Gas adsorption and desorption effects on cylinders and their importance for long-term gas records

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Abstract

It is well known that gases adsorb on many surfaces, in particular metal surfaces. There are two main forms responsible for these effects (i) physisorption and (ii) chemisorption. Physisorption is associated with lower binding energies in the order of 1–10 kJ mol\(^{-1}\) compared to chemisorption ranging from 100 to 1000 kJ mol\(^{-1}\). Furthermore, chemisorption forms only monolayers, contrasting physisorption that can form multilayer adsorption. The reverse process is called desorption and follows similar mathematical laws, however, it can be influenced by hysteresis effects. In the present experiment we investigated the adsorption/desorption phenomena on three steel and three aluminium cylinders containing compressed air in our laboratory and under controlled conditions in a climate chamber, respectively. We proved the pressure effect on physisorption for CO\(_2\), CH\(_4\) and H\(_2\)O by decanting a steel and an aluminium cylinder completely. The results are in excellent agreement with a monolayer adsorption model for both cylinders. However, adsorption on aluminium (0.3 ppm and 0 ppm for CO\(_2\) and H\(_2\)O) was about 20 times less than on steel (6 ppm and 30 ppm, respectively). In the climate chamber the cylinders were exposed to temperatures between −10 to +50°C to determine the corresponding temperature coefficients of adsorption. Again, we found distinctly different values for CO\(_2\) ranging from 0.0011 to 0.0133 ppm °C\(^{-1}\) for steel cylinders and −0.0003 to −0.0005 ppm °C\(^{-1}\) for aluminium cylinders. The reversed temperature dependence for aluminium cylinders is most probably due to temperature and gas consumption induced pressure changes. After correction, aluminium cylinders showed no temperature independence. Temperature coefficients for CH\(_4\), CO and H\(_2\)O adsorption were, within their error bands, insignificant. These results do indicate the need for careful selection and usage of gas cylinders for high precision calibration purposes such as requested in trace gas applications.
1 Introduction

Precision and accuracy of ambient air measurements depend on the stability of primary and secondary standards. Adsorption or desorption plays an important role in this stability. Besides the choice of the metal, also surface condition, surface coating or finish as well as humidity are critical for the gas composition (Matsumoto et al., 2005). The presented work was motivated by the fact that adsorption/desorption effects have been observed to play an important role not only in the laboratory, but also in the field during many experimental setups.

In the sorption theory one distinguishes several terms such as absorption, adsorption, sorption, desorption, physisorption and chemisorption. Adsorption is a surface adhesion process of atoms, ions, or molecules from a gas, liquid or dissolved solid (adsorbate) resulting in a layer on the adsorbent surface (main material). In contrast, absorption is a volume process in which permeation or dissolution of the absorbate in a liquid or solid material (absorbent) takes place. Sorption summarizes both processes while desorption is the reverse process.

Surface atoms of the bulk material, being specified by the fact that they are not fully surrounded by other adsorbent atoms, can therefore attract adsorbates. Adsorption itself splits into physisorption and chemisorption. The former being a general phenomenon forming mono- or multilayers whereas the latter depends on the chemical feature of both the adsorbate and adsorbent and forms only monolayers. Similar to surface tension, adsorption is a consequence of surface energy.

Physical adsorption, also known as physisorption, is a process governed by low electrostatic interactions between the electron configuration of the adsorbate and the adsorbent, in particular van der Waals forces. The involved energy is weak (10–100 meV corresponding to 1–10 kJ mol$^{-1}$) and therefore barely influences the electron structure of the substances involved and mainly appears under low temperature conditions (room energy). The upper energy limit involves the interaction with permanent electric dipoles of polar surfaces (salts) or with the image charges as present in electrically con-
ductible surfaces such as metals. For these processes the energies can reach those of chemisorption.

Chemisorption in contrast involves much higher energies in the range of 1 to 10 eV (100 to 1000 kJ mol\(^{-1}\)) and often requires an activation energy finally resulting in a structure that is similar to a chemical bond of either ionic or covalent type. Sorption and desorption can differ, in this case we deal with hysteresis, i.e. the quantity adsorbed differs from the corresponding quantity desorbed.

The definition of adsorption given by the International Union of Pure and Applied Chemistry (IUPAC) reads as follows: an increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces. Adsorption can also occur at the interface of a condensed and a gaseous phase (McNaught and Wilkinson, 1997).

Several mathematical models have been presented for adsorption. Freundlich and Küster (1894) were the first to describe this process with a purely empirical formula for gaseous adsorbates. Equation (1) expresses the pressure dependence by adjusting the empirical constants \(k\) and \(n\). \(x\) denotes the quantity adsorbed, \(m\) the mass of absorbent and \(P\) the pressure (Freundlich, 1906).

\[
x = kP^{1/n}
\]

Irving Langmuir (Langmuir, 1916, 1918) was the first to derive a scientifically based adsorption isotherm. It is based on four assumptions: (i) all of the adsorption sites are equivalent and each site can only accommodate one molecule; (ii) the surface is energetically homogeneous and adsorbed molecules do not interact; (iii) there are no phase transitions; (iv) at the maximum adsorption, only a monolayer is formed. Adsorption only occurs on localized sites on the surface, not with other adsorbates. His final result expresses the fraction of the adsorption sites occupied, \(\Theta\), as given in Eq. (2).

\[
\Theta = \frac{KP}{1 + KP}
\]
where $K$ is the ratio of the direct (adsorption) and reverse rate (desorption) constants ($k$, $k_{-1}$) and $P$ is the pressure. For low pressures $\Theta$ corresponds to $KP$ and for high pressure it approaches unity.

The four assumptions listed by Langmuir are often not fulfilled, in particular assumption (iv). This fact led to the BET model derived jointly by Brunauer, Emmett and Teller described in Brunauer et al. (1938) which relates to multilayer adsorption. Further extensions were made by Kisliuk (Kisliuk, 1957) by taking into account interactions of gas molecules in the adsorbed and gaseous phase. Since we neither use the BET nor the Kisliuk model, we omit corresponding equations.

Besides the pressure or gas (particle) density dependence there is also a temperature dependence of adsorption/desorption processes. According to the Polanyi–Wigner equation given in Eq. (3), the desorption rate is dependent on a frequency term, $\nu(\Theta)$, a coverage order term, $\Theta^n$, and an Arrhenius factor containing the activation energy for desorption.

$$k_{-1}(\Theta, t) = \frac{d\Theta}{dt} = \nu(\Theta) \cdot \Theta^n \cdot e^{-\frac{E_{A,des}(\Theta)}{RT(t)}}$$

(3)

In this work we mainly investigate the adsorption and its reverse process. In particular we present results for the pressure and temperature dependent adsorption process of trace gases (CO$_2$, CO, CH$_4$) as well as H$_2$O on two metal surfaces, namely steel and aluminium.

2 Methods

We ran two experiments in order to determine the pressure and temperature dependencies of gas adsorption on two different metal cylinder surfaces (steel and aluminium). In the first experiment we decanted 5 liters per minute from either a steel (50 L steel cylinder from Carbagas, Switzerland) or aluminium cylinder (30 L Scott-Marrin Luxfer aluminium cylinder) and monitored the mole fractions of CO$_2$, CH$_4$ and H$_2$O.
H$_2$O by a Picarro G2311f and G2401, in which case CO was measured in addition. Attached to the cylinders were pressure regulators from Tescom (type: 64-3441KA412 dual stage). The starting pressures were about 110 bar and 95 bar for the steel and aluminium cylinder, respectively. Due to the large gas flow which was maintained by the detector itself in the case of G2311f and by an external flow meter for the G2401, it took only about 14 (steel) and 8 (aluminium) hours, respectively to empty the cylinders. The mole fractions were monitored on a 0.1 s level with the G2311f instrument whereas on a 5 s level with the G2401. In parallel we recorded the pressure continuously. This experiment was performed at the University of Bern under normal laboratory conditions (room temperature at 22°C, room pressure about 950 mbar).

The second experiment was performed in the Climate Chamber at the Swiss Federal Institute of Metrology (METAS). The purpose of this experiment was to determine the temperature dependence of the adsorption process. Therefore, a temperature range from −10°C to +50°C was operated as documented in Fig. 1. The temperature was set to a fixed temperature for 2 h at each level. Within every two hours sequence we switched between the six cylinders and an additional reference cylinder outside the climate chamber using a 10-port VICI AG valve (type: EMT2CSD12MWE). Unfortunately, the electronics of the Vici valve was malfunctioning after the first night and therefore we had to replace it. Hence the experiment was extended in order to have two full temperature cycles for data evaluation. The temperature in the climate chamber was recorded directly from the cylinders using sensors of the type 80PK-1, −40 . . . + 260°C and recorded by a GMH3250 temperature sensor from Greisinger. The pressure transducers used were PTU-S-AC160-31AC for high pressures and PTU-S-AC6-31AC for low pressures from Swagelok. Measurements were displayed by a homemade LCD device and logged by a Labjack U12 from the Meilhaus Electronic GmbH.
3 Results

Figures 2 and 4 display the CO$_2$ mole fraction change for experiment 1 (emptying gas cylinders) for a stainless and an aluminium cylinder. According to Eq. (2), the corrected CO$_2$ mole fraction (CO$_{2,corr}$) can be calculated from the measured mole fraction (CO$_{2,meas}$) through the following formula:

$$CO_{2,corr} = CO_{2,meas} - CO_{2,ad} \left(1 - \frac{KP}{1 + KP}\right)$$ (4)

where $CO_{2,ad}$ corresponds to the adsorbed CO$_2$ molecules on the wall, expressed as CO$_2$ mole fraction times the occupied adsorption sites. $CO_{2,ad}$ and $K$ can be determined experimentally to fit the measured CO$_2$ mole fraction. This results in an adsorbed mole fraction of 9 ppm for $CO_{2,ad}$ and 0.6 bar$^{-1}$ for $K$. The former value can be compared with a monomolecular layer of CO$_2$ molecules on the inner cylinder wall area. Our steel cylinders have an outer diameter of 0.24 m, an inner diameter of 0.2 m and a length of 1.5 m. Therefore, the inner area corresponds roughly to 1 m$^2$, which is in excellent agreement with a monolayer corresponding to 1.09 m$^2$ when assuming a molecule diameter of 3.4 Å. This supports our assumption to use the Langmuir approach for a monomolecular layer in contrast to a multi-layer coverage. It is interesting to note that the water adsorption is about five times stronger as shown by an equal pressure behaviour of desorption (Fig. 3) as for CO$_2$. By taking into account the smaller molecule size, this corresponds to a two-molecular layer at maximum.

Similar considerations can be made for the aluminium cylinder which results in empirically derived values of 0.3 ppm for $CO_{2,ad}$ and 2 bar$^{-1}$ for $K$. The effect of adsorption is significantly less on an aluminium than on a steel surface, only about five percent of the adsorption sites are occupied. However, the Langmuir model still holds for this emptying experiment. It was also tested whether the decanting rate has an influence by performing tests with 5 and 0.25 L min$^{-1}$, respectively. The results are displayed in Fig. 4 and show similar increases towards lower pressures but there are obvious trends
superimposed that cannot be explained by the adsorption theory. These trends may be due to instrumental trends.

The second experiment conducted in a climate chamber followed expectations in that the temperature dependence of CO$_2$ adsorption is considerable for steel surfaces but again significantly smaller on aluminium. For the latter case it even changed sign to a slightly negative correlation with temperature, though statistically not robust. The pressure drop for gas consumption throughout this experiment was in the order of 14 and 24 bar with initial pressures around 150 and 120 bar for the steel and aluminium cylinders, respectively. The induced desorption changes are moderate and amount to about 0.01 ppm for both steel and aluminium cylinders according to Eq. (4). Also, the temperature induced pressure changes amounting to about 30 bar (150bar · $\Delta T/T$) are only twice as large. Hence no influence on the temperature dependencies is expected for steel cylinders. For the aluminium cylinders, though, these two influences are most probably the reason for the observed reversed temperature behaviour. All other measured gas species, i.e. CO, CH$_4$ and H$_2$O showed no temperature dependence as documented in Table 2, except for H$_2$O of the steel cylinder LK548528.

$$E_{A,des}(\Theta) = \ln(\text{CO}_2,\text{meas}(T_{\text{high}}) - \text{CO}_2,\text{meas}(T_{\text{low}})) \cdot R \left(\frac{1}{T_{\text{low}}} - \frac{1}{T_{\text{high}}}\right)$$

(5)

Desorption energies, $\Theta E_{A,des}(\Theta)$, for physisorption can be calculated from Eq. (5) or derived from the slope obtained when plotting the logarithm of the measuring CO$_2$ differences vs. the inverse temperature of experiment two as shown for steel cylinder 1 in Fig. 8. The slopes do slightly differ from $-1412$ to $-1686$ for positive and negative temperature gradients, respectively with a mean of $-1552$ for the overall correlation. Hence adsorption energies vary between $12,357$ and $13,919$ J mol$^{-1}$ with an average value of $12,897$ J mol$^{-1}$. This might point to a small contribution of thermal diffusion on measured CO$_2$ concentrations (Keeling et al., 2007). Similarly for aluminium cylinder 2, Fig. 10, the desorption energies are slightly different for positive or negative temperature gradients. However, the determination of the desorption energy for aluminium...
cylinders is difficult due to the very small, hardly measureable CO₂ change. Hence those, lower values than for steel cylinders should be taken with care.

4 Conclusions

The experiments performed clearly demonstrate that the aluminium cylinders are significantly more robust against adsorption/desorption processes for CO₂, CO, CH₄ and H₂O than steel cylinders. The desorption rate behaviour follows nicely a monomolecular layer desorption as described by the Langmuir equation and is about 30 times larger for steel than for aluminium surfaces. Also, the desorbed amount is about 30 times higher for steel (9 ppm) than for aluminium (0.3 ppm) and about 100 times larger than the WMO target value of 0.1 ppm for steel and still significantly above it for aluminium. Therefore, special attention has to be given to which end pressure the cylinders should be used for calibration purposes. The community is generally aware of this influence but it has not yet been quantified properly. It is noteworthy that desorption starts already close to 100 bar (1450 psig). At 30 bar it can already reach 0.5 ppm. The WMO target value of 0.1 ppm might already be reached at 60 bars compared to the value at 100 bar.

The temperature dependence that was observed for three steel and aluminium cylinders is 0.0014 to 0.0184 ppm °C⁻¹ and −0.0003 to −0.0005 ppm °C⁻¹, respectively. This might have an influence on the precision when facing large temperature fluctuations in the laboratories or when measuring in the field with large ambient temperature variations, but only for steel and not for aluminium cylinders.

The recommendation for high precision greenhouse gas determination is to use aluminium cylinders and to minimize temperature fluctuations in order to limit desorption and thermal diffusion effects.

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intercomparison initiatives, such as Round Robins organized by WMO/IAEA, the Cucumber program organized by UEA and others that were helpful in leading to these investigations.

References


Table 1. Cylinders used for the experiment with their identification and trace gas mole fractions.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
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<tbody>
<tr>
<td>1: LK502291</td>
<td>153.2</td>
<td>138.74</td>
<td>439.58</td>
<td>10.40</td>
<td>2058.0</td>
<td>0.88</td>
<td>Bern</td>
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<tr>
<td>2: CB09790</td>
<td>121.3</td>
<td>97.2</td>
<td>405.06</td>
<td>5.40</td>
<td>1977.04</td>
<td>2.38</td>
<td>Bern</td>
</tr>
<tr>
<td>3: LK548602</td>
<td>155.0</td>
<td>140.54</td>
<td>420.49</td>
<td>9.40</td>
<td>1967.04</td>
<td>0</td>
<td>Bern</td>
</tr>
<tr>
<td>4: CB09877</td>
<td>131.0</td>
<td>106.9</td>
<td>399.52</td>
<td>193.40</td>
<td>2080.04</td>
<td>28.41</td>
<td>Empa</td>
</tr>
<tr>
<td>5: LK548528</td>
<td>153.6</td>
<td>139.14</td>
<td>438.95</td>
<td>13.40</td>
<td>2058.04</td>
<td>2.94</td>
<td>Bern</td>
</tr>
<tr>
<td>5*: LK535353 &gt; 170</td>
<td>135.54</td>
<td>391.49</td>
<td>74.40</td>
<td>1995.04</td>
<td>17.73</td>
<td>Bern</td>
<td></td>
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<tr>
<td>6: CB09786</td>
<td>120.5</td>
<td>96.4</td>
<td>405.60</td>
<td>11.40</td>
<td>1977.04</td>
<td>4.94</td>
<td>Bern</td>
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<tr>
<td>7: CA03901</td>
<td>76</td>
<td>75</td>
<td>363.08</td>
<td>102.4</td>
<td>1796.04</td>
<td>1.17</td>
<td>NOAA</td>
</tr>
</tbody>
</table>

* Due to a leak cylinder LK548528 had to be exchanged with cylinder LK535353 during the experiment.
Table 2. Temperature dependencies of gas adsorption on steel and aluminium surfaces for CO₂, CO, CH₄ and H₂O applying a temperature range from −10 to +50 °C. NA when r² < 0.02.

<table>
<thead>
<tr>
<th>Cylinder</th>
<th>CO₂ [ppm °C⁻¹]</th>
<th>CO [ppb °C⁻¹]</th>
<th>CH₄ [ppb °C⁻¹]</th>
<th>H₂O [ppm °C⁻¹]</th>
<th>surface type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: LK502291</td>
<td>0.0061</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>steel</td>
</tr>
<tr>
<td>2: CB09790</td>
<td>−0.0005</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>aluminium</td>
</tr>
<tr>
<td>3: LK548602</td>
<td>0.0141</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>steel</td>
</tr>
<tr>
<td>4: CB09877</td>
<td>−0.0003</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>aluminium</td>
</tr>
<tr>
<td>5: LK548528</td>
<td>0.0184</td>
<td>NA</td>
<td>NA</td>
<td>0.113</td>
<td>steel</td>
</tr>
<tr>
<td>5*: LK535353</td>
<td>0.0014</td>
<td>NA</td>
<td>NA</td>
<td>0.00003</td>
<td>steel</td>
</tr>
<tr>
<td>6: CB09786</td>
<td>−0.0003</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>aluminium</td>
</tr>
</tbody>
</table>

* Due to a leak cylinder LK548528 had to be exchanged with cylinder LK535353 during the experiment.
Figure 1. Temperature exposed to the cylinders in the climate chamber. Every two hours the temperature changed by 10 °C. The actual temperature (red) is in good agreement with the set temperature (light blue) but delayed by 2.75 h (bold blue).
Figure 2. Emptying experiment within 14 h: CO$_2$ mole fraction of a steel cylinder vs. its pressure in red (only every 100 point of 0.1 s resolution data is shown). Langmuir monomolecular layer desorption model in blue (CO$_2$$_{ad}$ = 9 ppm, $K$ = 0.6 bar$^{-1}$).
Figure 3. Emptying experiment within 14 h: H$_2$O even shows a five times stronger desorption effect documented by the linear correlation with the CO$_2$ mole fraction.

\[ y = 5.1015x - 2098.9 \]
\[ R^2 = 0.9203 \]
**Figure 4.** Emptying experiment within 8 h: CO₂ mole fraction of an aluminium cylinder vs. its pressure in red (5 s resolution). Langmuir mono-molecular layer desorption model in blue (CO₂,ad = 0.3 ppm, K = 2 bar⁻¹, Eₐ,des = 10 kJ mol⁻¹) for a decanting rate of 5 L min⁻¹ upper panel and for 0.25 L min⁻¹ in the lower panel (CO₂,ad = 0.3 ppm, K = 10 bar⁻¹, Eₐ,des = 2.5 kJ mol⁻¹). Temperature corresponding to the pressure is displayed in green. Note that the decreasing trend is not explainable with the adsorption theory and is most probably due instrumental drift.
Figure 5. Emptying experiment within 8 h: H$_2$O and CO show no and CH$_4$ an extremely small desorption effect on this aluminium cylinder compared to the CO$_2$ mole fraction.
Figure 6. Temperature dependence for the CO₂ mole fraction for the steel cylinders 1, 3, 5.
Figure 7. Restricted temperature dependence for the CO$_2$ mole fraction for the steel cylinder 5a that was replaced on the 24 April because of a small leak at the regulator.
Figure 8. Logarithmic dependence the CO$_2$ mole fraction on the inverse temperature for the steel cylinder 1. Open red symbols correspond to negative and filled red symbols to positive temperature gradients in Fig. 1. The slopes do slightly differ from $-1487$ to $-1675$ for positive and negative temperature gradients, respectively with a mean of $-1552$ for the overall correlation. Hence adsorption energies vary between 12,357 and 13,919 J mol$^{-1}$ with an average value of 12,897 J mol$^{-1}$. Open and filled blue symbols correspond to the CO$_2$ concentrations vs. temperature.
Figure 9. Temperature dependence for the CO$_2$ mole fraction for the aluminium cylinders 2, 4, 6.
Figure 10. Logarithmic dependence the CO₂ mole fraction on the inverse temperature for the aluminium cylinder 2. Open red symbols correspond to negative and filled red symbols to positive temperature gradients in Fig. 1. The slopes do slightly differ from −659 to −637 for positive and negative temperature gradients, respectively with a mean of −667 for the overall correlation. Hence adsorption energies vary between 5476 and 5293 J mol⁻¹ with an average value of 5547 J mol⁻¹. Open and filled blue symbols correspond to the CO₂ concentrations vs. temperature.