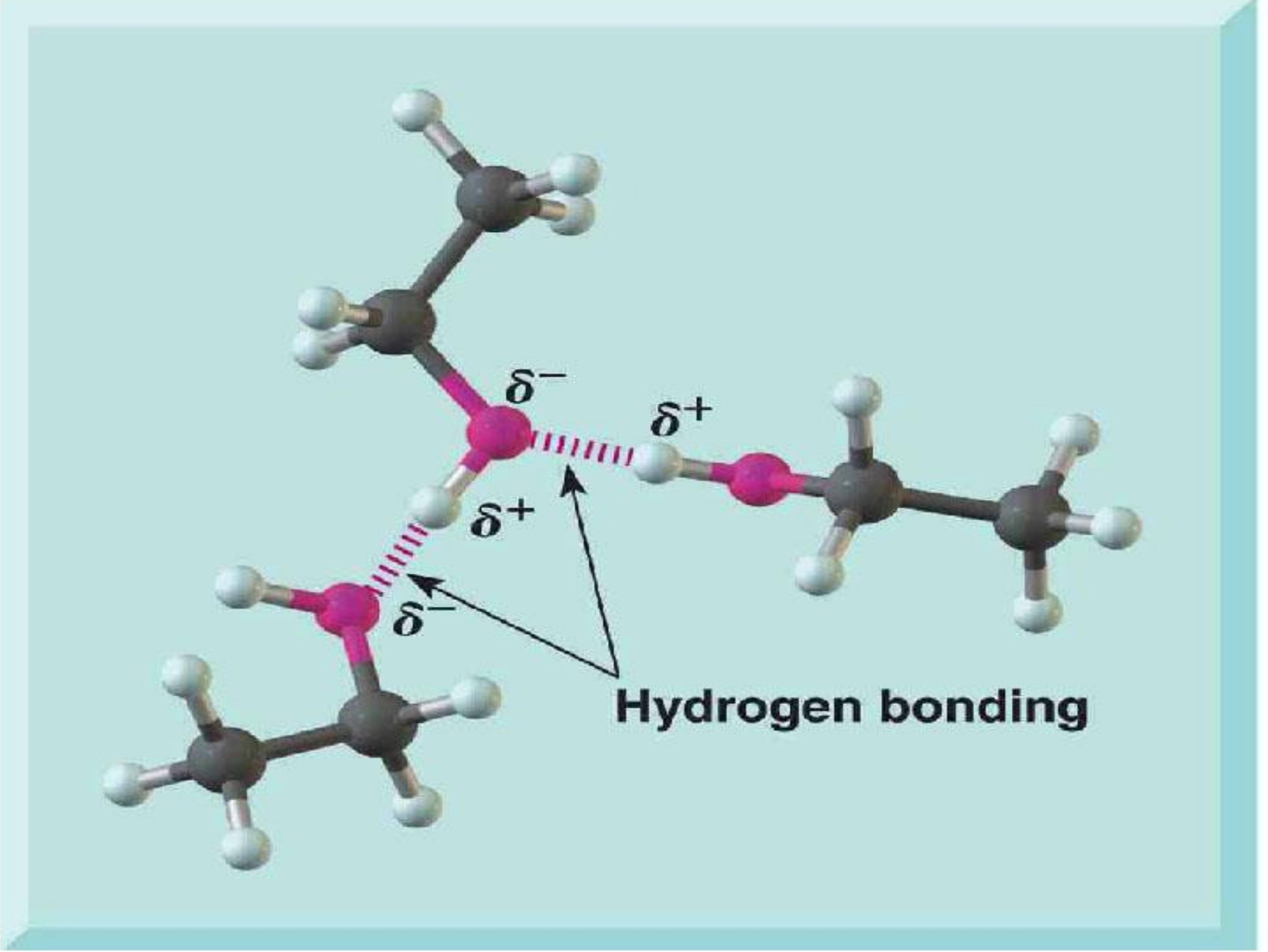
- Primary/1° : carbon with –OH is bonded to one other carbon.
- Secondary/2° : carbon with –OH is bonded to two other carbons.
- Tertiary/3° : carbon with –OH is bonded to three other carbons.



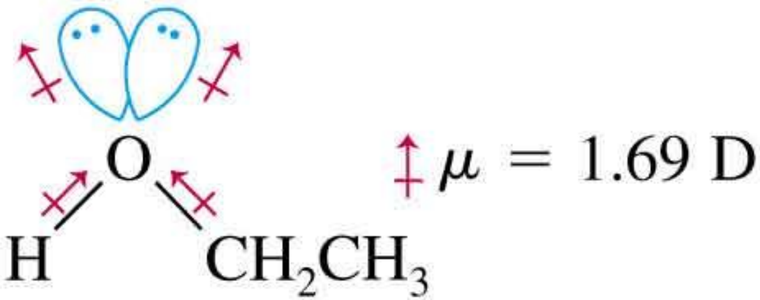


Physical Properties

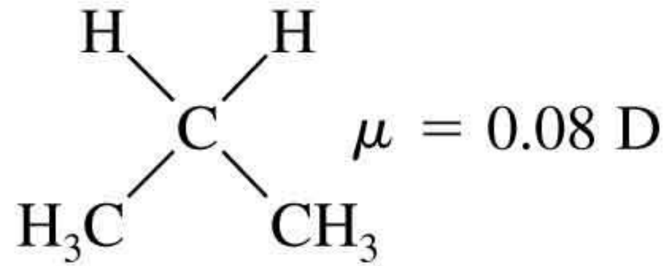
- Unusually high boiling points due to hydrogen bonding between molecules.
- Small alcohols are miscible in water, but solubility decreases as the size of the alkyl group increases.


δ⁻
δ⁺
δ⁺
δ⁻
Hydrogen bonding

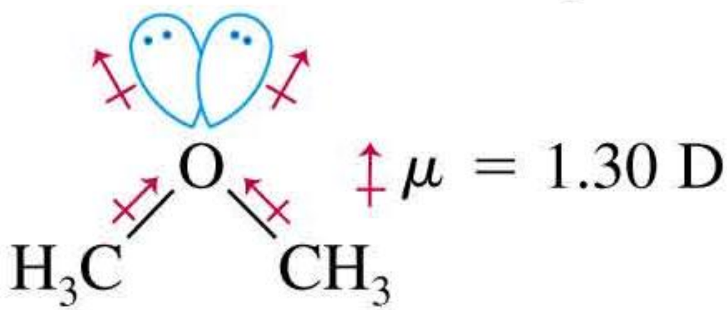
Boiling Points



ethanol, MW 46
bp 78°C



propane, MW 44
bp −42°C

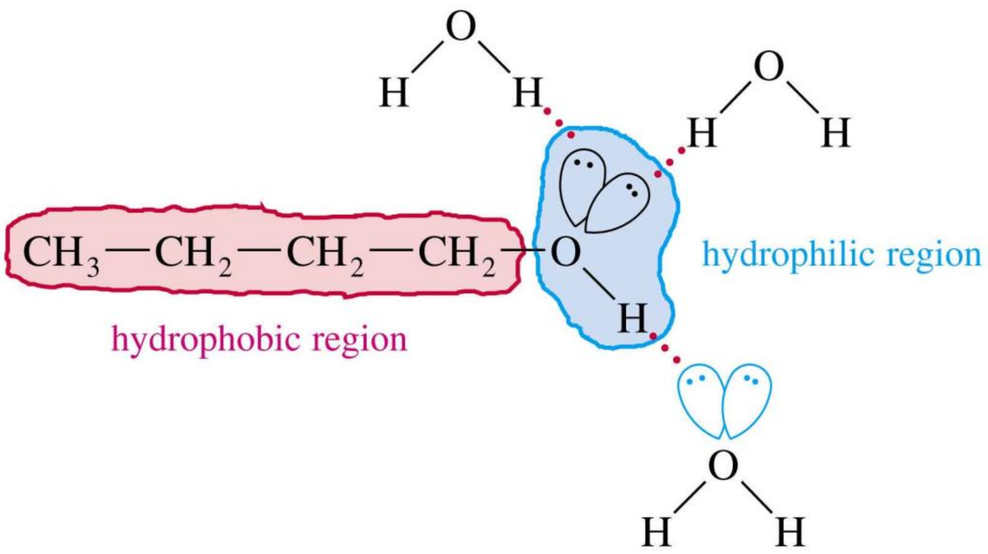


dimethyl ether, MW 46
bp −25°C

Solubility in Water

TABLE 10-2 Water Solubility of Alcohols (at 25°C)

Alcohol	*Solubility in Water*
methyl	miscible
ethyl	miscible
n-propyl	miscible
t-butyl	miscible
isobutyl	10.0%
n-butyl	9.1%
n-pentyl	2.7%
cyclohexyl	3.6%
n-hexyl	0.6%
phenol	9.3%
hexane-1,6-diol	miscible



Solubility decreases as the size of the alkyl group increases.

Structural Formula	Name	MW	bp (°C)	Solubility in Water
CH_3OH	Methanol	32	65	Infinite
CH_3CH_3	Ethane	30	-89	Insoluble
CH_3CH_2OH	Ethanol	46	78	Infinite
$CH_3CH_2CH_3$	Propane	44	-42	Insoluble
$CH_3CH_2CH_2OH$	1-Propanol	60	97	Infinite
$CH_3CH_2CH_2CH_3$	Butane	58	0	Insoluble
$CH_3(CH_2)_2CH_2OH$	1-Butanol	74	117	8 g/100 g
$CH_3(CH_2)_3CH_3$	Pentane	72	36	Insoluble
$HOCH_2(CH_2)_2CH_2OH$	1,4-Butanediol	90	230	Infinite
$CH_3(CH_2)_3CH_2OH$	1-Pentanol	88	138	2.3 g/100 g
$CH_3(CH_2)_4CH_3$	Hexane	86	69	Insoluble

Physical Properties of Alcohols, Ethers, and Epoxides

Property	Observation
Boiling point (bp) and melting point (mp)	• For compounds of comparable molecular weight, the **stronger** the intermolecular forces, the **higher** the bp or mp. $CH_3CH_2CH_2CH_3$ — VDW — bp 0 °C $CH_3OCH_2CH_3$ — VDW, DD — bp 11 °C $CH_3CH_2CH_2OH$ — VDW, DD, HB — bp 97 °C → **Increasing boiling point**
	• Bp's **increase** as the extent of hydrogen bonding **increases.** $(CH_3)_3C{-}OH$ — 3° — bp 83 °C $CH_3CH_2CH(OH)CH_3$ — 2° — bp 98 °C $CH_3CH_2CH_2CH_2{-}OH$ — 1° — bp 118 °C → **Increasing ability to hydrogen bond** **Increasing boiling point**
Solubility	• Alcohols, ethers, and epoxides having ≤ 5 C's are H_2O soluble because they each have an oxygen atom capable of hydrogen bonding to H_2O (Section 3.4C). • Alcohols, ethers, and epoxides having > 5 C's are H_2O insoluble because the nonpolar alkyl portion is too large to dissolve in H_2O. • Alcohols, ethers, and epoxides of any size are soluble in organic solvents.

Key: VDW = van der Waals forces; DD = dipole–dipole; HB = hydrogen bonding

Acidity of Alcohols

- pK_a range: 15.5-18.0 (water: 15.7)
- Acidity decreases as alkyl group increases.
- Halogens increase the acidity.
- Phenol is 100 million times more acidic than cyclohexanol!