Skills to Develop

• To understand the trends in properties and reactivity of the group 14 elements.

Tin and lead oxides and sulfides are easily reduced to the metal by heating with charcoal, a discovery that must have occurred by accident when prehistoric humans used rocks containing their ores for a cooking fire. However, because tin and copper ores are often found together in nature, their alloy—brass—was probably discovered before either element, a discovery that led to the Bronze Age. The heaviest element in group 14, lead, is such a soft and malleable metal that the ancient Romans used thin lead foils as writing tablets, as well as lead cookware and lead pipes for plumbing. (Recall that the atomic symbols for tin and lead come from their Latin names: Sn for stannum and Pb for plumbum.)

Although the first glasses were prepared from silica (silicon oxide, SiO$_2$) around 1500 BC, elemental silicon was not prepared until 1824 because of its high affinity for oxygen. Jöns Jakob Berzelius was finally able to obtain amorphous silicon by reducing Na$_2$SiF$_6$ with molten potassium. The crystalline element, which has a shiny blue-gray luster, was not isolated until 30 yr later. The last member of the group 14 elements to be discovered was germanium, which was found in 1886 in a newly discovered silver-colored ore by the German chemist Clemens Winkler, who named the element in honor of his native country.

$$\text{SiCl}_4(\text{l}) + 2\text{H}_2(\text{g}) \xrightarrow{\Delta} \text{Si}(\text{s}) + 4\text{HCl}(\text{g}) \quad (\text{3})$$

Preparation and General Properties of the Group 14 Elements

The natural abundance of the group 14 elements varies tremendously. Although oxygen is the most abundant element on Earth, the next most abundant is silicon, the next member of group 14. Pure silicon is obtained by reacting impure silicon with Cl$_2$ to give SiCl$_4$, followed by the fractional distillation of the impure SiCl$_4$ and reduction with H$_2$:

$$\text{SiCl}_4(\text{l}) + 2\text{H}_2(\text{g}) \xrightarrow{\Delta} \text{Si}(\text{s}) + 4\text{HCl}(\text{g}) \quad (\text{3})$$

Several million tons of silicon are annually produced with this method. Amorphous silicon containing residual amounts of
Hydrogen is used in photovoltaic devices that convert light to electricity, and silicon-based solar cells are used to power pocket calculators, boats, and highway signs, where access to electricity by conventional methods is difficult or expensive. Ultrapure silicon and germanium form the basis of the modern electronics industry (Figure \(\PageIndex{1}\)).

In contrast to silicon, the concentrations of germanium and tin in Earth’s crust are only 1–2 ppm. The concentration of lead, which is the end product of the nuclear decay of many radionuclides, is 13 ppm, making lead by far the most abundant of the heavy group 14 elements. No concentrated ores of germanium are known; like indium, germanium is generally recovered from flue dusts obtained by processing the ores of metals such as zinc. Because germanium is essentially transparent to infrared radiation, it is used in optical devices.

Tin and lead are soft metals that are too weak for structural applications, but because tin is flexible, corrosion resistant, and nontoxic, it is used as a coating in food packaging. A “tin can,” for example, is actually a steel can whose interior is coated with a thin layer (1–2 µm) of metallic tin. Tin is also used in superconducting magnets and low-melting-point alloys such as solder and pewter. Pure lead is obtained by heating galena (PbS) in air and reducing the oxide (PbO) to the metal with carbon, followed by electrolytic deposition to increase the purity:

\[
\text{PbS(s) +} \frac{3}{2}\text{O}_2(g) \xrightarrow{\Delta} \text{PbO(s) + SO}_2(g) \\
\text{PbO(s) + C(s) \xrightarrow{\Delta} Pb(l) + CO(g)} \\
\text{PbO(s) + CO(g) \xrightarrow{\Delta} Pb(l) + CO}_2(g)
\]

or

\[
\text{PbO(s) + CO(g) \xrightarrow{\Delta} Pb(l) + CO}_2(g)
\]

By far the single largest use of lead is in lead storage batteries. The group 14 elements all have ns^2np^2 valence electron configurations. All form compounds in which they formally lose either the two np and the two ns valence electrons or just the two np valence electrons, giving a +4 or +2 oxidation state, respectively. Because covalent bonds decrease in strength with increasing atomic size and the ionization energies for the heavier elements of the group are higher than expected due to a higher Z_{eff}, the relative stability of the +2 oxidation state increases smoothly from carbon to lead.

The relative stability of the +2 oxidation state increases, and the tendency to form catenated compounds decreases, from carbon to lead in group 14.

Recall that many carbon compounds contain multiple bonds formed by π overlap of singly occupied 2p orbitals on adjacent atoms. Compounds of silicon, germanium, tin, and lead with the same stoichiometry as those of carbon, however, tend to have different structures and properties. For example, CO\textsubscript{2} is a gas that contains discrete O=C=O molecules, whereas the most common form of SiO\textsubscript{2} is the high-melting solid known as quartz, the major component of sand. Instead of discrete SiO\textsubscript{2} molecules, quartz contains a three-dimensional network of silicon atoms that is similar to the structure of diamond but with an oxygen atom inserted between each pair of silicon atoms. Thus each silicon atom is linked to four other silicon atoms by bridging oxygen atoms.

The tendency to catenate—to form chains of like atoms—decreases rapidly as we go down group 14 because bond energies for both the E–E and E–H bonds decrease with increasing atomic number (where E is any group 14 element). Consequently, inserting a CH\textsubscript{2} group into a linear hydrocarbon such as n-hexane is exergonic (ΔG° = −45 kJ/mol),
whereas inserting an SiH$_2$ group into the silicon analogue of n-hexane (Si$_6$H$_{14}$) actually costs energy ($\Delta G^\circ \approx +25$ kJ/mol). As a result of this trend, the thermal stability of catenated compounds decreases rapidly from carbon to lead.

In Table 1 we see, once again, that there is a large difference between the lightest element (C) and the others in size, ionization energy, and electronegativity. As in group 13, the second and third elements (Si and Ge) are similar, and there is a reversal in the trends for some properties, such as ionization energy, between the fourth and fifth elements (Sn and Pb). As for group 13, these effects can be explained by the presence of filled $(n - 1)d$ and $(n - 2)f$ subshells, whose electrons are relatively poor at screening the outermost electrons from the higher nuclear charge.

**Table 1:** Selected Properties of the Group 14 Elements

<table>
<thead>
<tr>
<th>Property</th>
<th>Carbon</th>
<th>Silicon</th>
<th>Germanium</th>
<th>Tin</th>
<th>Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>atomic symbol</td>
<td>C</td>
<td>Si</td>
<td>Ge</td>
<td>Sn</td>
<td>Pb</td>
</tr>
<tr>
<td>atomic number</td>
<td>6</td>
<td>14</td>
<td>32</td>
<td>50</td>
<td>82</td>
</tr>
<tr>
<td>atomic mass (amu)</td>
<td>12.01</td>
<td>28.09</td>
<td>72.64</td>
<td>118.71</td>
<td>207.2</td>
</tr>
<tr>
<td>valence electron configuration*</td>
<td>2s$^2$2p$^2$</td>
<td>3s$^2$3p$^2$</td>
<td>4s$^2$4p$^2$</td>
<td>5s$^2$5p$^2$</td>
<td>6s$^2$6p$^2$</td>
</tr>
<tr>
<td>melting point/boiling point (°C)</td>
<td>4489 (at 10.3 MPa)/3825</td>
<td>1414/3265</td>
<td>939/2833</td>
<td>232/2602</td>
<td>327/1749</td>
</tr>
<tr>
<td>density (g/cm$^3$) at 25°C</td>
<td>2.2 (graphite), 3.51 (diamond)</td>
<td>2.33</td>
<td>5.32</td>
<td>7.27 (white)</td>
<td>11.30</td>
</tr>
<tr>
<td>atomic radius (pm)</td>
<td>77 (diamond)</td>
<td>111</td>
<td>125</td>
<td>145</td>
<td>154</td>
</tr>
<tr>
<td>first ionization energy (kJ/mol)</td>
<td>1087</td>
<td>787</td>
<td>762</td>
<td>709</td>
<td>716</td>
</tr>
<tr>
<td>most common oxidation state</td>
<td>+4</td>
<td>+4</td>
<td>+4</td>
<td>+4</td>
<td>+4</td>
</tr>
<tr>
<td>ionic radius (pm)$^\dagger$</td>
<td>≈29</td>
<td>≈40</td>
<td>53</td>
<td>69</td>
<td>77.5</td>
</tr>
<tr>
<td>electron affinity</td>
<td>−122</td>
<td>−134</td>
<td>−119</td>
<td>−107</td>
<td>−35</td>
</tr>
</tbody>
</table>

*The configuration shown does not include filled d and f subshells.

$^\dagger$The values cited are for six-coordinate $+4$ ions in the most common oxidation state, except for C$^{4+}$ and Si$^{4+}$, for which values for the four-coordinate ion are estimated.

$^\ddagger$X is Cl, Br, or I. Reaction with F$_2$ gives the tetrafluorides (EF$_4$) for all group 14 elements, where E represents any group 14 element.
<table>
<thead>
<tr>
<th>Property</th>
<th>Carbon</th>
<th>Silicon</th>
<th>Germanium</th>
<th>Tin</th>
<th>Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>(kJ/mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>electronegativity</td>
<td>2.6</td>
<td>1.9</td>
<td>2.0</td>
<td>2.0</td>
<td>1.8</td>
</tr>
<tr>
<td>standard reduction potential (E°, V)</td>
<td>0.21</td>
<td>−0.86</td>
<td>−0.18</td>
<td>−0.12</td>
<td>0.79</td>
</tr>
<tr>
<td>(for EO₂ → E in acidic solution)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>product of reaction with O₂</td>
<td>CO₂, CO</td>
<td>SiO₂</td>
<td>GeO₂</td>
<td>SnO₂</td>
<td>PbO</td>
</tr>
<tr>
<td>type of oxide</td>
<td>acidic (CO₂)</td>
<td>acidic neutral (CO)</td>
<td>amphoteric</td>
<td>amphoteric</td>
<td>amphoteric</td>
</tr>
<tr>
<td>product of reaction with N₂</td>
<td>none</td>
<td>Si₃N₄</td>
<td>none</td>
<td>Sn₃N₄</td>
<td>none</td>
</tr>
<tr>
<td>product of reaction with X₂⁺†</td>
<td>CX₄</td>
<td>SiX₄</td>
<td>GeX₄</td>
<td>SnX₄</td>
<td>PbX₂</td>
</tr>
<tr>
<td>product of reaction with H₂</td>
<td>CH₄</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
</tbody>
</table>

*The configuration shown does not include filled d and f subshells.*

†The values cited are for six-coordinate +4 ions in the most common oxidation state, except for C⁴⁺ and Si⁴⁺, for which values for the four-coordinate ion are estimated.

‡X is Cl, Br, or I. Reaction with F₂ gives the tetrafluorides (EF₄) for all group 14 elements, where E represents any group 14 element.

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**Reactions and Compounds of the Heavier Group 14 Elements**

Although silicon, germanium, tin, and lead in their +4 oxidation states often form binary compounds with the same stoichiometry as carbon, the structures and properties of these compounds are usually significantly different from those of the carbon analogues. Silicon and germanium are both semiconductors with structures analogous to diamond. Tin has two common allotropes: white (β) tin has a metallic lattice and metallic properties, whereas gray (α) tin has a diamond-like structure and is a semiconductor. The metallic β form is stable above 13.2°C, and the nonmetallic α form is stable below 13.2°C. Lead is the only group 14 element that is metallic in both structure and properties under all conditions.
Based on its position in the periodic table, we expect silicon to be amphoteric. In fact, it dissolves in strong aqueous base to produce hydrogen gas and solutions of silicates, but the only aqueous acid that it reacts with is hydrofluoric acid, presumably due to the formation of the stable SiF$_6^{2-}$ ion. Germanium is more metallic in its behavior than silicon. For example, it dissolves in hot oxidizing acids, such as HNO$_3$ and H$_2$SO$_4$, but in the absence of an oxidant, it does not dissolve in aqueous base. Although tin has an even more metallic character than germanium, lead is the only element in the group that behaves purely as a metal. Acids do not readily attack it because the solid acquires a thin protective outer layer of a Pb$^{2+}$ salt, such as PbSO$_4$.

All group 14 dichlorides are known, and their stability increases dramatically as the atomic number of the central atom increases. Thus CCl$_2$ is dichlorocarbene, a highly reactive, short-lived intermediate that can be made in solution but cannot be isolated in pure form using standard techniques; SiCl$_2$ can be isolated at very low temperatures, but it decomposes rapidly above $-150^\circ$C, and GeCl$_2$ is relatively stable at temperatures below 20$^\circ$C. In contrast, SnCl$_2$ is a polymeric solid that is indefinitely stable at room temperature, whereas PbCl$_2$ is an insoluble crystalline solid with a structure similar to that of SnCl$_2$.

The stability of the group 14 dichlorides increases dramatically from carbon to lead.

Although the first four elements of group 14 form tetrahalides (MX$_4$) with all the halogens, only fluorine is able to oxidize lead to the +4 oxidation state, giving PbF$_4$. The tetrahalides of silicon and germanium react rapidly with water to give amphoteric oxides (where M is Si or Ge):

$$\text{MX}_{4(s,l)} + 2\text{H}_2\text{O}_{(l)} \rightarrow \text{MO}_{2(s)} + 4\text{HX}_{(aq)} \label{1}$$

In contrast, the tetrahalides of tin and lead react with water to give hydrated metal ions. Because of the stability of its +2 oxidation state, lead reacts with oxygen or sulfur to form PbO or PbS, respectively, whereas heating the other group 14
elements with excess $O_2$ or $S_8$ gives the corresponding dioxides or disulfides, respectively. The dioxides of the group 14 elements become increasingly basic as we go down the group.

The dioxides of the group 14 elements become increasingly basic down the group.

Because the Si–O bond is even stronger than the C–O bond (~452 kJ/mol versus ~358 kJ/mol), silicon has a strong affinity for oxygen. The relative strengths of the C–O and Si–O bonds contradict the generalization that bond strengths decrease as the bonded atoms become larger. This is because we have thus far assumed that a formal single bond between two atoms can always be described in terms of a single pair of shared electrons. In the case of Si–O bonds, however, the presence of relatively low-energy, empty $d$ orbitals on Si and nonbonding electron pairs in the $p$ or $sp^n$ hybrid orbitals of O results in a partial $\pi$ bond (Figure \((\text{PageIndex}[3]\)). Due to its partial $\pi$ double bond character, the Si–O bond is significantly stronger and shorter than would otherwise be expected. A similar interaction with oxygen is also an important feature of the chemistry of the elements that follow silicon in the third period (P, S, and Cl). Because the Si–O bond is unusually strong, silicon–oxygen compounds dominate the chemistry of silicon.

**Figure \((\text{PageIndex}[3]\)):** Partial $\pi$ bond

Because silicon–oxygen bonds are unusually strong, silicon–oxygen compounds dominate the chemistry of silicon.

Compounds with anions that contain only silicon and oxygen are called silicates, whose basic building block is the $\text{SiO}_4^{4-}$ unit:

The number of oxygen atoms shared between silicon atoms and the way in which the units are linked vary considerably in different silicates. Converting one of the oxygen atoms from terminal to bridging generates chains of silicates, while converting two oxygen atoms from terminal to bridging generates double chains. In contrast, converting three or four oxygens to bridging generates a variety of complex layered and three-dimensional structures, respectively.
In a large and important class of materials called aluminosilicates, some of the Si atoms are replaced by Al atoms to give aluminosilicates such as zeolites, whose three-dimensional framework structures have large cavities connected by smaller tunnels (Figure \(\PageIndex{4}\)). Because the cations in zeolites are readily exchanged, zeolites are used in laundry detergents as water-softening agents: the more loosely bound Na\(^+\) ions inside the zeolite cavities are displaced by the more highly charged Mg\(^{2+}\) and Ca\(^{2+}\) ions present in hard water, which bind more tightly. Zeolites are also used as catalysts and for water purification.

Figure \(\PageIndex{4}\): Zeolites Are Aluminosilicates with Large Cavities Connected by Channels. The cavities normally contain hydrated cations that are loosely bound to the oxygen atoms of the negatively charged framework by electrostatic interactions. The sizes and arrangements of the channels and cavities differ in different types of zeolites. For example, in zeolite A the aluminosilicate cages are arranged in a cubic fashion, and the channels connecting the cavities intersect at right angles. In contrast, the cavities in faujasite are much larger, and the channels intersect at 120° angles. In these idealized models, the oxygen atoms that connect each pair of silicon atoms have been omitted.

Silicon and germanium react with nitrogen at high temperature to form nitrides (M\(_3\)N\(_4\)):

\[
\text{3Si}_{(l)} + 2N_{2(g)} \rightarrow \text{Si}_3N_4(s)
\]

Silicon nitride has properties that make it suitable for high-temperature engineering applications: it is strong, very hard, and chemically inert, and it retains these properties to temperatures of about 1000°C.
Because of the diagonal relationship between boron and silicon, metal silicides and metal borides exhibit many similarities. Although metal silicides have structures that are as complex as those of the metal borides and carbides, few silicides are structurally similar to the corresponding borides due to the significantly larger size of Si (atomic radius 111 pm versus 87 pm for B). Silicides of active metals, such as Mg$_2$Si, are ionic compounds that contain the Si$^{4-}$ ion. They react with aqueous acid to form silicon hydrides such as SiH$_4$:

\[
[Mg_2Si(s) + 4H^+(aq) \rightarrow 2Mg^{2+}(aq) + SiH_4(g)] \label{3A}
\]

Unlike carbon, catenated silicon hydrides become thermodynamically less stable as the chain lengthens. Thus straight-chain and branched silanes (analogous to alkanes) are known up to only n = 10; the germanium analogues (germanes) are known up to n = 9. In contrast, the only known hydride of tin is SnH$_4$, and it slowly decomposes to elemental Sn and H$_2$ at room temperature. The simplest lead hydride (PbH$_4$) is so unstable that chemists are not even certain it exists. Because E=E and E≡E bonds become weaker with increasing atomic number (where E is any group 14 element), simple silicon, germanium, and tin analogues of alkenes, alkynes, and aromatic hydrocarbons are either unstable (Si=Si and Ge=Ge) or unknown. Silicon-based life-forms are therefore likely to be found only in science fiction.

The stability of group 14 hydrides decreases down the group, and E=E and E≡E bonds become weaker.

The only important organic derivatives of lead are compounds such as tetraethyllead [(CH$_3$CH$_2$)$_4$Pb]. Because the Pb–C bond is weak, these compounds decompose at relatively low temperatures to produce alkyl radicals (R·), which can be used to control the rate of combustion reactions. For 60 yr, hundreds of thousands of tons of lead were burned annually in automobile engines, producing a mist of lead oxide particles along the highways that constituted a potentially serious public health problem. The use of catalytic converters reduced the amount of carbon monoxide, nitrogen oxides, and hydrocarbons released into the atmosphere through automobile exhausts, but it did nothing to decrease lead emissions. Because lead poisons catalytic converters, however, its use as a gasoline additive has been banned in most of the world.

\[\text{Figure \(\PageIndex{5}\)}\] Silicones Are Polymers with Long Chains of Alternating Silicon and Oxygen Atoms. The structure of a linear silicone polymer is similar to that of quartz, but two of the oxygen atoms attached to each silicon atom are replaced by the carbon atoms of organic groups, such as the methyl groups (–CH$_3$) shown here. The terminal silicon atoms are bonded to three methyl groups. Silicones can be oily, waxy, flexible, or elastic, depending on the chain length, the extent of cross-linking between the chains, and the type of organic group.

Compounds that contain Si–C and Si–O bonds are stable and important. High-molecular-mass polymers called silicones contain an (Si–O–)$_n$ backbone with organic groups attached to Si (Figure \(\PageIndex{5}\)). The properties of silicones are determined by the chain length, the type of organic group, and the extent of cross-linking between the chains. Without cross-linking, silicones are waxes or oils, but cross-linking can produce flexible materials used in sealants, gaskets, car polishes, lubricants, and even elastic materials, such as the plastic substance known as Silly Putty.
A child playing with Silly Putty, a silicone polymer with unusual mechanical properties. Gentle pressure causes Silly Putty to flow or stretch, but it cannot be flattened when hit with a hammer. This is called a "Non-Newtonian Fluid"

Example \(\PageIndex{2}\)

For each reaction, explain why the given products form.

a. \(\text{Pb}(s) + \text{Cl}_2(g) \rightarrow \text{PbCl}_2(s)\)

b. \(\text{Mg}_2\text{Si}(s) + 4\text{H}_2\text{O}(l) \rightarrow \text{SiH}_4(g) + 2\text{Mg(OH)}_2(s)\)

c. \(\text{GeO}_2(s) + 4\text{OH}^-(aq) \rightarrow \text{GeO}_4^{4-}(aq) + 2\text{H}_2\text{O}(l)\)

**Given:** balanced chemical equations

**Asked for:** why the given products form

**Strategy:**

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

**Solution:**

a. Lead is a metal, and chlorine is a nonmetal that is a strong oxidant. Thus we can expect a redox reaction to occur in which the metal acts as a reductant. Although lead can form compounds in the +2 and +4 oxidation states, \(\text{Pb}^{4+}\) is a potent oxidant (the inert-pair effect). Because lead prefers the +2 oxidation state and chlorine is a weaker oxidant than fluorine, we expect \(\text{PbCl}_2\) to be the product.

b. This is the reaction of water with a metal silicide, which formally contains the \(\text{Si}^{4-}\) ion. Water can act as either an acid or a base. Because the other compound is a base, we expect an acid–base reaction to occur in which water acts as an acid. Because \(\text{Mg}_2\text{Si}\) contains Si in its lowest possible oxidation state, however, an oxidation–reduction reaction is also a possibility. But water is a relatively weak oxidant, so an acid–base reaction is more likely. The acid \((\text{H}_2\text{O})\) transfers a proton to the base \((\text{Si}^{4-})\), which can accept four protons to form \(\text{SiH}_4\). Proton transfer from water produces the \(\text{OH}^-\) ion, which will combine with \(\text{Mg}^{2+}\) to give magnesium hydroxide.
c. We expect germanium dioxide (GeO$_2$) to be amphoteric because of the position of germanium in the periodic table. It should dissolve in strong aqueous base to give an anionic species analogous to silicate.

Exercise \PageIndex{2}

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. PbO$_2$(s) \xrightarrow{(\Delta)} 

b. GeCl$_4$(s) + H$_2$O(l) → 

c. Sn(s) + HCl(aq) → 

Answer:

a. \(\text{PbO}_2(\text{s}) \xrightarrow{(\Delta)} \text{PbO}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g})\)

b. GeCl$_4$(s) + 2H$_2$O(l) → GeO$_2$(s) + 4HCl(aq)

c. Sn(s) + 2HCl(aq) → Sn$^{2+}$(aq) + H$_2$(g) + 2Cl$^-$(aq)

Summary

The group 14 elements show the greatest diversity in chemical behavior of any group; covalent bond strengths decrease with increasing atomic size, and ionization energies are greater than expected, increasing from C to Pb. Because the covalent bond strength decreases with increasing atomic size and greater-than-expected ionization energies due to an increase in $Z_{\text{eff}}$, the stability of the +2 oxidation state increases from carbon to lead. The tendency to form multiple bonds and to catenate decreases as the atomic number increases. Consistent with periodic trends, metallic behavior increases down the group. Silicon has a tremendous affinity for oxygen because of partial Si–O π bonding. Dioxides of the group 14 elements become increasingly basic down the group and their metallic character increases. Silicates contain anions that consist of only silicon and oxygen. Aluminosilicates are formed by replacing some of the Si atoms in silicates by Al atoms; aluminosilicates with three-dimensional framework structures are called zeolites. Nitrides formed by reacting silicon or germanium with nitrogen are strong, hard, and chemically inert. The hydrides become thermodynamically less stable down the group. Moreover, as atomic size increases, multiple bonds between or to the group 14 elements become weaker. Silicones, which contain an Si–O backbone and Si–C bonds, are high-molecular-mass polymers whose properties depend on their compositions.

Contributors

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