

Chlorine

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Chlorine is a chemical element with symbol **Cl** and atomic number 17. The second-lightest of the halogens, it appears between fluorine and bromine in the periodic table and its properties are mostly intermediate between them. Chlorine is a yellow-green gas at room temperature. It is an extremely reactive element and a strong oxidising agent: among the elements, it has the highest electron affinity and the third-highest electronegativity, behind only oxygen and fluorine.

The most common compound of chlorine, sodium chloride (common salt), has been known since ancient times. Around 1630, chlorine gas was first synthesised in a chemical reaction, but not recognised as a fundamentally important substance. Carl Wilhelm Scheele wrote a description of chlorine gas in 1774, supposing it to be an oxide of a new element. In 1809, chemists suggested that the gas might be a pure element, and this was confirmed by Sir Humphry Davy in 1810, who named it from Ancient Greek: *χλωρός* *khlôros* "pale green" based on its colour.

Because of its great reactivity, all chlorine in the Earth's crust is in the form of ionic chloride compounds, which includes table salt. It is the second-most abundant halogen (after fluorine) and twenty-first most abundant chemical element in Earth's crust. These crustal deposits are nevertheless dwarfed by the huge reserves of chloride in seawater.

Elemental chlorine is commercially produced from brine by electrolysis. The high oxidising potential of elemental chlorine led to the development of commercial bleaches and disinfectants, and a reagent for many processes in the chemical industry. Chlorine is used in the manufacture of a wide range of consumer products, about two-thirds of them organic chemicals such as polyvinyl chloride, and many intermediates for the production of plastics and other end products which do not contain the element. As a common disinfectant, elemental chlorine and chlorine-generating compounds are used more directly in swimming pools to keep them clean and sanitary. Elemental chlorine at high concentrations is extremely dangerous and poisonous for all living organisms, and was used in World War I as the first gaseous chemical warfare agent.

Chlorine, ¹⁷Cl



A glass container filled with chlorine gas



Emission line spectra; 400–700 nm

General properties

| | |
|---------------------|-----------------------|
| Name, symbol | chlorine, Cl |
| Appearance | pale yellow-green gas |

Chlorine in the periodic table

| | |
|---|---|
| Atomic number (<i>Z</i>) | 17 |
| Group, block | group 17 (halogens), p-block |
| Period | period 3 |
| Element category | ☐ diatomic nonmetal |
| Standard atomic weight (<i>A</i> _r) | 35.45 ^[1] (35.446– 35.457) ^[2] |
| Electron configuration | [Ne] 3s ² 3p ⁵ |
| per shell | 2, 8, 7 |

Physical properties

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|--------------|-----|
| Phase | gas |
|--------------|-----|

In the form of chloride ions, chlorine is necessary to all known species of life. Other types of chlorine compounds are rare in living organisms, and artificially produced chlorinated organics range from inert to toxic. In the upper atmosphere, chlorine-containing organic molecules such as chlorofluorocarbons have been implicated in ozone depletion. Small quantities of elemental chlorine are generated by oxidation of chloride to hypochlorite in neutrophils as part of the immune response against bacteria.

Properties

Chlorine is the second halogen, being a nonmetal in group 17 of the periodic table. Its properties are thus similar to fluorine, bromine, and iodine, and are largely intermediate between those of the first two. Chlorine has the electron configuration $[\text{Ne}]3s^23p^5$, with the seven electrons in the third and outermost shell acting as its valence electrons. Like all halogens, it is thus one electron short of a full octet, and is hence a strong oxidising agent, reacting with many elements in order to complete its outer shell.^[26] Corresponding to periodic trends, it is intermediate in electronegativity between fluorine and bromine (F: 3.98, Cl: 3.16, Br: 2.96, I: 2.66), and is less reactive than fluorine and more reactive than bromine. It is also a weaker oxidising agent than fluorine, but a stronger one than bromine. Conversely, the chloride ion is a weaker reducing agent than bromide, but a stronger one than fluoride.^[26] It is intermediate in atomic radius between fluorine and bromine, and this leads to many of its atomic properties similarly continuing the trend from iodine to bromine upward, such as first ionisation energy, electron affinity, enthalpy of dissociation of the X_2 molecule ($X = \text{Cl}, \text{Br}, \text{I}$), ionic radius, and X–X bond length. (Fluorine is anomalous due to its small size.)^[26]

All four stable halogens experience intermolecular van der Waals forces of attraction, and their strength increases together with the number of electrons among all homonuclear diatomic halogen molecules. Thus, the melting and boiling points of chlorine are intermediate between those of fluorine and bromine: chlorine melts at -101.0 °C and boils at -34.0 °C . As a result of the increasing molecular weight of the halogens down the group, the density and heats of fusion and vaporisation of chlorine are again intermediate between those of bromine and fluorine, although all their heats of vaporisation are fairly low (leading to high volatility) thanks to their diatomic molecular structure.^[26] The halogens darken in colour as the group is descended: thus,

| | |
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| Melting point | 171.6 K (-101.5 °C , -150.7 °F) |
| Boiling point | 239.11 K (-34.04 °C , -29.27 °F) |
| Density at stp (0 °C and 101.325 kPa) | 3.2 g/L |
| when liquid, at b.p. | 1.5625 g/cm ³ ^[3] |
| Critical point | 416.9 K, 7.991 MPa |
| Heat of fusion | (Cl ₂) 6.406 kJ/mol |
| Heat of vaporisation | (Cl ₂) 20.41 kJ/mol |
| Molar heat capacity | (Cl ₂) 33.949 J/(mol·K) |

Vapour pressure

| P (Pa) | 1 | 10 | 100 | 1 k | 10 k | 100 k |
|----------|-----|-----|-----|-----|------|-------|
| at T (K) | 128 | 139 | 153 | 170 | 197 | 239 |

Atomic properties

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|-----------------------------|--|
| Oxidation states | 7, 6, 5, 4, 3, 2, 1, −1 (a strongly acidic oxide) |
| Electronegativity | Pauling scale: 3.16 |
| Ionisation energies | 1st: 1251.2 kJ/mol 2nd: 2298 kJ/mol 3rd: 3822 kJ/mol (more) |
| Covalent radius | 102±4 pm |
| Van der Waals radius | 175 pm |

Miscellanea

| | |
|--------------------------|--------------|
| Crystal structure | orthorhombic |
|--------------------------|--------------|

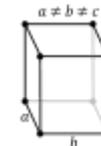
while fluorine is a pale yellow gas, chlorine is distinctly yellow-green. This trend occurs because the wavelengths of visible light absorbed by the halogens increase down the group.^[26] Specifically, the colour of a halogen, such as chlorine, results from the electron transition between the highest occupied antibonding π_g molecular orbital and the lowest vacant antibonding σ_u molecular orbital.^[27] The colour fades at low temperatures, so that solid chlorine at $-195\text{ }^\circ\text{C}$ is almost colourless.^[26]

Like solid bromine and iodine, solid chlorine crystallises in the orthorhombic crystal system, in a layered lattice of Cl_2 molecules. The Cl-Cl distance is 198 pm (close to the gaseous Cl-Cl distance of 199 pm) and the $\text{Cl}\cdots\text{Cl}$ distance between molecules is 332 pm within a layer and 382 pm between layers (compare the van der Waals radius of chlorine, 180 pm). This structure means that chlorine is a very poor conductor of electricity, and indeed its conductivity is so low as to be practically unmeasurable.^[26]

Isotopes

Chlorine has two stable isotopes, ^{35}Cl and ^{37}Cl . These are its only two natural isotopes occurring in quantity, with ^{35}Cl making up 76% of natural chlorine and ^{37}Cl making up the remaining 24%. Both are synthesised in stars in the oxygen-burning and silicon-burning processes.^[28] Both have nuclear spin 3/2+ and thus may be used for nuclear magnetic resonance, although the spin magnitude being greater than 1/2 results in non-spherical nuclear charge distribution and thus resonance broadening as a result of a nonzero nuclear quadrupole moment and resultant quadrupolar relaxation. The other chlorine isotopes are all radioactive, with half-lives too short to occur in nature primordially. Of these, the most commonly used in the laboratory are ^{36}Cl ($t_{1/2} = 3.0 \times 10^5\text{ y}$) and ^{38}Cl ($t_{1/2} = 37.2\text{ min}$), which may be produced from the neutron activation of natural chlorine.^[26]

The most stable chlorine radioisotope is ^{36}Cl . The primary decay mode of isotopes lighter than ^{35}Cl is electron capture to isotopes of sulfur; that of isotopes heavier than ^{37}Cl is beta decay to isotopes of argon; and ^{36}Cl may decay by either mode to stable ^{36}S or ^{36}Ar .^[29] ^{36}Cl occurs in trace quantities in nature as a cosmogenic nuclide in a ratio of about $(7-10) \times 10^{-13}$ to 1 with stable



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| Speed of sound | 206 m/s (gas, at 0 °C) |
| Thermal conductivity | $8.9 \times 10^{-3}\text{ W}/(\text{m}\cdot\text{K})$ |
| Electrical resistivity | $>10\ \Omega\cdot\text{m}$ (at 20 °C) |
| Magnetic ordering | diamagnetic ^[4] |
| CAS Number | 7782-50-5 |

History

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|--------------------------------------|-----------------------------|
| Discovery and first isolation | Carl Wilhelm Scheele (1774) |
| Recognized as an element by | Humphry Davy (1808) |

Most stable isotopes of chlorine

| iso | NA | half-life | DM | DE (MeV) | DP |
|------------------------------------|-------|-----------------------------|-------------------------|------------|-------------------------------------|
| ^{35}Cl | 76% | is stable with 18 neutrons | | | |
| ^{36}Cl | trace | $3.01 \times 10^5\text{ y}$ | β^- ϵ | 0.709 - | ^{36}Ar ^{36}S |
| ^{37}Cl | 24% | is stable with 20 neutrons | | | |

chlorine isotopes: it is produced in the atmosphere by spallation of ^{36}Ar by interactions with cosmic ray protons. In the top meter of the lithosphere, ^{36}Cl is generated primarily by thermal neutron activation of ^{35}Cl and spallation of ^{39}K and ^{40}Ca . In the subsurface environment, muon capture by ^{40}Ca becomes more important as a way to generate ^{36}Cl .^{[30][31]}

Source

- Wikipedia: Chlorine ()