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Quantification of the degree-of-isotopic-equilibrium of carbon and oxygen isotopes in mixtures of CO_2 gases

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Abstract

A model has been developed enabling to quantify the degree of scrambling of carbon and oxygen isotopes in mixtures of CO_2 gases with different isotopic compositions. If such isotope mixtures are quantitatively prepared ('synthesized') they are 'embodiments' ('realizations') of SI units, and can serve as 'calibrators' of measurements of C and O isotope amount ratios, thus establishing metrological traceability of the measurement results to the SI.

Absence of complete equilibrium will cause further isotope scrambling reactions *during* the isotope amount ratio measurements in the mass spectrometer until the realization of full isotopic equilibrium, but biasing the measurement results continuously before the equilibrium is attained. The concept of *isotope ratio space* has been conceived to describe this process.

This model fits the experimental data adequately and enables to determine the degree-of-isotopic-equilibrium in the gaseous mixture at any time during the mixing process. This creates the possibility to verify the achievement of the isotopic equilibrium prior to the (ion current ratio) measurements.

Keywords: CO_2; Isotope equilibration; Isotope ratio mass spectrometry; Synthetic isotope mixtures; Scrambling

1. Introduction

Isotope measurements relative to a conventional delta scale (via δ-reference samples) have led to an immensely rich harvest of results and derived conclusions on the basis of measurement results obtained as ratios-of-ion-current-ratios, $J = I(^{i}\mathrm{E})^{+}/I(^{j}\mathrm{E})^{+}$. These results, however, are not ratios-of-amount-ratios, $R = n(^{i}\mathrm{E})/n(^{j}\mathrm{E})$ of the isotopes concerned (the mass spectrometers used are strictly built as instruments which measure ratios-of-ion-current-ratios, J) and, therefore, conclusions are only valid for ratios-of-ion-current-ratios, $J_{i,j}$ and not necessarily for ratios-of-amount-ratios $R_{i,j} = K_{i,j}J_{i,j}$. In addition, isotope reference samples, frequently have an isotopic composition which is inadequately known and for which either the material or the certified value is inherently unstable in time (e.g. a water standard) or possibly not quite homogeneous (for a mineral standard). An improvement of the measurement results is achieved by replacing the reference sample by a 'synthesized' isotope mixture which has isotope amount ratios known from a quantitative preparation, thus making measurements relative to a 'well-known' reference sample, rather than to a merely 'designated' sample-by-human-consensus.

But, there are recurring practical problems inhibiting to obtain "absolute" measurement results, such as insufficient 'scrambling' (random mixing) of the isotopes before measurement, resulting in the fact that what is being measured, is not what was intended to be measured ('the measurand'). This simply prevents a valid metrological comparison of the measurement results, even when obtained against a common well-known reference sample.

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Only *primary* measurement standards (PMS) in the metrological meaning of the term, such as 'embodiments' ('realizations') of the SI units involved (mol/mol) in the form of 'synthesized' isotope amount ratios and then only if small enough full measurement uncertainty has been achieved [1–4], will enable to determine the size of these scrambling effects and open the possibility of adequate correction. If the values for the isotope amount ratios in these PMS are shown to be traceable to the SI, will metrological traceability of measurement results have been achieved and will measurement results (obtained in different laboratories and from different procedures) be comparable in order to determine their degree-of-equivalence. For example, if the SMOW and PDB measurement standards are compared for their C and/or O isotope amount ratios, either on CO_2 or on O_2 as the measurement gas, in order to determine their degree-of-equivalence, a '*differential*' measurement result cannot explain discrepancies introduced by the conversion procedures.

The route to achieve primary measurement standards for carbon is the preparation of synthetic isotope mixtures in the form of carbon dioxides, prepared by mixing CO_2 gas molecules of different isotopic composition using a gravimetric approach [1–4] "to synthesize the value of an isotope amount ratio". Such a project has been initiated about one year ago between IRMM (Geel) and NPL (Teddington) in the frame of the JEPPIM[1]-cooperation. The 'synthetically prepared isotope amount ratios' can then be used to calibrate the measured ion current ratios $J_{i/44} = I[^{i}(CO_2)^+]/I[^{44}(CO_2)^+]$ with $i = 45$–47 obtained from measurements on CO_2 gas (so without any involved correction for oxygen), resulting eventually into "absolute" isotope amount ratios $R_{13/12} = n(^{13}C)/n(^{12}C)$, $R_{18/16} = n(^{18}O)/n(^{16}O)$ and $R_{17/16} = n(^{17}O)/n(^{16}O)$ through the measurement model $R_{i/44} = K_{i/44}J_{i/44}$ [1].

However, in this process and during the measurements of the ion current ratios $J_{i/44}$, apparent anomalies are encountered, not of instrumental origin but actually due to lack of isotope equilibration, both in the prepared CO_2 mixtures as well as in the CO_2 starting materials. This has important consequences, not only for treating and evaluating the measured data, but also for the calculations of the residual correction factors $K_{i/44}$ for systematic unknown effects in the mass spectrometer (with their associated combined measurement uncertainties). It is clear that when the carbon and oxygen isotopes are not in full isotopic equilibrium in the CO_2 molecules, they do not obey a full statistical distribution in the CO_2 molecules; hence, the real carbon and oxygen isotope amount ratios cannot be derived from the ion current ratio measurements $J_{i/44}$ or not even from calculation of these values from mixing of starting materials if the latter themselves were not fully isotopically equilibrated. It is mandatory to verify the realization of *full* isotopic equilibrium in every CO_2 gas in each step of the mixing process. The quantification of the degree of completion of such a statistical isotope distribution is discussed in this paper. This quantification also helps to evaluate the uncertainty of any isotope amount ratio measurement result of species consisting of different isotopologues (i.e. a chemical species that differ only in isotopic composition) full equilibrium is not reached (or when it takes too long). The lack of any deviation from linearity (ln *R* versus time) is not automatically a clear quantification of the completeness of the status of equilibrium of the sample. Therefore, a distinct study of the evaluation of the equilibration process had to be made.

2. Distribution of carbon and oxygen isotopes within CO_2 molecules

The degree of isotope distribution over the entire CO_2 molecule (i.e. in *each* CO_2 molecule) when mixing CO_2 molecules of different isotopic composition, is of key importance when measuring the corresponding ion current ratios in the mass spectrometer [5]. Also the dynamics [7,8] of the distribution through the mixing process is essential for the CO_2 modeling, both on laboratory scale as well as in natural processes.

The gas mass spectrometric measurement procedure applied here and developed over the years for the re-determination of the Avogadro constant [3–8], creates opportunities which are not accessible in commercial 'delta'-machines. Monitoring isotope fractionation *during* [5] the measurements (by using kinetic gas theory), including a correction for adverse or uncontrolled fractionation, reveals crucial information on the degree-of-isotope-equilibration in the (CO_2) sample.

The general requirement for achieving complete isotopic equilibrium of the carbon and oxygen isotopes when mixing CO_2 gases is the availability of a catalyzing mechanism promoting isotope 'scrambling'. When mixing gaseous compounds of different isotopic composition, their equilibrium status is depending on the chemical and physical conditions in the process [9,10]. The speed, and consequently the time, required to reach a complete isotopic equilibrium in the gas mixture, are strongly temperature dependent. Also the presence of large adsorption/desorption surfaces inside a mixing container or at the inner surface of the spectrometer (inlet tubes, expansion vessel, ion source) affect the equilibration between isotopes. But hot surfaces as those of the high-temperature ionizing filament surface, are very suitable to progress isotope equilibration [11].

The purpose, however, of this paper is *not* to discuss theoretical aspects of isotope equilibration reaction dynamics, but to report a technique to evaluate and verify the 'degree of advancement' of isotope equilibration in CO_2 mixtures.

The carbon and the oxygen isotope amount fractions f_i (with $i = 13$, 17 and 18) can be calculated in the mixture according to simple mathematical equations:

$$f_{13} = \frac{f_{13}^1 n_1 + f_{13}^2 n_2}{n_1 + n_2}, \qquad f_{17} = \frac{f_{17}^1 n_1 + f_{17}^2 n_2}{n_1 + n_2},$$

$$f_{18} = \frac{f_{18}^1 n_1 + f_{18}^2 n_2}{n_1 + n_2} \tag{1}$$

where f_{13} is the carbon (^{13}C) isotope amount fraction of C in the mixture, while f_{17} and f_{18} are the oxygen isotope amount fractions (^{17}O and ^{18}O) of oxygen in the mixture. n_1 and n_2 are the amount of substance of CO_2 of the initial components used

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[1] JEPPIM: Joint European Program for Primary Isotope Measurements.

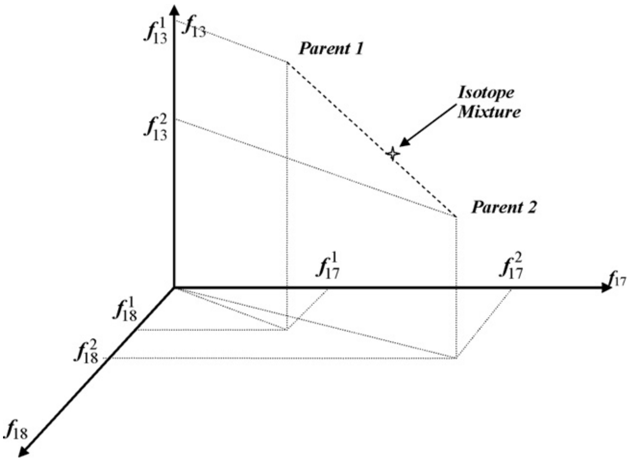

Fig. 1. Carbon and oxygen isotope amount fractions in the CO_2 molecules of the starting (parent) materials (Eq. (1)) visualized in a fictive "*isotope amount fraction space*", with the isotope amount fractions of carbon and oxygen of the mixture (at the dotted line) depending on the mixing ratio applied.

for mixing. Introducing $\gamma = n_1/n_2$, the mixing ratio, the set of Eq. (1) can be re-written as:

$$f_{13} = \frac{f_{13}^1\gamma + f_{13}^2}{\gamma + 1}, \qquad f_{17} = \frac{f_{17}^1\gamma + f_{17}^2}{\gamma + 1},$$
$$f_{18} = \frac{f_{18}^1\gamma + f_{18}^2}{\gamma + 1} \tag{2}$$

When the carbon and oxygen isotope amount fractions in the CO_2 molecules of the starting materials (f_i^1 and f_i^2 in Eq. (1)) are conceived in an "*isotope amount fraction space*" (Fig. 1), then the set of Eq. (2) creates a relation between the two CO_2 starting materials in this space. The isotope amount fractions of the CO_2 mixture are exactly on the (dotted line) line the position of which depends on the mixing ratio.

Isotope equilibrium takes place by (isotope) exchange reactions between the various CO_2 isotopologues (Table 1) present in the gas phase. Such reactions are more efficient at higher temperatures. However, when a statistical carbon and oxygen isotope distribution is not obeyed prior to the ion current ratio measurement, progressive continuous equilibration will take place *during* the measurement, due to the high operating temperatures in the spectrometer (inlet vessel, ion source, and, especially, at the ionization filament). An incompletely equilibrated sample will affect the molecular gas flow in the mass spectrometer, resulting in erroneous values for $J_{i/44}$ (Figs. 2 and 3), since $R_{i/44} = K_{i/44}J_{i/44}$, where $K_{i/44}$ is the correction factor for systematic, but as yet, unknown effects ($i = 45–47$).

Table 1
Symmetry numbers σ for the different CO_2 isotopologues required for the calculation of the equilibrium constants K_E

Different CO_2 isotopologues[a]	Symmetry number (σ)
$^{12}C^{16}O^{18}O$, $^{12}C^{17}O^{18}O$, $^{13}C^{16}O^{17}O$, $^{13}C^{16}O^{18}O$, $^{13}C^{17}O^{18}O$, $^{12}C^{16}O^{17}O$	1
$^{12}C^{16}O_2$, $^{12}C^{17}O_2$, $^{12}C^{18}O_2$, $^{13}C^{16}O_2$, $^{13}C^{18}O_2$, $^{13}C^{17}O_2$	2

[a] Isotopologues are chemical species that differ only in isotopic composition (example $^{12}C^{16}O_2$ and $^{12}C^{17}O_2$).

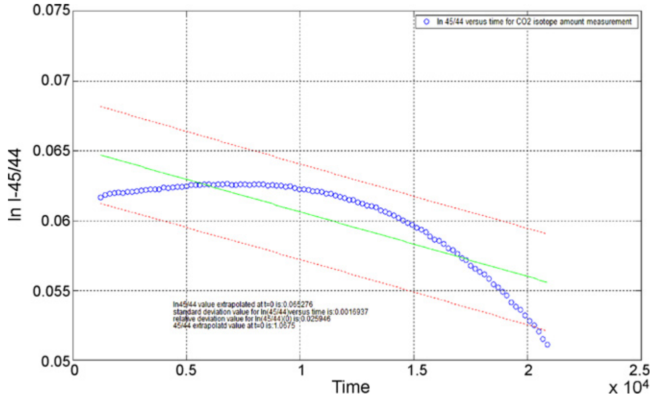

Fig. 2. The ion current ratio $J_{45/44} = I[^{45}(CO_2)^+]/I[^{44}(CO_2)^+]$ measured on non-equilibrated $^{13}CO_2$ vs. time. The non-equilibrated status of this parent material (needed to prepare the mixtures) clearly shows that the gas delivered by the company (Chemotrade, D) was already a mixture of at least two $^{13}CO_2$ gases before it was sent to IRMM. It required a complete isotope equilibration before it could be used in gas mixing.

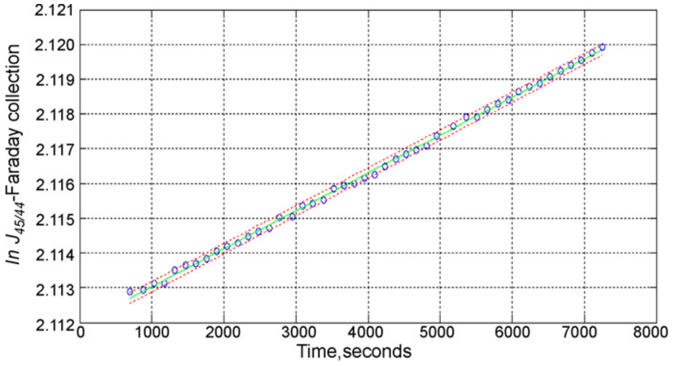

Fig. 3. The ion current ratio $J_{45/44} = I[^{45}(CO_2)^+]/I[^{44}(CO_2)^+]$ measured on a (complete) equilibrated gaseous $^{13}CO_2$ (parent gas) vs. time.

3. Mass spectrometric measurements

The procedure used for measuring the ion current ratios $J_{i/44}$ on CO_2 followed by calibration by means of synthesized isotope amount ratio values embodied in synthetic isotope mixtures, is an important ingredient of 'absolute' isotope amount ratio measurements by gas mass spectrometry. In this way, different sources of uncertainty can be identified [1,4,12,13].

In order to convert the measured ion current ratios $J_{i/44} = I[^{i}(CO_2)^+]/I[^{44}(CO_2)^+]$ into amount ratios $n[^{i}(CO_2)]/n[^{44}(CO_2)]$, a correction factor $K_{i/44}$ for all systematic unknown effects in the mass spectrometer is needed. The actual $K_{i/44}$ factor is a product of the different correction factors needed to correct for different effects (absorption, memory, gas inlet, isotope fractionation during fragmentation [22], isotope equilibrium, . . .).

$$\frac{n\ [^{i}(CO_2)]}{n\ [^{44}(CO_2)]} = R_{i/44} = K_{i/44}J_{i/44} \qquad \text{with} \quad i = 45–47. \tag{3}$$

or

$$R_{i/44} = K^{1}_{i/44}K^{2}_{i/44}K^{3}_{i/44}\ldots.J_{i/44} = K_{i/44}J_{i/44} \tag{4}$$

The equation shows correctly that in a mass spectrometer, isotope amount ratios are not directly accessible, but only via measurements of ratios of ion currents. The use of a molecular gas flow inlet system [4,5] results in a 'predictable' and verifiable mass discrimination [8] consistent with a mass-dependent effect known from kinetic gas theory to be $[M({}^{i}E)/M({}^{j}E)]^{\Phi}$, with M being the molar mass.

Under ideal gas conditions, the predicted value of Φ is 1/2. This can be verified by experimentally determining Φ in back-extrapolating long series of $J_{i/44}$ measurements to time zero ($t = 0$) using Eq. (5). This yields an experimental value close to 0.50. The built-in degree-of-ideal-gas-condition *during* the measurements (i.e. checking whether the gas effuses really as predicted by kinetic gas theory) has proven to be very powerful. It enables to check whether isobaric interferences occur, or when there are isotope-dependent problems caused by adsorption in the mass spectrometer [4,5]. It can *also* be used to verify the degree-of-statistical-isotope equilibrium in the samples measured.

Fig. 3 shows how the experimentally observed change of the ion current ratios over time can be monitored, with the help of Eq. (5):

$$\ln J_{i/44}(t) = \ln J_{i/44}(t_0) + \frac{([M^{i}(\mathrm{CO_2})^{-\Phi}] - [M^{44}(\mathrm{CO_2})^{-\Phi}])}{[M^{44}(\mathrm{CO_2})^{-\Phi}]} \times \ln\frac{I[{}^{44}(\mathrm{CO_2})^{+}]\,(t)}{I[{}^{44}(\mathrm{CO_2})^{+}]\,(t_0)} \tag{5}$$

From the slope $([M^{i}(\mathrm{CO_2})^{-\Phi}] - [M^{44}(\mathrm{CO_2})^{-\Phi}])/[M^{44}(\mathrm{CO_2})^{-\Phi}])$ of the relationship the value of the exponent Φ can be calculated and compared to the theoretical value of $\Phi = 1/2$. Thus, it is possible to identify and quantify the most important $K_{i/44}$-factor in Eq. (4). Of course a 'residual' $K_{i/44}$-factor is still possible. This can only be determined by the use of synthetically prepared mixtures of enriched isotopes [8].

4. The measurement model for sample equilibration

The preparation of synthetic isotope mixtures in $\mathrm{CO_2}$ requires a careful gravimetric (or volumetric) mixing procedure of two or more gaseous components ("parents") of different isotopic composition. In order to obtain the carbon and oxygen isotope amount ratios from the mixing procedures, the ion current ratios $J_{i/44} = I[{}^{i}(\mathrm{CO_2})^{+}]/I[{}^{44}(\mathrm{CO_2})^{+}]$ need to be measured on all starting materials and mixtures. Applying an extrapolation (to time $t = 0$) as described by Eq. (5), a value for $J_{i/44}$ corresponding to the original sample can be obtained.

By an iterative procedure, the final residual correction factors $K_{i/44}$ can be obtained [8,14–16]. These are factors to be used to calibrate measurements of unknown samples (Eq. (3)). 'Traceable' carbon and oxygen isotope amount ratios can be obtained in this way because offering the possibility of 'tracing' back results to synthetic isotope mixtures, i.e. to a realization of the measurement unit chosen (mol/mol). They should also be accompanied by GUM evaluated uncertainty budgets [17]. This way of thinking is only correct if the carbon and oxygen in the parent gases, as well as in the prepared synthetic isotope mixtures, are in complete isotopic equilibrium before measurement. During the $J_{i/44}$ measurements, variations others than expected by kinetic gas theory [14–16], have been observed.

During the first measurements, some slopes obtained were even negative (!) (Fig. 2), while kinetic gas theory (Fig. 3) predicts for $\ln J_{45/44} = I[{}^{45}(\mathrm{CO_2})^{+}]/I[{}^{44}(\mathrm{CO_2})^{+}]$ versus time t, a value for $\sqrt{M^{45}(\mathrm{CO_2})/M^{44}(\mathrm{CO_2})} = 1.0113\,(10)$. A possible explanation could be gas adsorption in the mass spectrometer also provides a mechanism for isotopic exchange [12] among the $\mathrm{CO_2}$ molecules. That can be observed during the first part of a measurement (during the first 7000 s in Fig. 2), when the distribution of the isotopic species shifts towards equilibrium but does not completely achieve it. However, this mechanism is not strong enough to generate the samples to complete equilibrium. It encounters this situation only for multiple isotope compounds, where in the mixing processes more than one atom of the same element (oxygen in the case of $\mathrm{CO_2}$) is exchanged.

The completeness of the isotope equilibration [11] in a given gas mixture, which starts in isotope exchange reactions between different isotopologues, needs to be evaluated. The time t needed to get a complete equilibrated gas, depends on the structure of the gas molecules and on the temperature and pressure at which the equilibration takes place.

The calculations to express these equilibrium constants for such isotope exchange reactions are based on Urey formalisms [9,10], applying '*ratios of reduced partition functions*' of the molecules and their products involved [18,19].

Consider the general case of an isotope exchange reaction when mixing only two gases, as described by the following equation:

$$AX' + BX \Leftrightarrow AX + BX' \tag{6}$$

their individual equilibrium constants K_{E} are given as:

$$K_{\mathrm{E}} = \frac{Q(AX)Q(BX')}{Q(AX')Q(BX)} \tag{7}$$

with Q the '*molar partition function*' for each isotopologue involved in the reaction.

According to the (simplified) Bigeleisen-Mayer [10,18] (isotope separation) theory, and introducing the notation 'molecular symmetry' [18,19] number σ, which is inversely proportional to the molar partition functions Q, Eq. (7) can be re-written as follows:

$$K_{\mathrm{E}} = \frac{Q(AX)Q(BX')}{Q(AX')Q(BX)} = \frac{(k/\sigma_{AX})(k/\sigma_{BX'})}{(k/\sigma_{AX'})(k/\sigma_{BX})} = \frac{(\sigma_{AX'}/\sigma_{AX})}{(\sigma_{BX'}/\sigma_{BX})} \tag{8}$$

It is assumed here that the temperature effect on the partition functions is very small [10], which enables neglecting k (differences in k are extremely small [18,19]). As a consequence, the equilibrium constants K_{E} can be calculated solely from the symmetry numbers σ of the molecular species involved (Table 1) for

Table 2
Most important exchange reactions when mixing CO_2 gases of different carbon and oxygen isotopic composition, associated by their particular equilibrium constants K_E

Equilibrium reaction	Equilibration constants, K_E
$^{12}C^{16}O_2 + {}^{12}C^{18}O \Leftrightarrow 2{}^{12}C^{16}O^{18}O$	$K_{E^{12}C^{16}O^{18}O} = 4$
$^{12}C^{16}O_2 + {}^{12}C^{17}O_2 \Leftrightarrow 2{}^{12}C^{16}O^{17}O$	$K_{E^{12}C^{16}O^{17}O} = 4$
$^{12}C^{17}O_2 + {}^{12}C^{18}O_2 \Leftrightarrow 2{}^{12}C^{17}O^{18}O$	$K_{E^{12}C^{17}O^{18}O} = 4$
$^{12}C^{16}O_2 + {}^{13}C^{16}O^{17}O \Leftrightarrow {}^{12}C^{16}O^{17}O + {}^{13}O^{16}O_2$	$K_{E^{13}C^{16}O_2} = 1$
$^{13}C^{16}O_2 + {}^{12}C^{16}O^{18}O \Leftrightarrow {}^{12}C^{16}O_2 + {}^{13}O^{16}O^{18}O$	$K_{E^{12}C^{16}O_2} = 1$
$^{12}C^{17}O_2 + {}^{13}C^{16}O_2 \Leftrightarrow {}^{12}C^{16}O_2 + {}^{13}O^{17}O_2$	$K_{E^{13}C^{17}O_2} = 1$

reactions amongst different isotopologues. The symmetry number σ, can be determined by a simply counting of the number of inter-changeable orientations of O and C within the molecule. These are given in Table 2.

When different CO_2 isotopologues are mixed, the following (most important) isotope exchange reactions take place:

$$^{12}C^{16}O_2 + {}^{12}C^{18}O_2 \Leftrightarrow\ 2{}^{12}C^{16}O^{18}O \tag{9}$$

$$^{12}C^{16}O_2 + {}^{12}C^{17}O_2 \Leftrightarrow\ 2{}^{12}C^{16}O^{17}O \tag{10}$$

$$^{12}C^{17}O_2 + {}^{12}C^{18}O_2 \Leftrightarrow\ 2{}^{12}C^{17}O^{18}O \tag{11}$$

$$^{12}C^{16}O_2 + {}^{13}C^{16}O^{17}O\ \Leftrightarrow {}^{12}C^{16}O^{17}O + {}^{13}C^{16}O_2 \tag{12}$$

$$^{13}C^{16}O_2 + {}^{12}C^{16}O^{18}O\ \Leftrightarrow {}^{12}C^{16}O_2 + {}^{13}O^{16}C^{18}O_2 \tag{13}$$

$$^{12}C^{17}O_2 + {}^{13}C^{16}O_2 \Leftrightarrow {}^{12}C^{16}O_2 + {}^{13}C^{17}O_2 \tag{14}$$

Obviously, more exchange reactions are possible, but the ones indicated here [9–14] carry enough information to compute the status of the isotope equilibration in the gaseous mixture (the others are superfluous).

Via the symmetry numbers (Table 1), the equilibrium constants $K_{E_{CO_2}}$ (Table 2) can be calculated. Eq. (15) exemplifies the calculation of $K_{E^{12}C^{16}O^{18}O}$ (from Eq. (9)):

$$K_{E^{12}C^{16}O^{18}O} = \frac{n^2(^{12}C^{16}O^{18}O)}{n(^{12}C^{16}O_2)n(^{12}C^{18}O_2)} = \frac{Q^2_{^{12}C^{16}O^{18}O}}{Q_{^{12}C^{16}O_2}Q_{^{12}C^{18}O_2}}$$
$$= \frac{(k/\sigma_{^{12}C^{16}O^{18}O})^2}{(k/\sigma_{^{12}C^{16}O_2})(k/\sigma_{^{12}C^{18}O_2})} = \frac{(2)(2)}{(1)} = 4 \tag{15}$$

with n being the amount of substance of the different species involved.

These equilibration constants (Table 2) provide the relation between the amounts of substance of CO_2 involved in the reactions discussed Eqs. (9)–(14).

$$n^2(^{12}C^{16}O^{18}O) = 4n(^{12}C^{16}O_2)n(^{12}C^{18}O_2) \tag{16}$$

$$n^2(^{12}C^{16}O^{17}O) = 4n(^{12}C^{16}O_2)n(^{12}C^{17}O_2) \tag{17}$$

$$n^2(^{12}C^{17}O^{18}O) = 4n(^{12}C^{17}O_2)n(^{12}C^{18}O_2) \tag{18}$$

$$\frac{n(^{12}C^{16}O^{17}O)}{n(^{12}C^{16}O_2{}^{16}O_2)} = \frac{n(^{13}C^{16}O^{17}O)}{n(^{13}C^{16}O_2)} \tag{19}$$

$$\frac{n(^{12}C^{16}O^{18}O)}{n(^{12}C^{16}O_2)} = \frac{n(^{13}C^{16}O^{18}O)}{n(^{13}C^{16}O_2)} \tag{20}$$

$$\frac{n(^{12}C^{16}O_2)}{n(^{12}C^{17}O_2)} = \frac{n(^{13}C^{16}O_2)}{n(^{13}C^{17}O_2)} \tag{21}$$

Assuming a mass independent ionization cross section, the isotope amount ratios can be written as:

$$R_{45/44} = \frac{n(^{12}C^{16}O^{17}O)}{n(^{12}C^{16}O_2)} + \frac{n(^{13}C^{16}O_2)}{n(^{12}C^{16}O_2)},$$
$$R_{46/44} = \frac{n(^{13}C^{16}O^{17}O)}{n(^{12}C^{16}O_2)} + \frac{n(^{12}C^{16}O^{18}O)}{n(^{12}C^{16}O_2)} + \frac{n(^{12}C^{17}O_2)}{n(^{12}C^{16}O_2)},$$
$$R_{47/44} = \frac{n(^{12}C^{17}O^{18}O)}{n(^{12}C^{16}O_2)} + \frac{n(^{13}C^{16}O^{18}O)}{n(^{12}C^{16}O_2)} + \frac{n(^{13}C^{17}O_2)}{n(^{12}C^{16}O_2)} \tag{22}$$

Introducing the notations x, y and z as:

$$x = \frac{n(^{12}C^{17}O_2)}{n(^{12}C^{16}O_2)} \tag{23}$$

$$y = \frac{n(^{13}C^{16}O_2)}{n(^{12}C^{16}O_2)} \tag{24}$$

$$z = \frac{n(^{12}C^{18}O_2)}{n(^{12}C^{16}O_2)} \tag{25}$$

The set of Eq. (22) can be transformed in:

$$R_{45/44} = \frac{n(^{13}C^{16}O_2)}{n(^{12}C^{16}O_2)} + 2\sqrt{\frac{n(^{12}C^{17}O_2)}{n(^{12}C^{16}O_2)}} = y + 2\sqrt{x} \tag{26}$$

$$R_{46/44} = \frac{n(^{13}C^{16}O^{17}O)}{n(^{12}C^{16}O_2)} + \frac{n(^{12}C^{16}O^{18}O)}{n(^{12}C^{16}O_2)} + \frac{n(^{12}C^{17}O_2)}{n(^{12}C^{16}O_2)}$$
$$= 2y\sqrt{x} + 2\sqrt{z} + x \tag{27}$$

$$R_{47/44} = \frac{n(^{12}C^{17}O^{18}O)}{n(^{12}C^{16}O_2)} + \frac{n(^{13}C^{16}O^{18}O)}{n(^{12}C^{16}O_2)} + \frac{n(^{13}C^{17}O_2)}{n(^{12}C^{16}O_2)}$$
$$= 2\sqrt{xz} + 2y\sqrt{z} + yx \tag{28}$$

Eqs. (26)–(28) will be used as basis for the definition of an *"isotopic equilibration surface"*. This is a '*virtual*' surface (specially created for this work) in which the carbon and oxygen isotopes are in a complete statistical equilibrium within the CO_2 molecules in a 'virtual' isotope ratio space.

This set of Eqs. (26)–(28), however, cannot be solved in this way because of an underestimation: a relation between the oxygen isotopes is missing [20,21].

When CO_2 gases of complete different isotopic compositions in C and O are mixed, B needs to be calculated separately, using the measured isotope amount ratios of both starting materials. The parameters B_1 and B_2 can than be evaluated assuming that relationship (29) between R_{17} and R_{18} is applicable for each "*parent*":

$$R_{17}^{a^2} = B_1^2 R_{18}^a, \qquad R_{17}^{b^2} = B_1^2 R_{18}^b \tag{29}$$

This means that for both parent gases a unique oxygen relationship is used in (28), however, based on measured isotope amount ratios measured on each parent (29). When indeed CO_2 starting materials deviate from natural levels (of carbon or oxygen isotopes) dissimilar values for B_1 and B_2 will be obtained.

According to Eq. (29), a relationship for R_{17} and R_{18} can be set up within the gravimetrically prepared mixture:

$$R_{17} = \frac{R^a_{17} + \gamma R^b_{17}}{1+\gamma}, \qquad R_{18} = \frac{R^a_{18} + \gamma R^b_{18}}{1+\gamma} \tag{30}$$

with γ the mass ratio of the parent gases in the mixture: $\gamma = m_2/m_1$.

Applying the relationship (30) with introducing $\varepsilon = R^b_{17}/R^a_{17}$, will result in

$$R_{17}^2(1+\gamma)^2 = R_{17}^{a^2}(1+\gamma\varepsilon)^2$$

and

$$R_{18}(1+\gamma) = \frac{R_{17}^{a^2}}{B_1^2} + \gamma\frac{R_{17}^{b^2}}{B_2^2} = R_{17}^{a^2}\left(\frac{1}{B_1^2} + \gamma\frac{\varepsilon^2}{B_2^2}\right) \tag{31}$$

This will lead to the *calculated* value B in the a mixture:

$$B^2 = \frac{R_{17}^2}{R_{18}} = \frac{(1+\gamma\varepsilon)^2}{(1+\gamma)\left((1/B_1^2) + \gamma(\varepsilon^2/B_2^2)\right)} \tag{32}$$

Eq. (32) now completes the set of Eqs. (26)–(28) for each type of CO_2 mixture as follows:

$$\begin{aligned} &R_{45/44} = y + 2\sqrt{x}, \qquad R_{46/44} = 2y\sqrt{x} + 2\sqrt{z} + x, \\ &R_{47/44} = 2\sqrt{xz} + 2y\sqrt{z} + yx, \qquad x = B^2\sqrt{z} \end{aligned} \tag{33}$$

By replacing y and z in the set of Eq. (33), two polynomials as a function of B and x can be obtained,

$$x\left(\frac{2}{B^2} - 3\right) + 2\sqrt{x}R_{45/44} - R_{46/44} = 0 \tag{34}$$

$$2x^{3/2}\left(\frac{1}{B^2} + 1\right) - xR_{45/44}\left(\frac{2}{B^2} + 1\right) + R_{47/44} = 0 \tag{35}$$

from which by introducing the notation $\xi = \sqrt{x}$, the first Eq. (34) is of the second order (36), while the polynomial (35) is of the third degree (37).

$$\xi^2\left(\frac{2}{B^2} - 3\right) + 2\xi R_{45/44} - R_{46/44} = 0 \tag{36}$$

$$2\xi^3\left(\frac{1}{B^2} + 1\right) - \xi^2 R_{45/44}\left(\frac{2}{B^2} + 1\right) + R_{47/44} = 0 \tag{37}$$

The (positive) solution of polynomial (36) is the following:

$$\xi = \frac{-R_{45/44} + \sqrt{R_{45/44}^2 + R_{46/44}((2/B^2) - 3)}}{((2/B^2) - 3)} \tag{38}$$

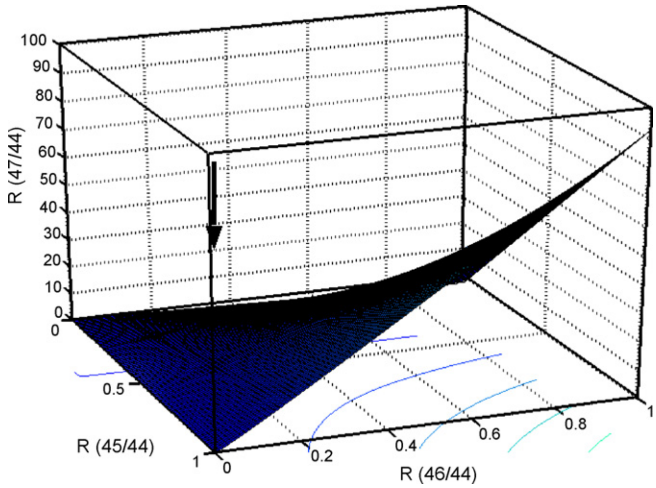

Fig. 4. The "*Isotopic equilibrium surface*" (based on Eq. (39)) as final proof for completeness of the isotopic equilibration in the sample, here visualized in a three-dimensional space. All points belonging to this surface fulfill the condition of Eq. (39), i.e. isotopic equilibrium within the sample.

With this value ξ (Eq. (38)) introduced in the polynomial (37) the "*Isotope equilibration surface*" is defined (39):

$$\begin{aligned} R_{47/44} = {} & \left(\frac{\sqrt{R_{45/44}^2 + R_{46/44}((2/B^2) - 3)} - R_{45/44}}{((2/B^2) - 3)}\right)^2 \\ & \times \left[R_{45/44}\left(\frac{2}{B^2} + 1\right) - 2\left(\frac{1}{B^2} + 1\right)\right. \\ & \left.\times \frac{\sqrt{R_{45/44}^2 + R_{46/44}((2/B^2) - 3)} - R_{45/44}}{((2/B^2) - 3)}\right] \end{aligned} \tag{39}$$

Taking the "*Isotope equilibrium surface*" (Eq. (39)) as ultimate proof for completeness of the isotopic equilibration in the sample, it is possible to visualize in a three-dimensional space the progress of the equilibration, i.e. the way how the ion current ratios are approaching this surface (Fig. 4). All points belonging to this surface fulfill the condition of Eq. (39); i.e. isotopic equilibrium within the sample. This surface is the geometrical locus of the sample, which is in complete isotopic equilibrium, whatever the isotopic enrichment will be. Obviously, it was an advantage in this study that the number of isotope amount ratios measured was only three and therefore could represented in a three-dimensional space (as a non-planar surface). For more complex gases (like SO_2), an *n*-dimensional space needs to be applied, which make the model much more difficult to use. In the mixing process, however, the two 'parent' gases (which are supposed to be in equilibrium, otherwise it must be done) could be represented as points on the 'Isotope Equilibrium Surface' and the resulted mixture will then be on the straight line (Fig. 1) at a position depending of the mixing ratio (Table 3). For evaluating the degree of advancement of the isotopic equilibrium in the carbon dioxide sample, only a tiny part of this surface is used (exemplified in Fig. 5 and described further).

Table 3
Ion current ratios observed on the CO_2 starting materials, the 'parent' gases used for the preparation of the CO_2 synthetic isotope mixtures [22]

Materials	$J_{45/44}$	$J_{46/44}$	$J_{47/44}$
$C^{18}O_2$	0.559 299 (21)	3.017 980 0 (50)	0.825 768 (47)
Natural CO_2	0.011 371 43 (86)	0.004 175 2 (33)	0.000 046 850 (10)
CL01	0.131 912 2 (10)	0.010 309 32 (19)	0.001 338 22 (16)
CL24	0.034 798 2 (23)	0.133 148 6 (26)	0.002 975 82 (10)
Natural CO_2 air liquide	0.011 725 00 (51)	0.004 123 89 (64)	0.000 046 436 (11)
IM-10‰	0.011 792 56 (43)	0.004 159 9 (15)	0.000 047 351 (21)
IM-20‰	0.011 589 51 (21)	0.004 059 0 (11)	0.000 045 498 1 (80)

Each measurement took about 2 h, and mean ion current ratios of the five successive measurements were obtained, with their associated standard measurement deviations (1 s).

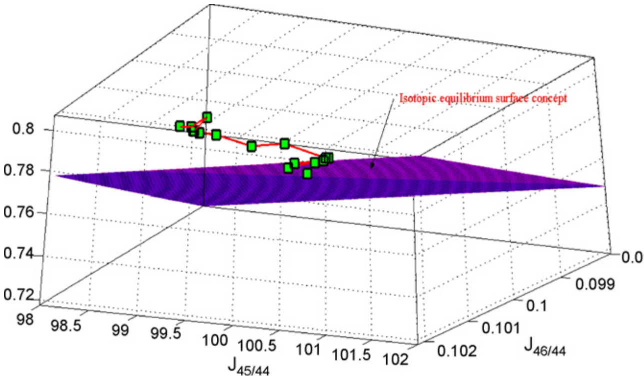

Fig. 5. Quantifying the isotopic equilibration of oxygen and carbon isotopes in the $^{13}CO_2$ gas. The 16 ion current ratio measurements $J_{i/44}$, with $i = 45$, 46 and 47 (Figs. 4–6) are compared to the virtual "*Isotope equilibrium surface*" (Eq. (41)) in the "*Isotope ratio space*".

In the space (Fig. 6), called the "*Isotopic equilibrium space*", the measured ion current ratios $J_{45/44}$, $J_{46/44}$ and $J_{47/44}$ can be found on the axes. The power of this approach is that *during* the isotope equilibration (performed artificially or taking place partially in the mass spectrometer during the measurement), its status can be observed at any time. When not complete, i.e. when the $J_{i/44}$ ion current ratio measurements have not yet exactly reached the surface, the process of equilibration needs to be continued further.

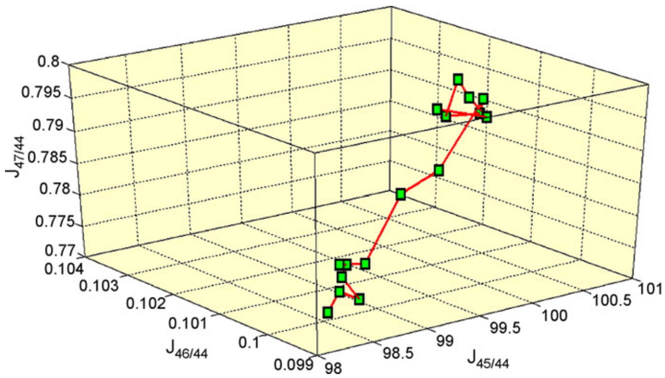

Fig. 6. Evolution of the isotope equilibration of oxygen and carbon isotopes in the $^{13}CO_2$ gas. The 16 ion current ratio measurements $J_{i/44}$, with $i = 45$, 46 and 47 (Figs. 4–6) are presented in the "*Isotope ratio space*", on their way to full equilibrium.

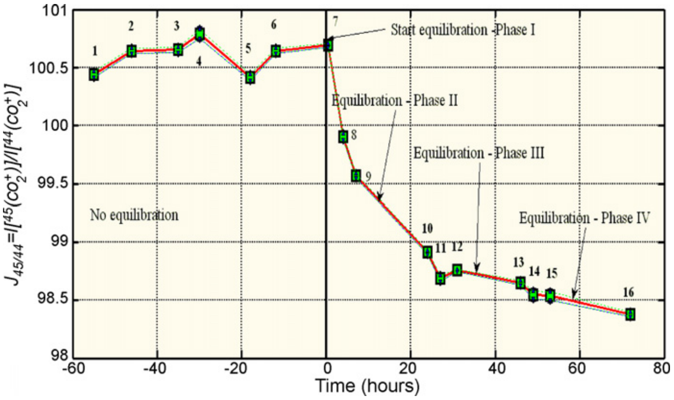

Fig. 7. The ion current ratio $J_{45/44} = I[^{45}(CO_2)^+]/I[^{44}(CO_2)^+]$ measured on the enriched $^{13}CO_2$ parent gas. The first seven $J_{45/44}$ measurements were made without intentional isotope equilibration. After measurement 7, a first equilibration had been made by means of Pt powder at 500 °C during 30 min, and $J_{45/44}$ measured again. This was repeated three more times.

The equilibration model has been exemplified here for a mixture of highly enriched $^{13}CO_2$ gases, employing Eq. (39) as starting point. In total, 16 ion current ratio measurements $J_{i/44} = I[^{i}(CO_2)^+]/I[^{44}(CO_2)^+]$ were performed by the MAT 271 gas mass spectrometer on the mixtures (presented consecutively in Figs. 7–9). For the first seven measurements no

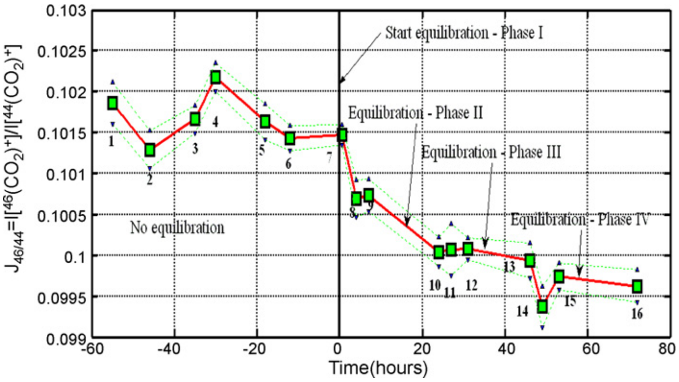

Fig. 8. The ion current ratio $J_{46/44} = I[^{46}(CO_2)^+]/I[^{44}(CO_2)^+]$ measured on the enriched $^{13}CO_2$ parent gas. The first seven $J_{46/44}$ measurements were made without intentional isotope equilibration. After measurement 7, a first equilibration had been made by means of Pt powder at 500 °C during 30 min, and $J_{46/44}$ measured again. This was repeated three more times.

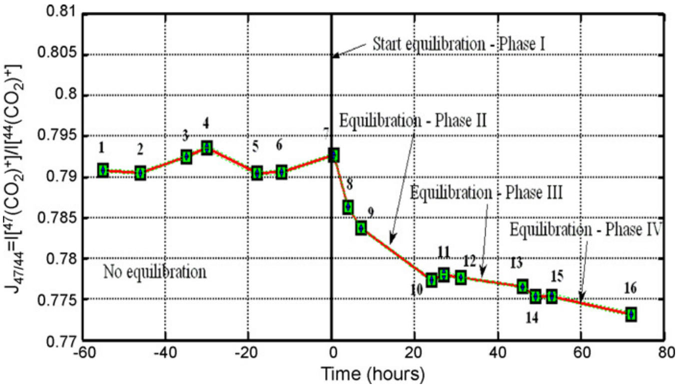

Fig. 9. The ion current ratio $J_{47/44} = I[^{47}(CO_2)^+]/I[^{44}(CO_2)^+]$ measured on the enriched $^{13}CO_2$ parent gas. The first seven $J_{47/44}$ measurements were made without intentional isotope equilibration. After measurement 7, a first equilibration had been made by means of Pt powder at 500 °C during 30 min, and $J_{47/44}$ measured again. This was repeated three more times.

(artificial) isotope equilibration had been made; hence, these measurements suffered from bad repeatabilities thus indicating that something was wrong with this sample.

About 60 h after the first measurement (at $t = 0$ on Figs. 7–9) a first sample equilibration was carried out by means of 100 mg Pt powder (200 mesh) at 500 °C for 30 min immediately followed by a new $J_{i/44}$ measurement. Already after the first equilibration, a significant decrease of all three ion current ratios $J_{i/44} = I[^{i}(CO_2)^+]/I[^{44}(CO_2)^+]$ was observed. Nine more measurements were made and, in between them, three more equilibrations of 30 min each were carried out (illustrated in Figs. 7–9).

The measured ion current ratios $J_{i/44} = I[^{i}(CO_2)^+]/I[^{44}(CO_2)^+]$ presented in an "*Isotope ratio space*" (Fig. 6) give a clear picture of the tendency to shift to the "*Isotope equilibrium surface*" (Fig. 5), with the distance to the surface becoming smaller when the sample approaches equilibrium. This means that the final distance yields the possibility of assessment the completeness of isotopic equilibrium in a gas mixture. It is the (geometrical) distance in the "isotope ratio space" with the coordinates being the measured ratios $J_{45/44}$, $J_{46/44}$ and $J_{47/44}$ and their distance to the surface considering the shortest distance from that point to the surface.

To calculate this distance (Δ) the following relationship between two points is used:

$$\text{distance} = \Delta = \sqrt{(R_{45/44} - J_{45/44})^2 + (R_{46/44} - J_{46/44})^2 + (R_{47/44} - J_{47/44})^2} \qquad (40)$$

However, the values $R_{i/44}$ (those with shortest distance to $J_{i/44}$) are not known but can be calculated by means of a 'minimization' approach, frequently called in mathematics a 'constraint non-linear optimization approach'. For the optimization the consideration of two additional constraints is required:

(a) The point $R_{i/44}$ must belong to the isotope equilibrium surface. That requires a slight transformation of Eq. (39):

$$R_{47/44} - \left(\frac{\sqrt{R_{45/44}^2 + R_{46/44}((2/B^2) - 3)} - R_{45/44}}{((2/B^2) - 3)}\right)^2 \times \left[R_{45/44}^2\left(\frac{2}{B^2} + 1\right) - 2\left(\frac{1}{B^2} + 1\right) \times \frac{\sqrt{R_{45/44}^2 + R_{46/44}((2/B^2) - 3)} - R_{45/44}}{((2/B^2) - 3)}\right] = 0 \qquad (41)$$

(b) Eq. (42) of the line between $R_{i/44}$ (surface) and the ion current ratio $J_{i/44}$ is:

$$a_1(R_{45/44} - J_{45/44}) + a_2(R_{46/44} - J_{46/44}) + a_3(R_{47/44} - J_{47/44}) = 0 \qquad (42)$$

The slopes a_i are calculated as the partial derivates of Eq. (39), and given by:

$$N = \nabla f = \begin{pmatrix} \dfrac{\partial f}{\partial R_{45/44}} \\ \dfrac{\partial f}{\partial R_{46/44}} \\ \dfrac{\partial f}{\partial R_{47/44}} \end{pmatrix} = \begin{pmatrix} a_1(R_{45/44}, R_{46/44}, R_{47/44}) \\ a_2(R_{45/44}, R_{46/44}, R_{47/44}) \\ a_3(R_{45/44}, R_{46/44}, R_{47/44}) \end{pmatrix} \qquad (43)$$

From Eq. (43), the three calculated values for $a_i(R_{45/44}, R_{46/44}, R_{47/44})$ are introduced in (42) resulting in the equation describing the perpendicular line to the surface. The two constraints (41) and (42) are now applied for the optimization approach of the distance Δ (Eq. (40)): the shortest 'distance' from the measured point $J_{i/44}$ in the 'isotope equilibrium surface' to the surface, representing the actual status of the isotope equilibrium in the gas mixture.

This optimization approach is too complicated and a very time consuming process, too difficult to calculate by hand, therefore the entire process was done with the help of the software Matlab 7.4.

On sample $^{13}CO_2$ the distances Δ to the isotopic equilibrium surface can now be calculated (as an example) for the 16 different ion current ratio measurements (presented in Figs. 7–9). This clearly shows that after measurement 7 (Figs. 7–9), i.e. after the isotope equilibration was started, the distance gradually becomes smaller, indicating that the isotope equilibration is on its way to completeness (Fig. 5).

5. Conclusions

The model presented enables to fit experimental mass spectrometric data adequately, thus opening the possibility to calculate the degree-of-isotopic-equilibrium in gaseous mixtures of isotopes at any time after mixing isotopes of different isotopic composition. This creates a warning signal for the degree-of-completion of an isotopic equilibrium prior to the ion current ratio measurements, thus preventing wrong measurement results.

The model is based on evaluating the distance of such ion current ratio presentation (inside the ‘isotope ratio space’) to a virtual “isotope equilibrium surface”, composed by the isotope amount ratios of the starting materials of the mixtures. This tool enables to quantify the degree-of-advancement of an isotope equilibration.

For gas isotope mixtures, which are not yet in full isotopic equilibrium, a (partial) isotope equilibration will take place inside the mass spectrometer during the ratio measurements, due to the large surfaces and high temperatures present in the spectrometer. Such uncontrolled equilibrations are only detectable by high precision ion current ratio measurements with measurement repeatabilities in the order of 10^{-5} relative of the ratio values. Measurements of this quality and potential for correction of systematic effects are essential for the preparation of primary isotope measurement standards.

Obviously, the distance to the “*Isotopic equilibrium surface*” is accompanied by measurement uncertainties, with the assumption on the oxygen isotopes’ relationship, as major uncertainty contribution to the calculation of the uncertainty of the surface (Eq. (39)).

Future work at IRMM aims at reducing this measurement uncertainty through the preparation of synthetic isotope mixtures in CO_2 form, from which absolute carbon and oxygen isotope amount ratios can be obtained without any assumption for the oxygen isotopic composition. Possible, minor “*residual distance*” to the “*Isotope equilibrium surface*” can be studied through measurement repeatabilities of the ion current ratio measurements.

Summarizing: It has been shown that it is possible to complete and to quantify the degree of ‘scrambling’ of carbon and oxygen isotopes in CO_2 mixtures, using platinum as catalyst at high temperatures.

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