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2007-N-13:

- Synthetic Strategies
- In order to reduce the incidence of dental cavities, water is fluoridated to a level of $1 \mathrm{mg} \mathrm{L}^{-1}$. In regions where the water is "hard" the calcium concentration is typically

For the dissolution of $\mathrm{CaF}_{2}(\mathrm{~s}) \rightleftharpoons \mathrm{Ca}^{2+}(\mathrm{aq})+2 \mathrm{~F}^{-}(\mathrm{aq}), Q_{\mathrm{sp}}=\left[\mathrm{Ca}^{2+}(\mathrm{aq})\right]\left[\mathrm{F}^{-}(\mathrm{aq})\right]^{2}$. If $Q_{\text {sp }}>K_{\text {sp }}$, then $\mathrm{CaF}_{2}(\mathrm{~s})$ will precipitate. If $Q_{\mathrm{sp}}<K_{\text {sp }}$, then $\mathrm{CaF}_{2}(\mathrm{~s})$ will completely dissolve.

The atomic mass of calcium is $40.08 \mathrm{~g} \mathrm{~mol}^{-1}$. A $100 \mathrm{mg} \mathrm{L}^{-1}$ solution contains
$\frac{100 \times 10^{-3}}{40.08}$ mol and has a concentration of $\frac{100 \times 10^{-3}}{40.08} \mathrm{M}$. $\left[\mathrm{Ca}^{2+}(\mathrm{aq})\right]=$ $2.495 \times 10^{-3}$ M.

The atomic mass of fluorine is $19.00 \mathrm{~g} \mathrm{~mol}^{-1}$. A $1 \mathrm{mg} \mathrm{L}^{-1}$ solution contains
$\frac{1 \times 10^{-3}}{19.00}$ mol and has a concentration of $\frac{1 \times 10^{-3}}{19.00} \mathrm{M} .\left[\mathrm{F}^{-}(\mathrm{aq})\right]=5.263 \times 10^{-5} \mathrm{M}$.
Hence, $Q_{\mathrm{sp}}=\left(2.495 \times 10^{-3} \mathrm{M}\right) \times\left(5.263 \times 10^{-5} \mathrm{M}\right)^{2}=6.911 \times 10^{-12} \mathrm{M}^{3}$. As $Q_{\mathrm{sp}}<K_{\mathrm{sp}}$, calcium fluoride will not precipitate.

Answer: No, it does not precipitate

- Consider the boiling points of the following monosubstituted benzenes.

|  | $\mathrm{C}_{6} \mathrm{H}_{6}$ | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~F}$ | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{Cl}$ | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{Br}$ | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}$ | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{I}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| b.p. | $80^{\circ} \mathrm{C}$ | $85^{\circ} \mathrm{C}$ | $132{ }^{\circ} \mathrm{C}$ | $156{ }^{\circ} \mathrm{C}$ | $182{ }^{\circ} \mathrm{C}$ | $188{ }^{\circ} \mathrm{C}$ |

Explain this order of boiling points.

Phenol $\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}\right)$ has an anomalously high boiling point compared to the other compounds as it forms strong hydrogen bonds.

The boiling points of the other compounds increase in the expected order, as the halogen increases in atomic number, the size and polarisability of its electron cloud increases and the strength of the intermolecular dispersion forces within the liquid increase.

The strengths of the dipole-dipole forces increase in the opposite order (greatest for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~F}$ as it contains the most electronegative halogen). This shows that dispersion forces are more important than dipole-dipole forces in this series of compounds.

- The primary buffering system in blood plasma is represented by the following equation:

$$
\mathrm{H}_{2} \mathrm{CO}_{3} \rightleftharpoons \mathrm{HCO}_{3}^{-}+\mathrm{H}^{+} \quad \mathrm{p} K_{\mathrm{a}}=6.1
$$

What is the ratio $\mathrm{HCO}_{3}: \mathrm{H}_{2} \mathrm{CO}_{3}$ at the normal plasma pH of 7.4 ?

The Henderson-Hasselbalch equation with [acid] $=\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]$ and [base] $=$ $\left[\mathrm{HCO}_{3}{ }^{-}\right]$can be used for this buffer system,

$$
\begin{aligned}
& \mathbf{p H}=\mathbf{p} K_{\mathrm{a}}+\log _{10}\left(\frac{[\text { base }]}{[\text { acid }]}\right) \\
& =6.1+\log _{10}\left(\frac{[\text { base }]}{\text { [acid] }]}\right)=7.4 \\
& \frac{[\text { base }]}{[\text { acid }]}=10^{(7.4-6.1)}=10^{1.3}=20
\end{aligned}
$$

Answer: [base] : [acid] = $\mathbf{2 0}: \mathbf{1}$
A typical person has 2 L of blood plasma. If such a person were to drink 1 L of soft drink with a pH of 2.5 , what would the plasma pH be if it were not buffered? (Assume all of the $\mathrm{H}^{+}$from the soft drink is absorbed by the plasma, but the volume of plasma does not increase.)

As $\mathbf{p H}=-\log _{10}\left[\mathrm{H}^{+}\right]$, the $\left[\mathrm{H}^{+}\right]$in the soft drink is,

$$
\left[\mathbf{H}^{+}\right]_{\text {soft drink }}=1 \mathbf{1 0}^{-2.5} \mathbf{M}
$$

## 1 L of soft drink therefore contains

$$
\text { number of moles }=\text { concentration } \times \text { volume }=\left(10^{-2.5} \mathrm{~mol} \mathrm{~L}^{-1} \times 1 \mathrm{~L}\right)=10^{-2.5} \mathrm{~mol}
$$

If this amount is present in 2 L of plasma,

$$
\left[\mathrm{H}^{+}\right]_{\text {plasma }}=\frac{\text { number of moles }}{\text { volume }}=\frac{10^{-2.5}}{2} \mathrm{M}
$$

Hence the $\mathbf{p H}$ of the unbuffered plasma is

$$
\mathrm{pH}=-\log _{10}\left[\mathrm{H}^{+}\right]=-\log _{10}\left(\frac{10^{-2.5}}{2}\right)=2.8
$$

What is the pH in this typical person with a normal $\mathrm{HCO}_{3^{-}}$concentration of 0.020 M ? Ignore any other contributions to the buffering.

Before the addition of the soft drink, $\left[\mathrm{HCO}_{3}{ }^{-}\right]=0.020 \mathrm{M}$ and, at $\mathbf{p H} 7.4,\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]=$ $\left[\mathrm{HCO}_{3}{ }^{-}\right] / 20=0.0010 \mathrm{M}$.

As the soft drink has $10^{-2.5} \mathrm{~mol}$ of $\mathbf{H}^{+}$, its concentration when added to the plasma will again be $\left[\mathrm{H}^{+}\right]=\frac{10^{-2.5}}{2} \mathrm{M}$ before buffering. Adding it will decrease the base concentration and increase the acid concentration so that,

$$
\begin{aligned}
& {\left[\mathrm{HCO}_{3}{ }^{-}\right]=\left(0.020-\frac{10^{-2.5}}{2}\right) M=0.018 \mathrm{M}} \\
& {\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]=\left(0.0010+\frac{10^{-2.5}}{2}\right) M=0.0026 \mathrm{M}}
\end{aligned}
$$

## Hence,

$$
\mathrm{pH}=(6.1)+\log _{10}\left(\frac{0.018}{0.0026}\right)=7.0
$$

- Alfred Werner, one of the founders of the field of coordination chemistry, made extensive studies of the metal complex $\left[\mathrm{PtCl}_{2}\left(\mathrm{NH}_{3}\right)_{2}\right]$. He showed that it existed in two isomeric forms and used this information to predict that the compound had a square-planar molecular geometry. What other molecular geometry would need to be considered for such a complex and on what basis did Werner reject this alternative geometry?

As the complex contains 4 ligands bonded to $\mathbf{P t}(\mathrm{II})$ (two $\mathrm{Cl}^{-}$and two $\mathbf{N H}_{\mathbf{3}}$ ), a tetrahedral geometry also needs to be considered. However, as the angles between all of the bonds in a tetrahedron are the same, tetrahedral $\left[\mathrm{PtCl}_{2}\left(\mathrm{NH}_{3}\right)_{2}\right.$ would not give rise to two isomers.

Draw and name the two isomers.


Why does platinum(II) form square-planar complexes?

There are a number of reasons why platinum(II) forms square-planar rather than tetrahedral complexes. These include:
(i) $\mathrm{Pt}($ II) is a relatively big cation and so repulsion between the ligands are not too large.
(ii) The Pt-ligands bonds are stronger as, with its $5 d^{8}$ configuration, $\mathrm{Pt}(\mathrm{II})$ is able to keep the $d_{x 2-y 2}$ orbital completely empty allowing the ligands to donate into it.

Although the tetrahedral form has less crowding between the ligands, there is no single $d$-orbital which is directed towards, and can bond with, the ligands.

Which one of the isomers is biologically active? What is its activity? Describe two features of the complex that play important roles in this biological activity.

Only the cis isomer is biologically active - it is a potent anti-cancer drug.
The cis chloride ligands are easily replaced, allowing Pt(II) to bind to DNA and stop cell replication. It appears that the cis-geometry of the Pt-DNA bonds is important in this. The flat nature of the complex means it can approach the DNA closer.

- Nitric oxide, a noxious pollutant, and hydrogen react to give nitrous oxide and water according to the following equation.

$$
2 \mathrm{NO}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{N}_{2} \mathrm{O}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

The following rate data were collected at $225^{\circ} \mathrm{C}$.

| Experiment | $\left[\mathrm{NO}_{0}(\mathrm{M})\right.$ | $\left[\mathrm{H}_{2}\right]_{0}(\mathrm{M})$ | Initial rate $\left(\mathrm{d}[\mathrm{NO}] / \mathrm{dt}, \mathrm{M} \mathrm{s}^{-1}\right)$ |
| :---: | :---: | :---: | :---: |
| 1 | $6.4 \times 10^{-3}$ | $2.2 \times 10^{-3}$ | $2.6 \times 10^{-5}$ |
| 2 | $1.3 \times 10^{-2}$ | $2.2 \times 10^{-3}$ | $1.0 \times 10^{-4}$ |
| 3 | $6.4 \times 10^{-3}$ | $4.4 \times 10^{-3}$ | $5.1 \times 10^{-5}$ |

Determine the rate law for the reaction.
Between experiments (1) and (2), $\left[\mathrm{H}_{2}\right]_{0}$ is constant and $[\mathrm{NO}]_{0}$ doubles. As the rate increases by a factor of $\frac{1.0 \times 10^{-4}}{2.6 \times 10^{-5}}=3.8 \sim 4$, the rate is second order with respect to $[\mathrm{NO}]_{0}$.

Between experiments (1) and (3), $\left[\mathrm{H}_{2}\right]_{0}$ doubles and $[\mathrm{NO}]_{0}$ is constant. As the rate increases by a factor of $\frac{5.1 \times 10^{-5}}{2.6 \times 10^{-5}}=2.0$, the rate is first order with respect to [ NO$]_{0}$.

Overall,

$$
\text { rate }=k[\mathrm{NO}]^{2}\left[\mathrm{H}_{2}\right]
$$

Calculate the value of the rate constant at $225^{\circ} \mathrm{C}$.
Using experiment (1),

$$
\begin{aligned}
& 2.6 \times 10^{-5} \mathrm{M} \mathrm{~s}^{-1}=k \times\left(6.4 \times 10^{-3} \mathrm{M}\right)^{2} \times\left(2.2 \times 10^{-3} \mathrm{M}\right) \\
& k=2.9 \times 10^{2} \mathrm{M}^{-2} \mathrm{~s}^{-1}
\end{aligned}
$$

$$
\text { Answer: } k=2.9 \times 10^{2} \mathrm{M}^{-2} \mathrm{~s}^{-1}
$$

Calculate the rate of appearance of $\mathrm{N}_{2} \mathrm{O}$ when $[\mathrm{NO}]=\left[\mathrm{H}_{2}\right]=6.6 \times 10^{-3} \mathrm{M}$.
rate of disappearance of $\mathrm{NO}=k[\mathrm{NO}]^{2}\left[\mathrm{H}_{2}\right]$

$$
\begin{aligned}
& =\left(2.9 \times 10^{2} \mathbf{M}^{2} \mathbf{s}^{-1}\right) \times\left(6.6 \times 10^{-3} \mathrm{M}\right)^{2} \times\left(6.6 \times 10^{-3} \mathrm{M}\right) \\
& =8.3 \times 10^{-5} \mathrm{M} \mathrm{~s}^{-1}
\end{aligned}
$$

The rate of appearance of $\mathrm{N}_{2} \mathrm{O}$ is half this value as, from the chemical equation, NO is disappearing at twice the rate than $\mathrm{N}_{2} \mathrm{O}$ is appearing.

$$
\text { Answer: } \mathbf{4 . 1} \times \mathbf{1 0}^{-5} \mathbf{M ~ s}^{-1}
$$

Suggest a possible mechanism for the reaction based on the form of the rate law.
Explain your answer.

Step 1: $\quad 2 \mathrm{NO}(\mathrm{g}) \rightleftharpoons \mathbf{N}_{2} \mathrm{O}_{\mathbf{2}}(\mathrm{g})$

This is a fast equilibrium and so $K=\frac{\left[\mathrm{N}_{2} \mathrm{O}_{2}(\mathrm{~g})\right]}{[\mathrm{NO}(\mathrm{g})]^{2}}$ or $\left[\mathrm{N}_{2} \mathrm{O}_{2}(\mathrm{~g})\right]=K[\mathrm{NO}(\mathrm{g})]^{2}$
Step 2: $\quad \mathrm{N}_{2} \mathrm{O}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{N}_{2} \mathrm{O}(\mathrm{g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \quad$ slow (i.e. rate determining) As this is rate determining,

$$
\text { rate }=k_{2}\left[\mathbf{N}_{2} \mathrm{O}_{2}\right]\left[\mathrm{H}_{2}\right]
$$

As $\left[\mathrm{N}_{2} \mathrm{O}_{2}(\mathrm{~g})\right]=K[\mathrm{NO}(\mathrm{g})]^{\mathbf{2}}$, this can be rewritten as,

$$
\operatorname{rate}=k K[\mathrm{NO}]^{2}\left[\mathrm{H}_{2}\right]
$$

This is consistent with the experimentally determined rate law with $\boldsymbol{k}_{\exp }=\boldsymbol{k}_{2} \boldsymbol{K}$.

- The diagram below shows the structure of perovskite, a mineral made up of calcium (at each of the corners), oxygen (in the centre of each of the faces), and titanium (at the centre of the cube). The unit cell dimension (edge length, $a$ ) for perovskite is 0.38 nm .


○ calcium


What is the chemical formula of perovskite?

There are eight $\mathrm{Ca}^{2+}$ ions on the corners of the cube. These are each shared between eight unit cells: number of $\mathrm{Ca}^{2+}$ ions $=8 \times 1 / 8=1$.

There is a single, unshared $\mathrm{Ti}^{4+}$ ion at the cube centre.
There are six $\mathbf{O}^{2-}$ ions at the centres of the faces of the cube. These are each shared between two cubes: number of $\mathrm{O}^{2-}$ ions $=6 \times 1 / 2=3$.

Overall, $\mathrm{Ca}^{2+}: \mathrm{Ti}^{4+}: \mathrm{O}^{2-}=1: 1: 3$. The formula is $\mathrm{CaTiO}_{3}$.

Answer: $\mathbf{C a T i O} 3$
What is the volume of the unit cell?

The length of the side of the cube $=a=0.38 \mathrm{~nm}$. As $V=a^{3}$,

$$
V=\left(0.38 \times 10^{-9} \mathrm{~m}\right)^{3}=5.5 \times 10^{-29} \mathrm{~m}^{3}
$$

Answer: $5.5 \times \mathbf{1 0}^{-29} \mathbf{m}^{3}$
What is the density of perovskite? Give your answer in $\mathrm{g} \mathrm{cm}^{-3}$.

## Marks

 5As the atomic mass is the mass of a mole, the mass of one atom is $\frac{M}{N_{\mathrm{a}}}$. From above, each unit cell contains $1 \mathbf{C a}^{2+}, 1 \mathrm{Ti}^{4+}$ and $3 \mathrm{O}^{2-}$. The mass of one cell is therefore:

$$
\begin{aligned}
\text { mass of cell } & =\frac{M_{\mathrm{Ca}}}{N_{\mathrm{a}}}+\frac{M_{\mathrm{Ti}}}{N_{\mathrm{a}}}+3 \frac{M_{\mathrm{O}}}{N_{\mathrm{a}}}=\frac{1}{N_{\mathrm{a}}}(40.08+47.88+16.00) \mathrm{g} \\
& =\frac{1}{N_{\mathrm{a}}} \times 135.96 \mathrm{~g}=2.258 \times 10^{-22} \mathrm{~g}
\end{aligned}
$$

As $1 \mathrm{~cm}=0.01 \mathrm{~m}, 1 \mathrm{~cm}^{3}=(0.01)^{3} \mathrm{~m}^{3}=1 \times 10^{-6} \mathrm{~m}^{3}$. From above, $\mathrm{V}=5.5 \times 10^{-29} \mathrm{~m}^{3}$ so,

$$
\text { volume }=5.5 \times 10^{-29} / 1 \times 10^{-6} \mathrm{~cm}^{3}=5.5 \times 10^{-23} \mathrm{~cm}^{3} .
$$

Hence,

$$
\text { density }=\frac{\text { mass }(\mathrm{g})}{\text { volume }\left(\mathrm{cm}^{3}\right)}=\frac{2.258 \times 10^{-22} \mathrm{~g}}{5.5 \times 10^{-23} \mathrm{~cm}^{3}}=4.1 \mathrm{~g} \mathrm{~cm}^{-3}
$$

What is the density of perovskite? Give your answer in $\mathrm{g} \mathrm{cm}^{-3}$.

As the atomic mass is the mass of a mole, the mass of one atom is $\frac{M}{N_{\mathrm{a}}}$. From above, each unit cell contains $1 \mathrm{Ca}^{2+}, 1 \mathrm{Ti}^{4+}$ and $3 \mathrm{O}^{2-}$. The mass of one cell is therefore:

$$
\begin{aligned}
\text { mass of cell } & =\frac{M_{\mathrm{Ca}}}{N_{\mathrm{a}}}+\frac{M_{\mathrm{Ti}}}{N_{\mathrm{a}}}+3 \frac{M_{\mathrm{O}}}{N_{\mathrm{a}}}=\frac{1}{N_{\mathrm{a}}}(40.08+47.88+16.00) \mathrm{g} \\
& =\frac{1}{N_{\mathrm{a}}} \times 135.96 \mathrm{~g}=2.258 \times 10^{-22} \mathrm{~g}
\end{aligned}
$$

As $1 \mathrm{~cm}=0.01 \mathrm{~m}, 1 \mathrm{~cm}^{3}=(0.01)^{3} \mathrm{~m}^{3}=1 \times 10^{-6} \mathrm{~m}^{3}$. From above, $\mathrm{V}=5.5 \times 10^{-29} \mathrm{~m}^{3}$ so,

$$
\text { volume }=5.5 \times 10^{-29} / 1 \times 10^{-6} \mathrm{~cm}^{3}=5.5 \times 10^{-23} \mathrm{~cm}^{3} .
$$

Hence,

$$
\text { density }=\frac{\text { mass }(\mathrm{g})}{\text { volume }\left(\mathrm{cm}^{3}\right)}=\frac{2.258 \times 10^{-22} \mathrm{~g}}{5.5 \times 10^{-23} \mathrm{~cm}^{3}}=4.1 \mathrm{~g} \mathrm{~cm}^{-3}
$$

- Write balanced ionic equations for the reactions that occur in each of the following. If no reaction occurs, write "NO REACTION".

Excess 16 M ammonia solution is added to solid silver iodide.

No reaction (See E19 of Lab Handbook)
Excess 4 M ammonia solution is added to a 1 M magnesium sulfate solution.
$\mathbf{M g}^{2+}(\mathrm{aq})+2 \mathrm{NH}_{3}(\mathrm{aq})+2 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathbf{M g}(\mathrm{OH})_{2}(\mathrm{~s})+2 \mathrm{NH}_{4}{ }^{+}(\mathrm{aq})$

Excess 4 M hydrochloric acid is added to solid cadmium sulfide.
No reaction (See E5 of Lab Handbook)

Excess 4 M sodium hydroxide solution is added to 1 M zinc nitrate solution.

$$
\mathrm{Zn}^{2+}(\mathrm{aq})+4 \mathrm{OH}^{-}(\mathrm{aq}) \rightarrow\left[\mathrm{Zn}(\mathrm{OH})_{4}\right]^{2-}(\mathrm{aq})
$$

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Draw the structure(s) of the major organic product(s) formed in each of the following reactions. Give the names of the products where requested.

Marks 6


Name(s): 2-methylhept-5-yn-2-ol


Name(s): (Z)-3,6-diethyloct-4-ene


THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Compound $\mathbf{X}$ undergoes an addition reaction on treatment with hydrogen gas in the presence of a palladium on carbon catalyst to form a mixture of cyclic alkanes.


X

Clearly draw all possible products that can form from this reaction, taking care to represent the stereochemistry of the products clearly.


Clearly label each isomer drawn above as either chiral or achiral (not chiral).
Circle one of the isomers and provide a full systematic name for this compound below. Make sure you include all relevant stereochemical descriptors.

| cis-1,6-dimethylcyclodecane | trans-1,6-dimethylcyclodecane |
| :--- | :--- |

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Compound $\mathbf{Y}$ can be readily analysed by ${ }^{1} \mathrm{H}$ NMR spectroscopy.

On the diagram of $\mathbf{Y}$, write the letters $\mathbf{a}, \mathbf{b}, \mathbf{c}$, etc. as necessary to identify each unique hydrogen environment giving rise to a signal in the ${ }^{1} \mathrm{H}$ NMR spectrum.


Sketch the ${ }^{1}$ H NMR spectrum of compound $\mathbf{Y}$. Label each signal in the spectrum with $\mathbf{a}, \mathbf{b}, \mathbf{c}$, etc. to correspond with your assignments on the diagram of $\mathbf{Y}$. Make sure you show the splitting pattern (number of fine lines) you expect to see for each signal. Also write the relative number of hydrogens you expect above each signal.


How would you distinguish between compounds $\mathbf{Y}$ and $\mathbf{Z}$ using chemical reactions, spectroscopic analysis or other means?
(1) $Y$ is optically active. $Z$ is not. A polarimeter could be used to check optical rotation.
(2) Hydrolyse both compounds to the acids with $\mathrm{H}^{+} / \mathrm{H}_{2} \mathrm{O}$. Y will give optically pure acid (the ( $R$ )-enantiomer). $Z$ will give a racemic mixture of acids. React each product with an optically pure amine. The product from $Y$ will give a single compound, whilst the product from $Z$ will give a mixture of two diastereomers.

- Complete the two-step mechanism for the reaction given below. Draw partial charges, curly arrows and intermediate structures as appropriate to illustrate the bonding changes that take place.


Marks

- Complete the following table.
Starting material

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- Show clearly the reagents you would use to carry out the following chemical conversion. Draw constitutional formulas for any intermediate compounds. NOTE: More than one step is necessary.


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