Dissolution of Marble in Hydrochloric Acid

**Equipment:**
goblet

**Chemicals:**
marble or „limestone“ (calcium carbonate) in pieces (f.e. old marble plate)
hydrochloric acid (1 molar)

**Safety:**
It is highly recommended to wear safety glasses.

**Procedure:**
Hydrochloric acid, an aqueous solution of hydrogen chloride, HCl, is poured over two or three pieces of marble (or limestone).

**Observation:**
Foam develops that contains carbon dioxide.

**Explanation:**
Calcium carbonate is dissolved by hydrochloric acid, thereby forming gaseous carbon dioxide:

\[
\text{CaCO}_3|s + 2 \text{H}^+|w \rightarrow \text{Ca}^{2+}|w + \text{H}_2\text{O}|l + \text{CO}_2|g
\]

\[\Sigma \mu^\varphi: -1128.8 > -1184.6 \text{ kG}\]

\(\Rightarrow\) chemical drive \(\Delta^\varphi: +55.8 \text{ kG}\)

The drive of the reaction is positive, i.e. the combined reactants have a higher chemical potential than the products and subsequently the reaction takes place spontaneously.

Necessary chemical potentials \((T = 298 \text{ K}, \; p = 101 \text{ kPa})\):

<table>
<thead>
<tr>
<th>Substance</th>
<th>Chemical potential (\mu^\varphi) [kG]</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{CaCO}_3</td>
<td>s</td>
</tr>
<tr>
<td>\text{H}^+</td>
<td>w</td>
</tr>
<tr>
<td>\text{Ca}^{2+}</td>
<td>w</td>
</tr>
<tr>
<td>\text{H}_2\text{O}</td>
<td>l</td>
</tr>
<tr>
<td>\text{CO}_2</td>
<td>g</td>
</tr>
</tbody>
</table>
**Disposal:**
After the complete dissolution of the marble pieces, the produced solution is neutralised and flushed down the drain with water.
Ammonia Fountain

**Equipment:**
- 2-L round-bottomed flask
- dropping funnel
- 250-mL round-bottomed flask with two necks for dropping funnel and glass tube
- glass tube (diameter: 7-8 mm)
- L-shaped glass tube (diameter: 7-8 mm)
- flexible tube
- ring stands, clamps and ring
- glass tube with tapered end (length: approx. 30 cm, diameter: 7-8 mm)
- two rubber stoppers with one hole and one with two holes
- small rubber stopper (that fits the glass tube)
- crystallisation dish or beaker
- blow-dryer

**Chemicals:**
- concentrated ammonia solution
- sodium hydroxide pellets
- deionised water
- phenolphthalein solution
- diluted hydrochloric acid

**Safety:**
- sodium hydroxide (NaOH): C R35 S26-37/39-45
- phenolphthalein solution (C₁₂H₁₄O₄) (in ethanol): R10

Ammonia is a colourless, highly corrosive and irritant gas which is especially harmful to the respiratory system and the eyes. Therefore, the round-bottomed flask has to be filled in a fume hood. It is also necessary to wear safety glasses and protective gloves.

To avoid implosion-related incidents caused by the stress of the vacuum created during the experiment damaged glassware (with “stars”, cracks etc.) should never be used.

**Procedure:**

**Preparation:** A relatively dry sample of ammonia gas can be prepared by dropping concentrated ammonia solution onto granular sodium hydroxide. Therefore, 15 g of NaOH pellets are put into the 250-mL round-bottomed flask with two necks. The dropping funnel is attached to one neck, and the second neck is closed using a one-hole rubber stopper with a glass tube in it. The 2-L round bottomed flask is closed using a two-hole rubber stopper with an L-shaped glass tube in one of the holes and the other hole open. The 2-L
flask is mounted upside-down to a stand, and a flexible tube is used to connect the glass tubes of the two flasks together.

The dropping funnel is filled with 30 mL concentrated ammonia solution that is dripped into the 250-mL flask. The developed dry gas fills the 2L-flask by downward displacement of air. After the reaction, the 2-L flask is sealed with a one-hole stopper that has the tapered glass tube in it. The tapered end should be inside the flask, and extend about half of the way into the bulb of the flask. The flask is heated by a blow-dryer and subsequently the non-tapered end of the glass tube is sealed with a small rubber stopper.

**Procedure:** The crystallisation dish is filled with deionised water, and the indicator phenolphthalein and a few drops of hydrochloric acid are added to the water. The inverted 2L-flask is clamped on the stand over the crystallisation dish so that the bottom end of the glass tube is immersed deeply in the water and secured by a ring. Then the small rubber stopper is removed.

**Observation:**

The water begins to go up in the glass tube because of slight underpressure in the flask. When the first drops reaches the bulb the speed of the process increases more and more until the water shoots into the glass flask like a fountain. Additionally, the solution turns pink. The water level rises until the flask is nearly completely filled.

**Explanation:**

Ammonia gas is extremely soluble in water (1 L water can dissolve 702 L ammonia gas at 20°C!). The fountain experiment demonstrates the violence with which ammonia is absorbed by water. The process can be explained thermodynamically by use of the chemical potential:

\[
\text{NH}_3|_g \rightarrow \text{NH}_3|_w \\
\mu^\ominus: -16.4 > -26.4 \quad \text{kG}
\]

\[ \Rightarrow \text{chemical drive } \Delta G^\ominus: +10.0 \text{ kG} \]

The drive of the reaction is positive, i.e. the reaction takes place spontaneously.

The first few water drops that enter the round-bottomed flask dissolve part of the ammonia gas, thereby reducing its volume considerably. This causes a decrease in pressure in the flask, and more water is drawn from the reservoir into the bulb. As more and more water rushes into the flask, more and more of the ammonia gas dissolves creating a larger pressure difference, thereby speeding up the flow of the water.

The aqueous ammonia solution is a weak base because of the protolysis reaction:

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-.
\]

This alkaline effect of ammonia is revealed by the indicator phenolphthalein, which changes its colour to pink.

**Disposal:**

The solution is neutralised with hydrochloric acid and poured down the drain.
**Carbide Lamp**

**Equipment:**
- washing bottle with dropping funnel
- rubber tubing
- glass tube with tapered end
- matches or pocket lighter
- wooden splint
- test tube

**Chemicals:**
- calcium carbide (ideal grain size: 20 – 40 mm)
- deionised water

**Safety:**
- calcium carbide (CaC₂): F R15 S8-43.6
- ethyne (acetylene) (C₂H₂): F+ R5-6-12 S9-16-33
- calcium hydroxide (Ca(OH)₂): Xi R41 S(22-24-26-39

Ethyne is extremely flammable and forms explosive mixtures with air ("detonating gas"). Because the gas is poisonous particularly with regard to contaminants it is necessary to work in a fume hood. It is also required to wear safety glasses.

**Procedure:**
The dropping funnel is filled with water and some lumps of calcium carbide are placed in the washing bottle. Water is dripped (cautiously!) onto the calcium carbide until a vigorous generation of gas begins. Then the cock of the dropping funnel is closed and the escaping gas is collected in the test tube. The existence of an explosive mixture can be tested by ignition with a burning splint. When the explosion danger is overcome, i.e. most of the air in the washing bottle is displaced by ethyne, the gas can be ignited directly at the tapered end of the glass tube by the splint (eventually it is necessary to drip again some water onto the carbide). For avoiding any explosion danger it is recommended to fill the washing bottle with nitrogen before starting the experiment.

**Observation:**
The produced gaseous ethyne burns with a bright and sooty flame. Additionally, an unpleasant garlic-like ordour can be noticed.

**Explanation:**
As the calcium carbide reacts with water it produces ethyne (acetylene) according to
\[
\text{CaC}_2|_{\text{s}} + 2 \ \text{H}_2\text{O}|_{\text{l}} \rightarrow \text{Ca(OH)}_2|_{\text{w}} + \text{C}_2\text{H}_2|_{\text{g}}
\]

\[\Sigma \mu^\varphi: \quad -542.2 \ > \ -658.4 \quad \text{kG}\]

\[\implies \text{chemical drive } \mathcal{J}^\varphi: +116.2 \ \text{kG}\]

The drive of the reaction is positive, i.e.
the reactants combined have a higher chemical potential than the products and subsequently the reaction takes place spontaneously.

Necessary chemical potentials \((T = 298 \ \text{K}, \ p = 101 \ \text{kPa}):\)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Chemical potential (\mu^\varphi [\text{kG}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{CaC}_2</td>
<td>_{\text{s}}</td>
</tr>
<tr>
<td>\text{H}_2\text{O}</td>
<td>_{\text{l}}</td>
</tr>
<tr>
<td>\text{Ca}^{2+}</td>
<td>_{\text{w}}</td>
</tr>
<tr>
<td>\text{OH}^-</td>
<td>_{\text{w}}</td>
</tr>
<tr>
<td>\text{C}_2\text{H}_2</td>
<td>_{\text{g}}</td>
</tr>
</tbody>
</table>

A positive chemical potential, like in the case of ethyne, does not mean that the substance cannot be produced by normal reactions of stable substances \((\text{with negative } \mu)\). It only means that the substance tends to decompose into its elements \(\text{(however, this process might proceed very slowly because of inhibitions, like in the case of benzene)}\).

The “burning test” demonstrates that the produced ethyne reacts with oxygen in the air describable by

\[
2 \ \text{C}_2\text{H}_2|_{\text{g}} + 5 \ \text{O}_2|_{\text{g}} \rightarrow 4 \ \text{CO}_2|_{\text{g}} + \text{H}_2\text{O}|_{\text{l}}.
\]

In earlier times, the gas extracted from the above reaction was used to power miners’ lamps and bicycle lights because of its bright flame. It is still used today for welding because of its high combustion temperature.

The characteristic “carbide odour”, however, is not caused by ethyne but by the toxic gas phosphine released by the contaminant calcium phosphide on contact with water.

Pure calcium carbide forms colourless, transparent crystals. Mostly the technical product is commercially available which is composed of greyish black or brown lumps. The colour is caused by contamination with carbon and iron oxide. Other contaminants are calcium oxide, calcium phosphide mentioned above, calcium sulfide, calcium nitride and silicium carbide.

**Disposal:**

After the burning of the produced ethyne, the residue should completely react with water in the fume hood. The produced solution of calcium hydroxide is neutralised and flushed down the drain with water.
Annealing of Silver Oxide

**Equipment:**
glass equipment with high-melting test tube and ground-glass joint (see figure on the right)
small balloon
ring stand, clamp
water jet pump
burner
wooden splint

**Chemicals:**
silver oxide

**Safety:**
silver oxide (Ag₂O): O, C  R8-34-44  S26-36/37/39-45

It is necessary to wear safety glasses and protective gloves.

**Procedure:**
**Preparation:** Approx. 2 g silver oxide are filled in the test tube and the balloon is put over the top part (as in the figure above). The whole equipment is mounted and clamped on the stand. It is then evacuated by a water jet pump.
**Procedure:** The blackish brown silver oxide is moderately heated by a burner, until the whole oxide was decomposed.

**Observation:**
The substance gradually changes its colour to whitish. The generation of a gas is detectable by the slow blowing up of the balloon. Subsequently, the gas can be identified as oxygen with a glowing splint. White shiny silver metal remains in the test tube.

In a simplified version of the experiment silver oxide can be filled in a normal high-melting test tube and heated. The glowing splint is then placed directly into the mouth of the test tube.

**Explanation:**
The thermal decomposition of silver oxide can be described by:
\[
2 \text{Ag}_2\text{O}|s \rightarrow 4 \text{Ag}|s + \text{O}_2|g
\]

\[\Sigma \mu^\ominus: \quad -22.4 < 0\]

\[\Rightarrow \text{chemical drive } \mathcal{A}^\ominus: -22.4 \text{ kG}\]

The decomposition does not take place at room temperature due to the negative drive. However, since a gas, that means a substance with strongly negative temperature coefficient \(\alpha\), should be formed we expect that this process will begin at a high enough temperature.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Chemical potential (\mu^\ominus) [kG]</th>
<th>Temperature coefficient (\alpha) [G/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(_2)O</td>
<td>s</td>
<td>-11.2</td>
</tr>
<tr>
<td>Ag</td>
<td>s</td>
<td>0</td>
</tr>
<tr>
<td>O(_2)</td>
<td>g</td>
<td>0</td>
</tr>
</tbody>
</table>

The minimum temperature \(T_D\) for the decomposition of Ag\(_2\)O is obtained from the condition that the combined chemical potentials of the initial and final substances must be equal and the chemical drive \(\mathcal{A}\) changes its sign:

\[\mathcal{A} = \mathcal{A}_0 + \alpha \cdot (T_D - T_0) = 0.\]

We obtain

\[T_D = T_0 - \frac{\mathcal{A}_0}{\alpha}.\]

Inserting the \(\mathcal{A}^\ominus\) and \(\alpha\) values which are calculated according to \(\alpha = 2 \cdot \alpha_{\text{Ag}_2\text{O}} - 4 \cdot \alpha_{\text{Ag}} - \alpha_{\text{O}_2}\) results in \(T_D \approx 465 \text{ K}\).

**Disposal:**
The silver residue is collected for reworking in a special container.
Boiling by Cooling

**Equipment:**
1-L round-bottomed flask
heating mantle or burner with wire gauze
rubber stopper
beaker
plastic tray
ring stand, clamp

**Chemicals:**
water
crushed ice

**Safety:**
To avoid implosion-related incidents caused by the stress of the vacuum created during the experiment damaged glassware (with “stars”, cracks etc.) never should be used. It is also necessary to always wear safety glasses.

**Procedure:**
The round-bottomed flask is one half filled with water and a few boiling stones are added. The water is heated until boiling using a heating mantle or burner, and allowed to boil for a few minutes so that most of the air is driven out of the flask. The flask is removed from the heat, tightly stoppered and allowed to cool for a little while to make a good seal. Then the inverted flask is clamped on the stand over a plastic tray, secured by a ring and ice water is poured cautiously over the flask.

**Observation:**
The water inside the flask begins to boil heavily. When the pouring is stopped the boiling process also comes to an end after a little while. But the boiling starts up again by pouring more ice water over the flask. The whole “procedure” can be repeated several times.

**Explanation:**
The boiling process can be described by the following equation:

\[ \text{H}_2\text{O}|l \rightarrow \text{H}_2\text{O}|g. \]

Liquid water has a smaller chemical potential than water vapour under standard conditions (298 K, 101 kPa), i.e. the drive is negative and the process will not take place.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Chemical potential ( \mu^\circ ) [kG]</th>
<th>Pressure coefficient ( \beta ) [G/Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>l</td>
<td>-237.2</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>g</td>
<td>-228.6</td>
</tr>
</tbody>
</table>
But the chemical potential of gases, and therefore also that of water vapour, is strongly pressure dependent as shown by a high pressure coefficient. At sufficiently low pressure the chemical potential of water vapour will fall below the value of liquid water so that the water will boil at temperatures significantly less than 100°C.

The flask is completely filled with water, i.e. liquid water is in equilibrium with water vapour. The cooling of its upper part causes the water vapour to condense and the pressure of the vapour to quickly drop to a low value.
Iron(III) Thiocyanate Equilibrium

**Equipment:**
- large goblet
- three smaller goblets
- glass rod

**Chemicals:**
- iron(III) nitrate solution (approx. 0.1 M)
- ammonium thiocyanate solution (approx. 0.1 M)
- deionised water

**Safety:**
- iron(III) nitrate nonahydrate (Fe(NO₃)₃ ⋅ 9 H₂O): O, Xi R8-36/38 S26
- ammonium thiocyanate (NH₄SCN): Xn R20/21/22-32-52/53 S13-61

It is necessary to wear safety glasses.

**Procedure:**
10 mL iron(III) nitrate and 10 mL ammonium thiocyanate solution are filled in the large goblet. The blood-red mixture is diluted with water until its colour changes to pale orange. Subsequently, the solution is divided into three approximately equal parts. The solution in the first small goblet is then treated with 20 mL of excess iron(III) solution, that in the third with 20 mL of excess thiocyanate solution.

**Observation:**
The colour gets again blood-red in both cases. The second goblet acts as reference.

**Explanation:**
Between iron hexaquo complex cations and thiocyanate anions on the one hand and the blood-red iron thiocyanate complex on the other hand exists an equilibrium which can be described by the following simplifying equation:

\[
[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + 3 \text{SCN}^- \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_3(\text{SCN})_3] + 3 \text{H}_2\text{O}.
\]

The application of the mass action law results in

\[
K_c = \frac{c([\text{Fe}(\text{H}_2\text{O})_3(\text{SCN})_3])}{c([\text{Fe}(\text{H}_2\text{O})_6]^{3+}) \cdot c(\text{SCN}^-)^3}.
\]

Water as solvent is treated as pure substance; therefore, it does not appear in the formula.
Dilution with water lowers the concentration of the complex, but also the concentrations of the free ions. Therefore, the denominator will decrease much faster than the numerator. Because the quotient is a constant, the so-called equilibrium constant $\hat{K}_c$, the numerator has to also decrease: The equilibrium is displaced towards the reactant side, i.e. some iron thiocyanate complex has to decompose again into iron hexaquo complex cations and thiocyanate anions. The pale orange colour of the resulting solution is caused by the iron hexaquo complex.

The addition of excess iron(III) ions, however, results in an increase of the denominator. More iron thiocyanate complex has to be formed in order to use up this extra reactant (along with the other reactant thiocyanate) and re-establish the equilibrium. Similarly, the addition of excess thiocyanate also causes a shift of the equilibrium to the product side.

**Disposal:**

The solutions are poured in a special jar for hazardous waste disposal.
Drinking Duck

Materials:
duck
beaker
possibly support
bell jar
possibly lifting gear

Chemicals:
water

Procedure and observation:
The beaker is filled with water and the felt of the duck’s head is wetted. After a while the duck begins to “drink” periodically, i.e. it slowly swings back and forth, dips its beak into the water, backs up again and after a few oscillations restarts the game.
After repeated „drinking“ the bell jar is placed over the duck and the beaker. After a while the duck stands still. When the bell jar is removed the duck will begin to “drink” again. By means of an appropriate equipment the movement of the duck can be utilised to lift up a weight.

Explanation:
Technically, the „drinking duck“ is a kind of „matter engine“ which utilises the difference between the chemical potentials of liquid water ($\mu_1$) and water vapour in the air ($\mu_2$). Due to the phenomenon of mass action the chemical potential of water vapour strongly diluted in air is lowered below that of liquid water and the evaporation process

$$H_2O|l \rightarrow H_2O|g$$

can take place voluntarily.
The flow of vapour from the felt into the ambient air caused by the potential gradient, $\mu_1 \rightarrow \mu_2$, is coupled with an entropy flow. The vapour transports approximately three times more entropy than was previously contained in the liquid water. Therefore, the wet felt cools down and entropy begins to flow off from the interior of the head, thereby cooling it inside compared to the body. Some of the vapour of the internal liquid (with a very low boiling point) condenses and the reduced pressure forces the liquid to rise up in the tube thereby gradually changing the centre of gravity of the duck. Finally the duck tips over and tilts into the water. At this moment the lower end of the tube comes out of contact with the liquid surface, part of the liquid drains back into the body and the vapour pressure in head and body is equalised. The bird returns to its upright position and the „game“ can start again.
As long as the head of the duck remains wet the process of “drinking” will recur periodically.

When the bell jar is placed over the duck and the beaker the chemical potentials of water and (saturated) water vapour will become equal and therefore the potential difference necessary for the “drive” is zero. The duck stops drinking.
The use of the drinking duck in the lifting gear proves that it is in fact a matter engine. For a lossless machine working between two reservoirs with fixed potentials $\mu_1$ and $\mu_2$ the
energy $W$ can be utilised (negative sign!) when the amount of matter $n$ is transferred from $\mu_1$ (the higher potential of liquid water) to $\mu_2$ (the lower potential of water vapour in ambient air):

$$W = n(\mu_2 - \mu_1).$$