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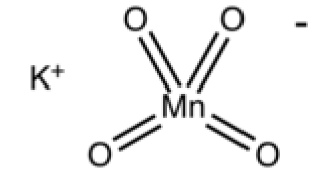
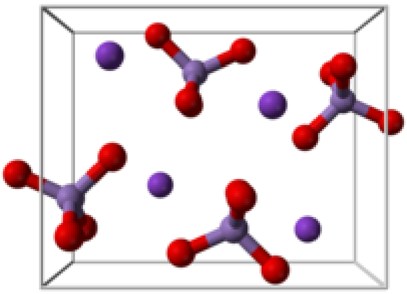
Potassium permanganate

Potassium permanganate is an inorganic compound with the chemical formula $KMnO_4$ and composed of K^+ and MnO_4^-. It is a purplish-black crystalline salt, that dissolves in water to give intensely pink or purple solutions.

Potassium permanganate is widely used in chemical industry and laboratories as a strong oxidizing agent, and also as a medication for dermatitis, for cleaning wounds, and general disinfection. It is on the WHO Model List of Essential Medicines, the safest and most effective medicines needed in a health system.[5] In 2000, worldwide production was estimated at 30,000 tonnes.[5]

Potassium permanganate





Names	
IUPAC name	Potassium manganate(VII)
Other names	Potassium permanganate Chameleon mineral Condy's crystals Permanganate of potash Hypermangan
Identifiers	
CAS Number	7722-64-7 (https://commonchemistry.cas.org/detail?cas_rn=7722-64-7) ✓
3D model (JSmol)	Interactive image (https://chemapps.stolaf.edu/jmol/jmol.php?model=%5BK%2B%5D.%5BO-%5

Contents

Uses

Almost all applications of potassium permanganate exploit its oxidizing properties.[6] As a strong oxidant that does not generate toxic byproducts, $KMnO_4$ has many niche uses.

Medical uses

Potassium permanganate is used for a number of skin conditions.[7] This includes fungal infections of the foot, impetigo, pemphigus, superficial wounds, dermatitis, and tropical ulcers.[8][7] It is on the World Health Organization's List of Essential Medicines, the safest and most effective medicines needed in a health system.[5]

Water treatment

Potassium permanganate is used extensively in the water treatment industry. It is used as a regeneration chemical to remove iron and hydrogen sulfide (rotten egg smell) from well water via a "Manganese Greensand" Filter. "Pot-Perm" is also obtainable at pool supply stores and is used additionally to treat waste water. Historically it was used to disinfect drinking water[9][10] and can turn the water pink.[11] It currently finds application in the control of nuisance organisms such as zebra mussels in fresh water collection and treatment systems.[12]

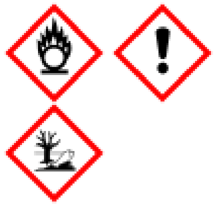
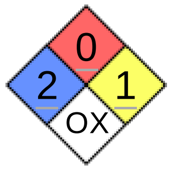
Synthesis of organic compounds

A major application of $KMnO_4$ is as a reagent for the synthesis of organic compounds.[13] Significant amounts are required for the synthesis of ascorbic acid, chloramphenicol, saccharin, isonicotinic acid, and pyrazinoic acid.[6]

$KMnO_4$ is used in qualitative organic analysis to test for the presence of unsaturation. It is sometimes referred to as **Baeyer's reagent** after the German organic chemist Adolf von Baeyer . The reagent is an alkaline solution of potassium permanganate. Reaction with double or triple bonds (-C=C- or -C≡C-) causes the color to fade from purplish-pink to brown. Aldehydes and formic acid (and formates) also give a positive test.[14] The test is antiquated.

	D%5BMn%5D%28%3DO%29%28%3DO%29%3DO)
ChEMBL	ChEMBL3833305 (https://www.ebi.ac.uk/chembldb/index.php/compound/inspect/ChEMBL3833305)
ChemSpider	22810 (http://www.chemspider.com/Chemical-Structure.22810.html)
DrugBank	DB13831 (https://www.drugbank.ca/drugs/DB13831)
ECHA InfoCard	100.028.874 (https://echa.europa.eu/substance-information/-/substanceinfo/100.028.874)
EC Number	231-760-3
KEGG	D02053 (https://www.kegg.jp/entry/D02053) ✓
PubChem CID	516875 (https://pubchem.ncbi.nlm.nih.gov/compound/516875)
RTECS number	SD6475000
UNII	00OT1QX5U4 (https://fdasis.nlm.nih.gov/srs/srsdirect.jsp?regno=00OT1QX5U4)
UN number	1490
CompTox Dashboard (EPA)	DTXSID2034839 (https://comptox.epa.gov/dashboard/DTXSID2034839)
InChI	
InChI=1S/K.Mn.4O/q+1;;;;;-1 ✓	

Key: VZJVWSHVAAUDKD-UHFFFAOYSA-N ✓	
SMILES	
[K+].[O-][Mn](=O)(=O)=O	
Properties	
Chemical formula	$KMnO_4$
Molar mass	158.034 g/mol
Appearance	Purplish-bronze-gray needles Magenta–rose in solution[1]
Odor	odorless
Density	2.7 g/cm^3[2]:4.83
Melting point	240 °C (464 °F; 513 K) (decomposes)
Solubility in water	76 g/L (25 °C)[2] 250 g/L (65 °C)
Solubility	decomposes in alcohol and organic solvents
Magnetic susceptibility (χ)	+20.0·10^{-6} cm^3/mol[2]:4.134
Refractive index (n_D)	1.59
Structure[3]	
Crystal structure	Orthorhombic, oP24
Space group	Pnma, No. 62
Lattice constant	a = 0.909 nm, b = 0.572 nm, c = 0.741 nm
Formula units (Z)	4
Thermochemistry	
Heat capacity (C)	119.2 J/mol K
Std molar entropy (S°_{298})	171.7 J K^{-1} mol^{-1}
	−813.4 kJ/mol

Std enthalpy of formation ($\Delta_f H^{\ominus}_{298}$)	
Gibbs free energy ($\Delta_f G^\circ$)	-713.8 kJ/mol
Pharmacology	
ATC code	D08AX06 (WHO (https://www.whocc.no/atc_ddd_index/?code=D08AX06)) V03AB18 (WHO (https://www.whocc.no/atc_ddd_index/?code=V03AB18))
Hazards	
GHS pictograms	
NFPA 704 (fire diamond)	
Lethal dose or concentration (LD, LC):	
LD_{50} (median dose)	1090 mg/kg (oral, rat)[4]
Related compounds	
Other anions	Potassium manganate
Other cations	Sodium permanganate Ammonium permanganate Calcium permanganate Silver permanganate
Related compounds	Manganese heptoxide

Except where otherwise noted, data are given for materials in their standard state (at 25 °C [77 °F], 100 kPa).

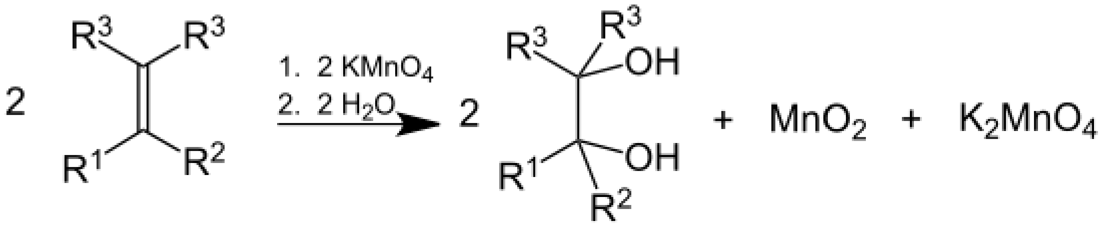
✗ verify (what is ✓✗ ?)

Infobox references

Potassium permanganate

Clinical data	
License data	US DailyMed: Potassium_permanganate (https://dailymed.nlm.nih.gov/dailymed/search.cfm?labeltype=all&query=Potassium_permanganate)
Identifiers	
CompTox Dashboard (EPA)	DTXSID2034839 (https://comptox.epa.gov/dashboard/DTXSID2034839)
ECHA InfoCard	100.028.874 (https://echa.europa.eu/substance-information/-/substanceinfo/100.028.874)

A solution of $KMnO_4$ in water, in a volumetric flask



Analytical use

Potassium permanganate can be used to quantitatively determine the total oxidizable organic material in an aqueous sample. The value determined is known as the *permanganate value*. In analytical chemistry, a standardized aqueous solution of $KMnO_4$ is sometimes used as an oxidizing titrant for redox titrations (permanganometry). As potassium permanganate is titrated, the solution becomes a light shade of magenta, which darkens as excess of the titrant is added to the solution. In a related way, it is used as a reagent to determine the Kappa number of wood pulp. For the standardization of $KMnO_4$ solutions, reduction by oxalic acid is often used.[15]

Aqueous, acidic solutions of $KMnO_4$ are used to collect gaseous mercury in flue gas during stationary source emissions testing.[16]

In histology, potassium permanganate was used as a bleaching agent.[17][18]

Fruit preservation

Ethylene absorbents extend storage time of bananas even at high temperatures. This effect can be exploited by packing bananas in polyethylene together with potassium permanganate. By removing ethylene by oxidation, the permanganate delays the ripening, increasing the fruit's shelf life up to 4 weeks without the need for refrigeration.[19][20][21]

Survival kits

Potassium permanganate is sometimes included in survival kits: as a hypergolic fire starter (when mixed with glycerol antifreeze from a car radiator;[22][23][24] as a water sterilizer - and for creating distress signals on snow.[25]

Fire service

Potassium permanganate is added to "plastic sphere dispensers" to create backfires, burnouts, and controlled burns. Polymer spheres resembling ping-pong balls containing small amounts of permanganate are injected with ethylene glycol and projected towards the area where ignition is desired, where they spontaneously ignite seconds later.[26][27] Both handheld[27] and helicopter-[26] or boat-mounted[27] plastic sphere dispensers are used.

Other uses

Potassium permanganate is one of the principal chemicals used in the film and television industries to "age" props and set dressings. Its ready conversion to brown MnO_2 creates "hundred-year-old" or "ancient" looks on Hessian cloth (burlap), ropes, timber, and glass.[28]

Potassium permanganate can be used to oxidize cocaine paste to purify it and increase its stability. This led to the Drug Enforcement Administration launching Operation Purple in 2000, with the goal of monitoring the world supply of potassium permanganate; however, potassium permanganate derivatives and substitutes were soon used thereafter to avoid the operation.[29]

In agricultural chemistry, it is used for estimation of available nitrogen in soil.

History

In 1659, Johann Rudolf Glauber fused a mixture of the mineral pyrolusite (manganese dioxide, MnO_2) and potassium carbonate to obtain a material that, when dissolved in water, gave a green solution (potassium manganate) which slowly shifted to violet and then finally red.[30] This report represents the first description of the production of potassium permanganate.[31] Just under 200 years later, London chemist Henry Bollmann Condy had an interest in disinfectants; he found that fusing pyrolusite with sodium hydroxide (NaOH) and dissolving it in water produced a solution with disinfectant properties. He patented this solution, and marketed it as 'Condy's Fluid'. Although effective, the solution was not very stable. This was overcome by using potassium hydroxide (KOH) rather than NaOH. This was more stable, and had the advantage of easy conversion to the equally effective potassium permanganate crystals. This crystalline material was known as 'Condy's crystals' or 'Condy's powder'. Potassium permanganate was comparatively easy to manufacture, so Condy was subsequently forced to spend considerable time in litigation to stop competitors from marketing similar products.[32]

Early photographers used it as a component of flash powder. It is now replaced with other oxidizers, due to the instability of permanganate mixtures.

Preparation

Potassium permanganate is produced industrially from manganese dioxide, which also occurs as the mineral pyrolusite. In 2000, worldwide production was estimated at 30,000 tonnes.[6] The MnO_2 is fused with potassium hydroxide and heated in air or with another source of oxygen, like potassium nitrate or potassium chlorate.[6] This process gives potassium manganate:

$$2\ MnO_2 + 4\ KOH + O_2 \rightarrow 2\ K_2MnO_4 + 2\ H_2O$$

(With sodium hydroxide, the end product is not sodium manganate but an Mn(V) compound, which is one reason the potassium permanganate is more commonly used than sodium permanganate. Furthermore, the potassium salt crystallizes better.[6])

The potassium manganate is then converted into permanganate by electrolytic oxidation in alkaline media:

$$2\ K_2MnO_4 + 2\ H_2O \rightarrow 2\ KMnO_4 + 2\ KOH + H_2$$

Other methods

Although of no commercial importance, potassium manganate can be oxidized by chlorine or by disproportionation under acid conditions.[33] The chlorine oxidation reaction is

$$2\ K_2MnO_4 + Cl_2 \rightarrow 2\ KMnO_4 + 2\ KCl$$

And the acid-induced disproportionation reaction may be written as

$$3\ K_2MnO_4 + 4\ HCl \rightarrow 2\ KMnO_4 + MnO_2 + 2\ H_2O + 4\ KCl$$

A weak acid such as carbonic acid is sufficient for this reaction:

$$3\ K_2MnO_4 + 2\ CO_2 \rightarrow 2\ KMnO_4 + 2\ K_2CO_3 + MnO_2$$

Permanganate salts may also be generated by treating a solution of Mn^{2+} ions with strong oxidants such as lead dioxide (PbO_2), sodium bismuthate ($NaBiO_3$), or peroxydisulfate. Tests for the presence of manganese exploit the vivid violet color of permanganate produced by these reagents.

Structure

$KMnO_4$ forms orthorhombic crystals with constants: a = 910.5 pm, b = 572.0 pm, c = 742.5 pm. The overall motif is similar to that for barium sulfate, with which it forms solid solutions.[34] In the solid (as in solution), each MnO_4^- centres are tetrahedral. The Mn–O distances are 1.62 Å.[35]

Reactions

Organic chemistry

Dilute solutions of $KMnO_4$ convert alkenes into diols (glycols). This behaviour is also used as a qualitative test for the presence of double or triple bonds in a molecule, since the reaction decolorizes the initially purple permanganate solution and generates a brown precipitate (MnO_2). In this context, it is sometimes called *Baeyer's reagent*. However, bromine serves better in measuring unsaturation (double or triple bonds) quantitatively, since $KMnO_4$, being a very strong oxidizing agent, can react with a variety of groups.

Under acidic conditions, the alkene double bond is cleaved to give the appropriate carboxylic acid:[36]

$$CH_3(CH_2)_{17}CH{=}CH_2 + 2\ KMnO_4 + 3\ H_2SO_4 \rightarrow CH_3(CH_2)_{17}COOH + CO_2 + 4\ H_2O + K_2SO_4 + 2\ MnSO_4$$

Potassium permanganate oxidizes aldehydes to carboxylic acids, such as the conversion of *n*-heptanal to heptanoic acid:[37]

$$5\ C_6H_{13}CHO + 2\ KMnO_4 + 3\ H_2SO_4 \rightarrow 5\ C_6H_{13}COOH + 3\ H_2O + K_2SO_4 + 2\ MnSO_4$$

Even an alkyl group (with a benzylic hydrogen) on an aromatic ring is oxidized, e.g. toluene to benzoic acid.[38]

$$5\ C_6H_5CH_3 + 6\ KMnO_4 + 9\ H_2SO_4 \rightarrow 5\ C_6H_5COOH + 14\ H_2O + 3\ K_2SO_4 + 6\ MnSO_4$$

Glycols and polyols are highly reactive toward $KMnO_4$. For example, addition of potassium permanganate to an aqueous solution of sugar and sodium hydroxide produces the chemical chameleon reaction, which involves dramatic color changes associated with the various oxidation states of manganese. A related vigorous reaction is exploited as a fire starter in survival kits. For example, a mixture of potassium permanganate and glycerol or pulverized glucose ignites readily.[22] Its sterilizing properties are another reason for inclusion of $KMnO_4$ in a survival kit.

By itself, potassium permanganate does not dissolve in many organic solvents. If an organic solution of permanganate is desired, "purple benzene" may be prepared, either by treating a two phase mixture of aqueous potassium permanganate and benzene with a quaternary ammonium salt,[39] or by sequestering the potassium cation with a crown ether.[40]

Reaction with acids

The reaction of permanganate with concentrated hydrochloric acid gives chlorine. The Mn-containing products from redox reactions depend on the pH. Acidic solutions of permanganate are reduced to the faintly pink manganese(II) ion (Mn^{2+}) and water. In neutral solution, permanganate is only reduced by three electrons to give manganese dioxide (MnO_2), wherein manganese is in a +4 oxidation state. This is the material that stains one's skin when handling $KMnO_4$. $KMnO_4$ spontaneously reduces in an alkaline solution to green K_2MnO_4, wherein manganese is in the +6 oxidation state.

A curious reaction occurs upon addition of concentrated sulfuric acid to potassium permanganate. Concentrated sulfuric acid reacts with $KMnO_4$ to give Mn_2O_7, which can be explosive.[41] Although no reaction may be apparent, the vapor over the mixture will ignite paper impregnated with alcohol. Potassium permanganate and sulfuric acid react to produce some ozone, which has a high oxidizing power and rapidly oxidizes the alcohol, causing it to combust. As the reaction also produces explosive Mn_2O_7, this should only be attempted with great care.[42][43]

Thermal decomposition

Solid potassium permanganate decomposes when heated:

$$2\ KMnO_4 \rightarrow K_2MnO_4 + MnO_2(s) + O_2$$

Here, the oxidation state of manganese changes as the potassium permanganate (oxidation state +7) decomposes to potassium manganate (oxidation state +6) and manganese dioxide (oxidation state +4). Oxygen gas is also liberated.

Safety and handling

Potassium permanganate poses risks as an oxidizer.[44] Contact with skin will result in a long lasting brown stain.[45]

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External links

- International Chemical Safety Card 0672 (https://www.ilo.org/dyn/icsc/showcard.display?p_lang=en&p_card_id=0672&p_version=2)
- "Potassium permanganate" (https://druginfo.nlm.nih.gov/drugportal/name/potassium%20permanganate). *Drug Information Portal*. U.S. National Library of Medicine.
- National Pollutant Inventory: Manganese and compounds Fact Sheet (http://www.npi.gov.au/resource/manganese-compounds)
- The use of potassium permanganate in fish ponds (https://web.archive.org/web/20110606090007/http://edis.ifas.ufl.edu/fa032)