Viking: There is water vapor in the martian atmosphere with contents of several 10 pr µm (equivalent to 10 g per square meter)

Modeling teaches that adsorption and condensation of water are characteristic for the interaction between atmosphere and the uppermost soil layers (mm - cm). Adsorption water behaves liquid-like, it is expected to support there chemical reactions also at present.
Adsorption water-driven processes on Mars, D. Möhlmann, DLR-PF, Berlin

Sublimation of water ice (Sonntag, 1990):

\[ p[Pa] = 611.2 \exp(\frac{22.46 (T[K] - 273.15)}{T[K] - 0.53}) \]

\[ (-65^\circ C < T[^\circ C] < 0.01^\circ C) \]

when \( T[K] >> 0.53 \),

\[ p[Pa] = 611.2 \exp(\frac{22.46 - 273.15}{T[K]}) = 3.47 \times 10^{12} \exp\left(\frac{6134.949}{T[K]}\right) \]

This corresponds with a molecular weight of water of 18.015

Resulting in a "Sublimation Enthalpy" of \( \Delta H_{\text{ice}} = 50.622 \text{ kJ mol}^{-1} \)

The evaporation enthalpy of water is of \( \Delta H_{\text{water}} = 45.054 \text{ kJ mol}^{-1} \) (at 0° C)

Hydration enthalpies of minerals are reported to have values up to \( \Delta H_{\text{mineral}} \approx 100 \text{ kJ mol}^{-1} \), and more.
Bulk water: 45 kJ/mol, Water ice: 50 kJ/mol.
Adsorption water is stronger bond.

Strongest bonds (surface forces) start at about 0.07 g/g.

The ratio $S = E/Z$ of the evaporation rate $E$ of adsorption water and the sublimation rate $Z$ is proportional to

$$S = e^{\frac{(\varepsilon_{\text{ads}} - \varepsilon_{\text{ice}})}{kT}}.$$  

This is for adsorption bond energies of $\varepsilon \approx 0.8$ eV of about $S^{-1} \approx 7.35 \times 10^6$. Thus, adsorption water can survive ice (it evaporates million times slower than ice sublimes under equal conditions). Adsorption water is expected to exist in Martian regions which are completely free of ice (dried out).

**Conclusion:** Adsorption water must (at least temporarily) exist also at present in the upper martian surface as a consequence of the atmospheric water content and the soil - atmosphere interaction.
Terrestrial model substances (minerals) can explain the observed water content of the upper martian surface by adsorption water. But, chemisorbed water is expected to be present too. Relative abundance ratios (physisorbed/chemisorbed) are yet unknown.
Adsorption water-driven processes on Mars, D. Möhlmann, DLR-PF, Berlin

Mass ratio of adsorption water (mass \( m \)) and dry soil (mass \( M \))

\[
\frac{m}{M} = n \Sigma S
\]

(\( n \) - number of monolayers, \( \Sigma \) = surface mass density of one layer of adsorption water (\( \Sigma = 3 \times 10^{-7} \text{ kg m}^{-2} \)), \( S \) - specific surface of the soil material (Ballou et al. 1978 - \( S = 1.7 \times 10^4 \text{ m}^2 \text{ kg}^{-1} \)).

\[
\Rightarrow \frac{m}{F} = \frac{n\Sigma SM}{F} = \frac{n\Sigma SV\rho}{F} = n\Sigma S\rho h, \quad \Rightarrow h = \frac{m/F}{n\Sigma S\rho}
\]

The amount of 10 pr m of water can be adsorbed (at one monolayer) within an uppermost layer of 1.31 mm depth (in case of \( S = 1.7 \times 10^4 \text{ m}^2 \text{ kg}^{-1} \)).

A value of \( m/M = 1\% \) corresponds to \( n = (m/M)/(SS) = 1.96 \).

A relative content of 1 % (by weight or mass) of adsorption water in soil corresponds to the presence of about 2 monolayers (in case of \( S \) according to Ballou et al., 1978).
The presence of adsorption water is expected to have an influence on physical (mechanical, electrical, optical, thermal) properties of the upper martian soil.

Adsorption water is expected to exist (at least temporarily) in the upper martian surface with a content of about 3% to 4% by weight (or temporarily more).
Adsorption water-driven processes on Mars, D. Möhlmann, DLR-PF, Berlin

Experiments to study adsorption water supported and UV-driven chemistry on haematite (Jung, Sattler, Möhlmann, DLR- TT,RS - Cologne, 2003)

Result: Chemistry works with adsorption water, oxidizing OH-radicals are produced and act oxidizing.

\[ \text{Fe}_2\text{O}_3 + 3 \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{3+} + 6 \text{H}^- \]

\[ \text{Fe}^{3+}_{\text{aq.}} + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{Fe}^{2+}_{\text{aq.}} + \text{H}^+ \]

Production of OH-radicals measured by Production of CO\(_2\) (oxidation product of Isopropanol, which was added)
Adsorption water-driven processes on Mars, D. Möhlmann, DLR-PF, Berlin

Oxidation of Methane:

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{CH}_3\text{OH} \\
\text{CH}_3\text{OH} & \rightarrow \text{HCHO} \\
\text{HCHO} & \rightarrow \text{HCOOH} \\
\text{HCOOH} & \rightarrow \text{CO}_2
\end{align*}
\]

Methane    Methanol    Formaldehyde    Formic acid

Mars-relevant experiment set-up: Inst. of Nonclassical Chemistry, University of Leipzig (Staudt, Wecks) and DLR Inst. of Planetary Research, Berlin (Möhlmann):

- 10 g wetted haematite (water:5% by weight)
- UV-source (HBO 100)
- Atmosphere of 100% methane (25°C, 1013 bar) (no heating, IR is filtered out)
- 50 ml cuvette (reaction volume)
Adsorption water-driven processes on Mars, D. Möhlmann, DLR-PF, Berlin

Haematite and (adsorption-) water:

\[
\text{Fe}_2\text{O}_3 + 3 \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{3+} + 6 \text{H}^-
\]

Photo-Fenton-reaction (UV-triggered reduction of iron):

\[
\text{Fe}^{3+}_{\text{aq.}} + \text{H}_2\text{O} \rightarrow \text{OH}^* + \text{Fe}^{2+}_{\text{aq.}} + \text{H}^+
\]

The resulting OH-radicals act extremely oxidizing. OH-radicals have a high oxidation potential.

Application to Mars: Haematite, UV and adsorption water are (at least locally and temporarily) present. Oxidizing OH-radicals are expected to be effective.

Methane is present on Mars with about 10 ppb\(_v\). (Formisano, 2004).

Oxidation of methane is expected. Proof by detecting resulting oxidation products (methanol, formaldehyde, formic acid, CO\(_2\)).

Gas-chromatic detection of oxidation products of methane (after 4 hours of irradiation)
Adsorption water-driven processes on Mars, D. Möhlmann, DLR-PF, Berlin

Ehrenreich and Widdell (1994) have isolated photosynthetic bacteria, which use the energy of sunlight to drive the fixation of CO₂ to „organic carbon“ in (CH₂O)ₙ: 

\[ \text{Fe(II)} + \text{CO}_2 + \text{H}_2\text{O} \xrightarrow{\text{UV, sunlight}} \text{Fe(III)} + (\text{CH}_2\text{O})_n \]

Suggested by Nealson & Stahl (1997) “to stimulate thought ...” (A)

Can microbes (and other organisms ?) regulate their water balance by using adsorption water from their surfaces (via aquaporines, e.g.)?

Reference: http://ntmf.mf.wau.nl/aquaporin/images/mechan_aqpl.jpg
Adsorption water-driven processes on Mars, D. Möhlmann, DLR-PF, Berlin

Adsorption water in the upper martian surface is an actual challenge to martian surface chemistry and possibly also to exobiology:

* **Adsorption water makes possible and/or supports a martian surface chemistry, also at present:** These processes are energetically driven by photons (UV). Current martian surface chemistry is mainly (non-thermal) photo-chemistry.

* **Existing iron oxides (as haematite), UV and adsorption water are a cause for the production of oxidizing OH-radicals,** which are expected to contribute to the oxidation of organics (Methane, carbonaceous meteorites).

* **Adsorption water mobilizes acids (as sulfuric acid), which can modify earlier formed carbonates** (surface cover by sulfates, e.g.).

* **Adsorption water covered catalytic surfaces** of minerals are expected to be essential agents in **non-thermal photo-chemical** processes. **Photon driven non-thermal redox-processes** on catalytic surfaces might together with atmospheric CO$_2$ cause a non-biogenic production of organics (?). Related experiments are in preparation.

* **Adsorption water deposits also on the surfaces (cell walls) of microbes etc.** There, it can be a source of water for the microbial metabolism. **Physico-chemical processes can be supported by adsorption water.** To study the relevance of adsorption water for life-processes is a current challenge to exobiology. Related experiments are in preparation.