PHYSICAL PROPERTIES

Physical Properties of Haloalkanes

Dipole Moment of The Halogen Derivatives

$$\mu = 4.8 \times \delta \times d$$

Where δ represents the charge and d is the bond length. These two factors, namely the charge and distance, counteract each other. Larger halogens tend to have longer bonds but weaker electronegativity. Consequently, the overall outcome is an increase in the bond dipole moment in the following order.

$$C - I < C - Br < C - F < C - Cl$$

$$\mu: \quad 1.29\ D \quad 1.48\ D \quad 1.51\ D \quad 1.56\ D$$

The electronegativities of the halogen increase in the order

$$I < Br < Cl < F$$

Table: Molecular dipole moments of methyl halides

X	CH_3X	CH_2X_2	CHX_3	CX_4
F	1.82 D	1.97D	1.65 D	0
Cl	1.94 D	1.60 D	1.03 D	0
Br	1.79 D	1.45 D	1.02 D	0
I	1.64 D	1.11 D	1.00 D	0

Boiling Point

(a) Regarding the halogens within a group of alkyl halides, the boiling point increases as you move down the periodic table. Alkyl fluorides exhibit the lowest boiling points, while alkyl iodides display the highest boiling points. This pattern aligns with the order of increasing polarizability among the halogens. (Polarizability refers to how easily the electron distribution around an atom can be distorted by an adjacent electric field and plays a significant role in determining the strength of induced-dipole/induced-dipole and dipole/induced-dipole attractions.) Forces relying on induced dipoles are most potent when the halogen is the highly polarizable iodine and weakest when the halogen is the nonpolarizable fluorine.

Table: Boiling points of some alkyl halide in ºC (1 atm)

Formula	X = F	X = Cl	X = Br	X = I
CH_3-X	-78	-24	3	42
CH_3-CH_2X	-32	12	38	72
CH_3-CH_2-CH_2X	-3	47	71	103
CH_3-$(CH_2)_3$-CH_2X	65	108	129	157
CH_3-$(CH_2)_4$-CH_2X	92	134	155	180

Fluorine is unique among the halogens is that increasing the number of fluorine's does not lead to higher and higher boiling point.

(b) The boiling points of methane's chlorinated derivatives elevate as the quantity of chlorine atoms increases, mainly due to the enhancement of induced-dipole/dipole attractive forces.

Compound	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
B.P.	–24ºC	40ºC	61ºC	77ºC

Table

	$CH_3 - CH_2F$	CH_3-CHF_2	CH_3-CF_3	CF_3-CF_3
B.P.	-32°C	-25°C	-47°C	-78°C

Density

Alkyl fluorides and chlorides have lower density, while alkyl bromides and iodides exhibit higher density compared to water.

Table

	$CH_3 - (CH_2)_6$-CH_2F	$CH_3 - (CH_2)_6$-CH_2Cl	$CH_3 - (CH_2)_6$-CH_2Br	$CH_3 - (CH_2)_6$-CH_2I
Density (20°C)	0.80 g/mL	0.89 g/mL	1.12 g/mL	1.34 g/mL

Due to the insolubility of alkyl halides in water, a mixture of an alkyl halide and water forms two distinct layers. When the alkyl halide is a fluoride or chloride, it remains in the upper layer, while water occupies the lower layer. Conversely, when the alkyl halide is a bromide or iodide, it settles in the lower layer, and water is in the upper layer. The introduction of multiple halogen atoms through polyhalogenation results in increased density.

For instance, compounds like CH_2Cl_2, $CHCl_3$, and CCl_4 are all denser than water.