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Quantitative measurements of helium-4 in the gas phase of Pd + D₂O electrolysis

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Abstract

A method for the mass spectrometric quantitative determination, down to the sub-ppb level, of the ⁴He content in the gaseous products of cold fusion Pd + D₂O electrolytic cells is described. The data collected in an experiment lasting over 1000 h provided a time picture of the phenomena. Measurements of the ²⁰Ne content have also been performed in order to check air contamination. The methods and controls employed are suitable for use with non-dedicated mass spectrometers which cannot be operated in vacuum static conditions.

Keywords: Pd + D₂O electrolysis; Cold fusion; ⁴He determination; Mass spectrometry

1. Introduction

In the framework of an experimental investigation which has been under way since 1989 involving calorimetric and nuclear measurements on electrolytic Pd + D systems, our aim has been to observe simultaneously any power excess and those nuclear products that have been hypothesized. In recent experiments we have performed quantitative measurements of the amount of ⁴He in the electrolysis gases. In this paper we report the method used and the results obtained in a multicell experiment lasting for about 1200 h. A complete account of the experiment and of the relation between the various types of measurements is given in a companion paper [1]. Helium measurements in the electrolysis gases have previously been performed at various levels of detection limits, but almost always in a limited number of samples which did not allow a time

pattern in the collected data to be sought. Therefore, we have developed a method suitable for a non-dedicated instrument which, even if not achieving the detection limits available at the most specialized institutions, can provide sufficient data with an adequate detection limit to give a time picture of the phenomena under study.

2. Experimental

2.1. General

The mass spectrometer employed (model 12-60-MT-7 built by Nuclide Analysis Associated, now operated by PATCO) was a single focusing 12" 60° magnetic instrument equipped with a Nier-type electron ion source designed and used for several years for high temperature chemistry studies by coupling to a Knudsen effusion molecular source [2]. The resolving power was adjusted to 660 (as measured by the single-peak half-height width at the ⁴He mass) to a compromise between sensitivity and discrimination capabilities. The detector was an electron multiplier operated at a gain, measured on mass 28, of 3 × 10⁵. The operating conditions were as follows: emission current, 1 mA; ionizing

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electron energy, 100 eV; accelerating voltage, c. 4500 V. With respect to the abundance sensitivity, the experimental conditions can be envisaged by noting that, at the typical operating pressure in the ion source of ca. 10^{-5} mbar, while the gas sample was being admitted with a D_2 signal of the order of tenths of nanoamperes the tail of the peak at the ^4He mass was approximately 1 pA.

The Knudsen molecular source assembly was removed and replaced with an inlet line assembled with conventional small flange KF 25 fittings. The inlet line consisted of a cold finger filled with active charcoal and cooled with liquid nitrogen. This line could be pumped with an auxiliary diffusion pump and was connected to the mass spectrometer ion source via a Balzers UDV035 dosing valve and a short quartz tube ending immediately before the first plates of the ion source itself.

The overall experiment has been described separately [1]. It suffices here to note that five electrolytic cells, with 0.2 M LiOD as electrolyte and Pd cathodes (in our notation cells 2, 4, 7, 8 and 10) were used, and a further cell with a Pt cathode (cell 1) constituted the reference cell providing a parallel blank.

Boil-off nitrogen was used as a carrier gas to sweep the electrolysis cells. Each cell was connected in series to its specific $D_2 + O_2$ external recombiner, and the stream of gas coming from the different cells could be directed, by a manifold valve system, through a stainless steel trap filled with Pd sponge and collected in a stainless steel volume of 500 cm^3 . Two of these trap-and-vessel systems were available to maintain flushing even when the Pd sponge had to be regenerated. The passage through the recombiner and the Pd sponge greatly reduced the deuterium content in the gas reaching the collecting vessel [1,3]. Pyrex glass was used for the cells and the recombiners. Nylon 66 tubes (cell lines 2, 7, 8 and 10) or stainless steel tubes (cell lines 1 and 4) were used; surprisingly, a relatively low ^4He background was measured for both materials (see below). Connections in the lines were made using Swagelock fittings; where this was not possible, as in the case of stainless steel–Pyrex joints, epoxy resin adhesives, of the type employed in high vacuum technology, were used. The stainless steel vessels were evacuated with a fore vacuum pump three times in sequence and filled with boil-off nitrogen before connection to the collecting line.

2.2. Helium measurement procedure

The procedure used was inspired by the classical work of Nier [4] and the experiment reported by Bush et al. [5]. However, since our mass spectrometer is unsuitable for measurements in vacuum static conditions, i.e. without any pumping, which are known to be

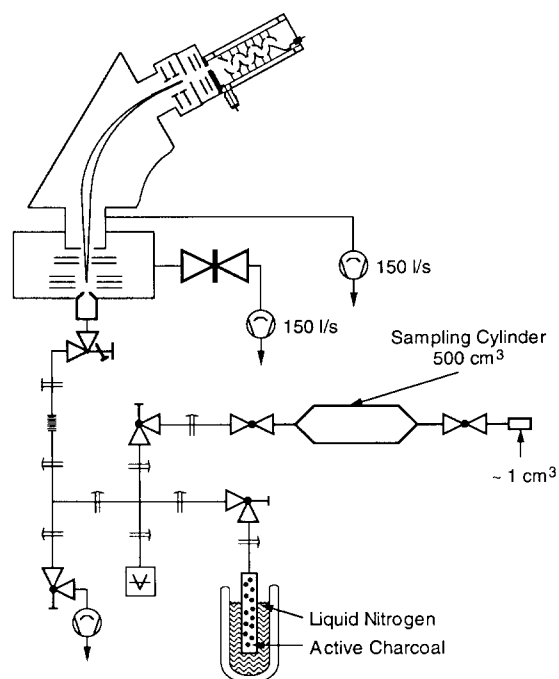


Fig. 1. Scheme of the inlet line used.

the most sensitive conditions, a different method had to be used. The sampling cylinder, filled with the gaseous mixtures collected as described, was connected to the inlet line (Fig. 1) maintained under vacuum with an auxiliary diffusion pump. After the auxiliary pump had been shut off, the sample was allowed to expand into the line (volume of roughly 1000 cm^3) where, within a few minutes, the main constituent of the gaseous mixture (nitrogen) was adsorbed down to a pressure of 10^{-2} Torr by activated charcoal (c. 30 g maintained at liquid nitrogen temperature). It should be noted that this adsorption stage was not primarily directed at the deuterium component of the gaseous sample, which was already greatly reduced by the collecting procedure, but instead at reducing the overall pressure prior to the admission. This allowed the dosing valve to be opened sufficiently wide without making the ion source pressure to rise to values which could cause noise and result in a severe deterioration in resolving power. The sample was subsequently admitted to the mass spectrometer ion source (volume ca. 5000 cm^3) whose pumping was shut off, shortly before the opening of the dosing valve, with a gate valve which was added to our pumping system for this purpose. Owing to the differential pumping between the analyser and the ion source sections of the mass spectrometer provided by two 150 l s^{-1} oil diffusion pumps, the partial pressure of the gases admitted rose when the dosing valve was opened and subsequently decreased, with kinetics dependent on the gas itself, as a consequence of the pumping through the low conductance connection to the analyser section. This behaviour is

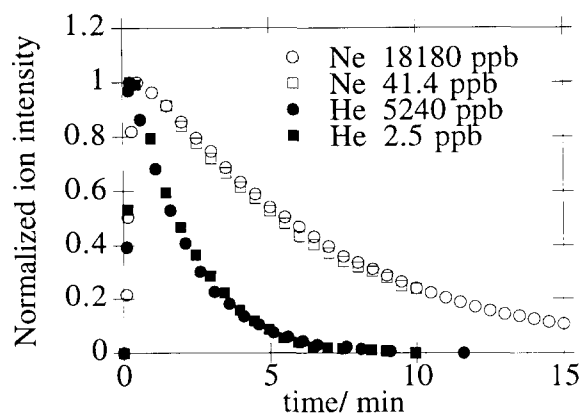


Fig. 2. Examples of the time dependence of the $^4\text{He}^+$ and $^{20}\text{Ne}^+$ ion intensity with various amounts of air admitted (neon, 500 cm^3 and 1.14 cm^3 ; helium, 500 cm^3 and 0.24 cm^3).

shown in Fig. 2 where it can be seen that no significant variation in the time dependence of the helium signal detected was observed for quite a large variation of the helium content in the sample admitted. Therefore the helium content could be measured by either the time integral of the signal or the maximum value of the signal itself. Both methods were used in the first part of the experiment with differences in the results ranging between 2% and 3%.

A typical example of a recording is shown in Fig. 3. The initial part shows how it is possible, by performing a scan by discrete variations of the accelerating voltage, to measure the background while following the helium signal and, subsequently, the deuterium ion intensity. Moreover, the detection of the deuterium signal at precisely the correct voltage span from the helium focusing conditions allowed the correct assignment to helium of the signal followed as a function of time to be checked. Indeed, if for some reason the deuterium signal was being recorded by mistake, no signal would have been found at that particular mass increment of the accelerating voltage focusing conditions. However, whenever the helium signal appeared to be unusual a quick check of the correct value of the onset ionization potential was performed as a matter of course.

The helium signal in the final portion of the recording shown in Fig. 3 is due to the admission of some air (ca. 1 cm^3) previously trapped into a known volume at the tip of the sampling cylinder on the opposite side to that used for the connection to the inlet line (see Fig. 1). By assuming that the helium content of the air (trapped in open air on the roof of the department building) was equal to the tabulated value (5.24 ppm), the amount of helium admitted was also known. This procedure allowed an in-situ calibration to be used to check the procedure and immediately identify any measurement which appeared unusual or of interest. This same procedure, together with similar ones, provided a conversion factor between the maximum ion

intensity measured and the amount of helium in the 500 cm^3 sampling cylinder. The 45 specific calibration runs performed through the experiment (with the admission of different quantities of helium, in the range from ppb to ppm) provided a value of $63 \pm 8 \text{ pA ppb}^{-1}$ for the conversion factor. No time dependence was observed. In order to measure the helium concentrations of the samples, this average value has been preferred to the direct point-to-point calibrations mentioned above as it was deemed that a more conservative estimate of the overall error could be made. Thus the dispersion of the values quoted (the error in the ion intensity measurement is negligible) has been assumed to be representative of the standard deviation to be applied, as a percentage error, to our overall measurements. It is reassuring that the procedure showed good linearity in the range of helium concentrations of interest; the average sensitivities found were 56 pA ppb^{-1} and 64 pA ppb^{-1} with helium contents in the

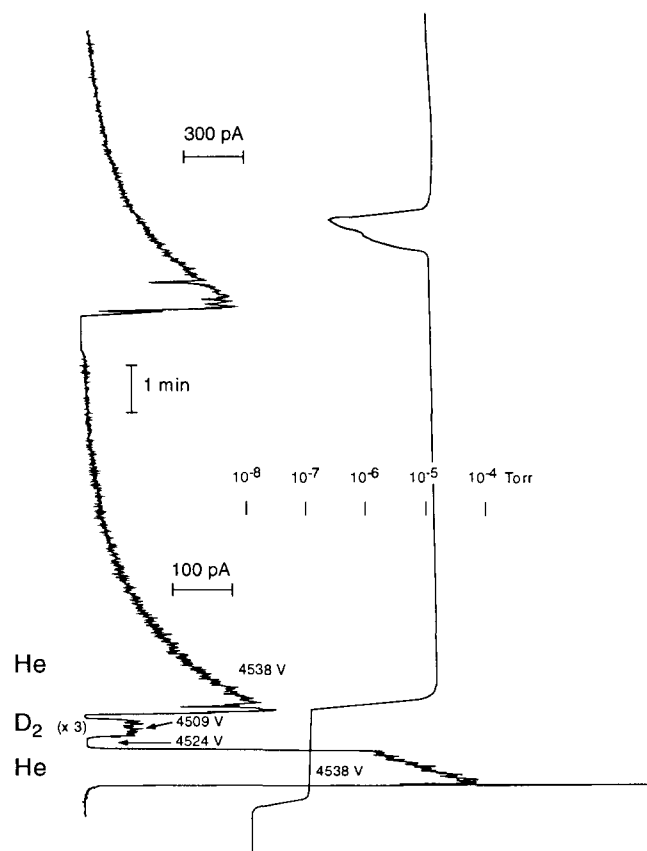


Fig. 3. Typical helium measurement. The ion intensity increases to the right while time increases in the vertical direction. The trace on the right (shifted in space out not in time) is the recording of the ion source pressure. The first rise of pressure shown is due to shutting of the pumping, while the second rise is due to admission of the sample. The mass spectrometer is tuned on ^4He at the beginning of the recording. The enlarged portion shows how a discrete voltage scan can be performed to check the background between helium and deuterium (at 4524 V) and to measure the deuterium (at 4509 V).

sample cylinder of 5.24 ppm and 10.4 ppb respectively. With the present ion intensity detection limit of the order of 1 pA at the operating pressure, and with a signal-to-noise ratio greater than 2, the helium detection limit attained with the procedure described can be given as ca. 3×10^{11} atoms or 1×10^{-8} cm³ stp or 0.02 ppb in a sampling volume of 500 cm³. An estimated detection limit is discussed because no attempt was made to handle air samples smaller than 50 μ l or 6×10^{12} atoms. The detection limit attained is higher than that reported for a specialized mass spectrometer operated in a completely static way. However, while the expected ⁴He amounts are well above this limit, no memory problems are encountered at these concentration levels with the semidynamic procedure described.

At the levels of helium concentration mentioned care must be taken to avoid any contamination in sample handling. The connection to the lines of our prefilled, and therefore helium-free, sampling cylinders was a possible source of air contamination, as was the procedure used to switch the collection between the different lines which could have been the origin of a mutual contamination between the lines. Therefore, the question arose of how much time should be allowed for the stream of gas coming from the collecting lines to sweep away any gas not fully representative of the cell gas composition. A rather conservative approach has been adopted by measuring the ⁴He content of a vessel filled with air as a function of the time elapsed after its connection to the lines. The depletion curve derived fell to the ppb level in slightly less than 2 h. On the basis of these experimental results a period of at least 2 h, but generally 3 h or more (in the case of overnight collections), was allowed to elapse after connecting the sampling cylinders to the collecting lines. This procedure should eliminate the contamination mentioned.

The background measured for the single inlet line, using the same procedure as for the samples, was routinely checked and was always found to be barely detectable despite the use of conventional KF-25 fittings which make use of sealing materials known to be prone to helium permeation. The low background was believed to be due to the limited duration of the procedure; the time between shutting off the auxiliary diffusion pump and the end of the measurement was typically no more than 20–30 min.

2.3. Helium: results

We were aware from the beginning of the preliminary measurements that the lines used to collect the sample were not perfectly tight. Indeed, the concentration of helium measured in the sample cylinder, in the absence of any electrolysis and even without the electrolyte, was typically of the order of ppb, although the

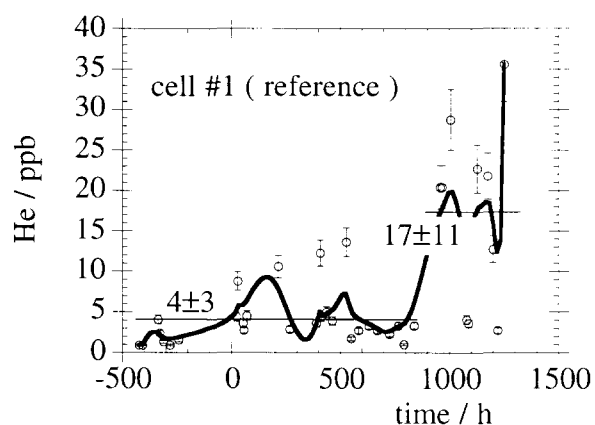


Fig. 4. ⁴He concentrations for the reference cell 1. The smoothing function fitted points towards an increase in the background after 900 h (see text).

boil-off nitrogen, if taken directly from the liquid phase, generally showed helium concentrations at the level of our detection limit and always lower than tenths of ppb. In this respect, as will become clearer in the following, it must be pointed out that the differences between the lines should be attributed to the connections between the various portions of the lines themselves and not to the material from which they were made. As a consequence the general philosophy of the measurements in the first part of the experiment has been to examine the helium concentration in each cell as a function of time by searching for any significant increase above the background of that particular cell. An increase over the levels measured for reference cell 1, which provided a parallel blank, was also sought. Therefore, in order to keep the sealing properties of the lines constant, even the slightest mechanical stress on the cell assembly and lines has carefully been avoided up to 900 h of the experiment. After this period, for reasons connected with the concurrent neutron measurement, some mechanical manipulation of the cell assembly was necessary. Therefore a modification of the sealing properties of the line connections may have occurred. Indeed, data for the reference cell 1 (Fig. 4) could be considered to support the hypothesis of an effect of the mechanical manipulation at 900 h. Therefore, taking a conservative approach, all data recorded after 900 h were discarded.

Comparison of the helium measurements of cells 2, 7 and 8 with those for cell 1 showed that none of these cells exhibited variations large enough to be considered significant with confidence. The ⁴He concentrations detected were in the range from 1 to 18 ppb.

In contrast, significant amounts of helium were detected for the cells 4 and 10 (Fig. 5). Fig. 5 also shows that there is a definite build-up of the helium detected in cell 4 with respect to both the background measured

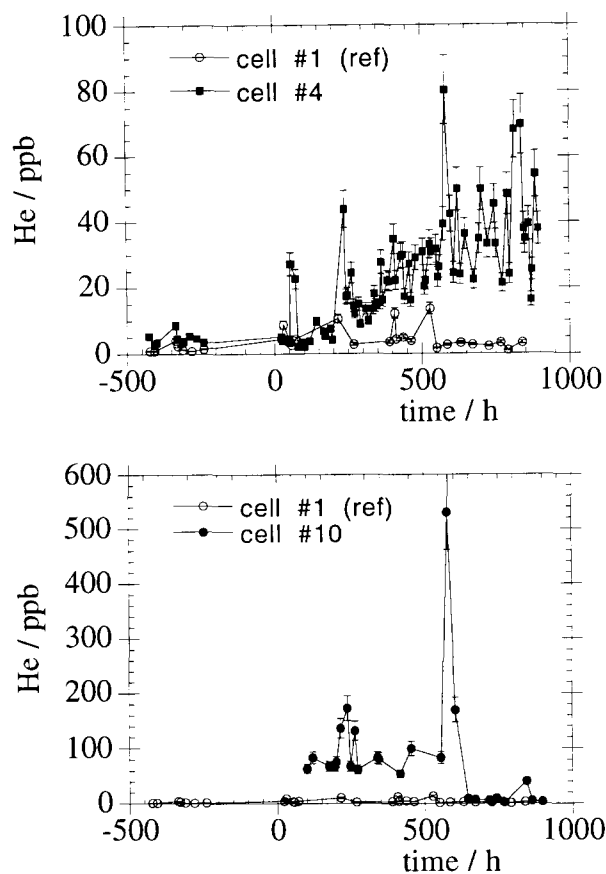


Fig. 5. ^4He concentrations found for cells 4 and 10 compared with those of the reference cell 1. Note the different ordinate scale employed.

for roughly 250 h before the beginning of the electrolysis and the parallel blank of the reference cell 1.

In the case of cell 10, for which no comparable data were obtained before the beginning of the electrolysis, much larger values than those for cell 4 were found from the start of the measurements. This fairly constant value of about 70 ppb, on which some prominent spikes are apparent, was believed to be due to the large background of that particular collecting line. However, shortly after 600 h and after an impressive peak has been recorded, the amount of helium detected dropped to very low values (some ppb) typical of reference cell 1. In contrast, an obvious correlation with the electrolysis conditions of cell 10 was not readily apparent [1]. Thus this quite dramatic decrease could be due to either spontaneous closure of the leak affecting the line (which is improbable but not impossible) or to a reduction of the helium release in the interior. As a consequence we were led to examine the experiment in a different way with respect to the original aim. Indeed, a method had to be devised in order to confirm or disprove the hypothesis of the occurrence of air leakage.

2.4. Neon: measurement procedure

Neon was selected as a marker of the presence of air since it was the only component, other than helium, that would not condense at liquid nitrogen temperature during the inlet procedure.

The most abundant isotope of neon, ^{20}Ne of mass 19.99244 and ionization potential (IP) 21.6 eV, can be measured mass spectrometrically by discriminating its contribution to the nominal mass 20 from other possibilities. In our case the principal possible interfering ions were CD_4^+ (20.05600 amu, IP = 13.19 eV), ND_3^+ (20.04537 amu, IP = 11.52 eV), D_2O^+ (20.02311 amu, IP = 12.60 eV), $\text{H}_2^{18}\text{O}^+$ (20.01481 amu, IP = 12.59 eV) and Ar^{2+} (19.98119 amu, IP = 43 eV) (a minor superposition of $^{18}\text{OD}^+$ (20.013262 amu) and HF^+ (20.00623 amu) is among the possibilities). The mass resolving power employed led to a partial resolution from the higher masses which allowed us to make fairly good estimates of the true separated ion intensities. The presence in the spectrum of the doubly ionized argon peak Ar^{2+} , which could not have been mass resolved, was avoided by reducing the operating value of the ionizing electron energy to 40 eV, below the onset of this process.

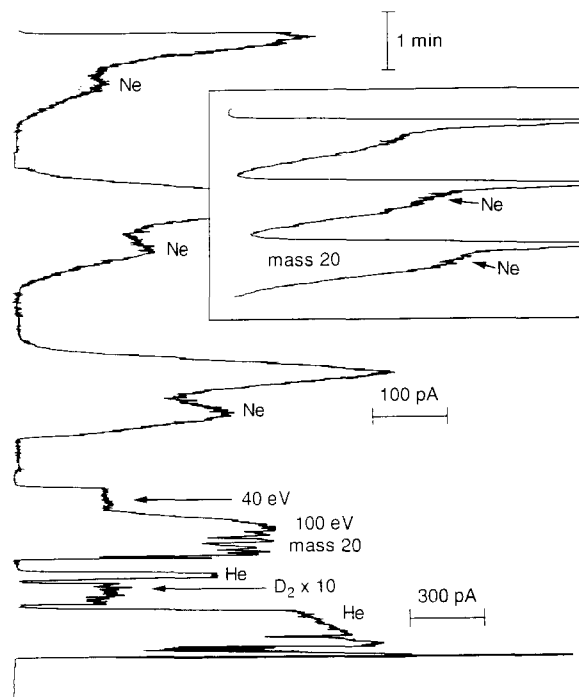


Fig. 6. Example of almost simultaneous helium and neon measurement. The ion intensity increases to the right while time increases in the vertical direction. The first part of the recording is similar to that of Fig. 3. Magnetic scanning across mass 20 is performed several times after the ionization energy has been reduced to 40 eV. The inset shows a different and rather extreme case where a larger superposition of masses is apparent.

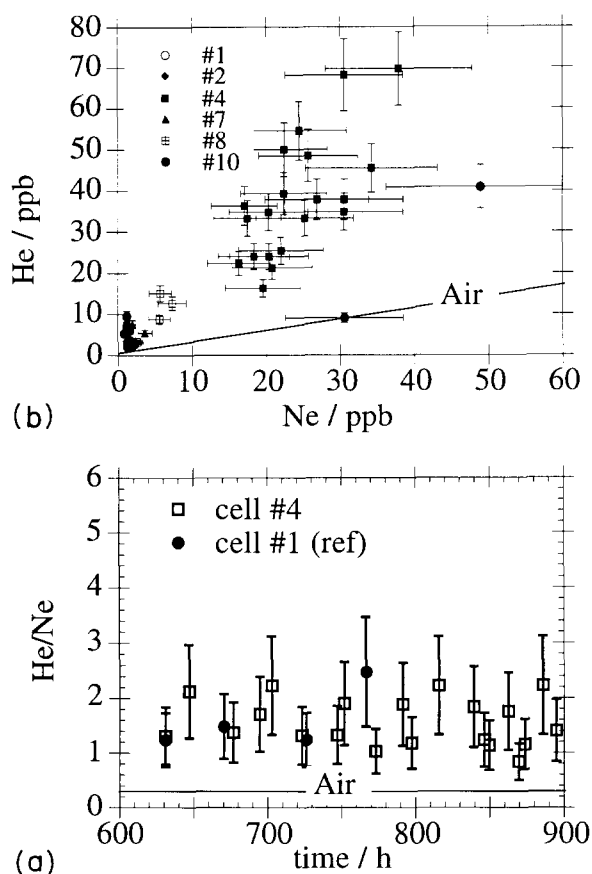


Fig. 7. (a) Helium-to-neon ratios measured as a function of time for cells 1 and 4; (b) helium versus neon detected for all the cells.

As in the case of helium (see Fig. 2), the neon signal measured as a function of time was found to be independent of the amount admitted to the ion source. In addition, as expected, it exhibited a different kinetic behaviour, lasting for a longer time than helium. These features allowed measurement, in any single admission of sample, first the helium maximum value and then the neon intensity–time dependence, from which a satisfactory back-extrapolation could be made. Calibrations similar to those described for helium were also made, leading to a conversion factor of 24 pA ppb^{-1} . However, the error on the neon measurement was taken as twice that of helium because, as shown in a typical recording (Fig. 6) and in an extreme case (inset to Fig. 6), the neon peak had various degrees of superimposition with the other contributions to mass 20 (mainly D_2O^+). However, whenever possible, the assignment of the peak to the neon ion has been checked with appearance potential determinations and always found to be consistent with the tabulated value of 21.6 eV, and through the control of the isotopic abundance distribution of masses 20 and 22 (the intensity of isotope 21 was almost always too low).

2.5. Neon results

First it must be recalled that after the beginning of the neon measurements (ca. 600 h) and before the limit on the reliability of data (ca. 900 h) the only cell with helium values greater than the background (either the internal background or that provided by the parallel blank) was cell 4. The helium-to-neon ratios measured for this cell, together with those measured for the reference cell are reported as a function of time in Fig. 7(a). Despite being definitely greater than the ratio found in air, the values found for cell 4 values can be superimposed almost exactly on those of cell 1 for which, of course, no helium release is expected. Therefore there seems no doubt that some form of preferential inflow of helium occurred.

It should be noted that the experimental results should not be attributed to the materials used in making up cells and collecting lines. Indeed, cells and lines 1 and 4 were identical but there was a difference in a factor of 8 in the helium detected; in addition, the helium concentrations for cell 10 were up to 50 times larger than those of cells 2, 7 and 8 even though all four cells were the same. Thus it must be concluded that the helium contamination from air did not occur by permeation through the materials of cells or lines but by some sort of leakage in the connections; the similar variations with time of the amount of helium detected supports this conclusion.

Other important evidence which emerges from the data in Fig. 7(a) is the correlation between helium and neon concentrations. This can be seen better in Fig. 7(b) where the helium detected in all the cells is plotted against the neon observed. A good correlation is quite apparent here: when helium increases, neon also increases. The simplest way to explain the experimental results shown, without invoking the release of both helium and neon from the cathode, is that of a combined leakage mechanism or, possibly, a concur-

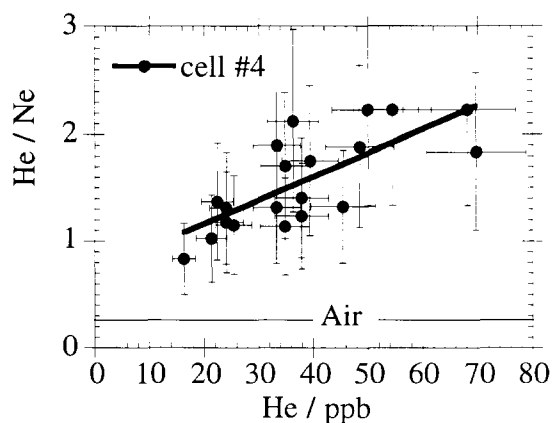


Fig. 8. He/Ne ratio versus helium concentrations for cell 4. The time span is the same as in Fig. 7(a).

rent helium inflow from the outside and release in the interior. Some support for this last hypothesis can be obtained from the data of Fig. 8, from which an increase in the He/Ne ratio with respect to the amount of helium detected can be hypothesized. Indeed, the alternative explanation, i.e. a combination of inflow mechanisms varying with the amount of helium detected, and thus with the amount of air entering, would be expected to give He/Ne ratio moving towards that in air on increasing helium and not vice versa.

3. Discussion

In this discussion we consider only the helium data presented here intentionally ignoring the heat power excess results [1] in order to obtain an independent assessment of the reliability of our present experimental results.

It seems reasonable to assume that, if there is a leakage, an increase with respect to the normal helium content in the air surrounding the cells should result in an increase in the helium found in the collected sample. In fact, since the beginning of the experiment, much attention has been paid to the presence of various possible sources of helium, like NMR machines, in our department. Therefore the helium content in the cell room with respect to that collected on the roof in open air has been checked at intervals. These checks were performed in an entirely similar way to that used for the sample; the only difference was the much smaller collecting volume employed. Quite large variations in the helium content, up to about four times that expected, have been observed. Nevertheless, in contrast with expectation, no correlation is apparent, on a reasonable time-scale, between the most prominent spike of helium detected in cell 10 and the helium content of the air surrounding the cells (Fig. 9).

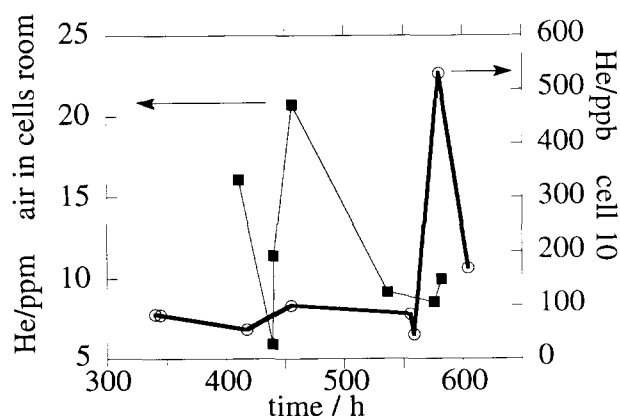


Fig. 9. Helium concentrations found in the air surrounding the cells and in cell 10. The lines are not significant and are drawn only as an aid to the eye.

It should also be noted that many quite large variations in the composition of the gaseous mixture occurred during the experiment as a consequence of either the electrolysis variations or the occasional shutting-off of the recombiners. However, the helium concentrations measured in the collected samples were completely independent of these composition variations. At first glance, whatever the helium inflow mechanism, this behaviour seems to be quite unexpected.

With respect to the helium time dependence the manipulation performed at 900 prevented observation of the expected drop in the helium detected to background level at the end of the electrolysis. If no significance is attached to such manipulation, whose influence on the sealing properties of all the lines is not proved, the failure to observe such an obvious drop points towards the occurrence of air contamination due to the spontaneous opening and closing of leak paths. However, if these spontaneous changes in the sealing properties are believed to have occurred, the evidence for air contaminations from the neon data, observed after 600 h on cell 4, cannot be extended rigorously with complete confidence to the most relevant helium measurements which pertain to a different cell and different period (cell 10 at $t < 600$ h). Moreover, it should be pointed out that the parallel blank from reference cell 1 exhibited a fairly low background throughout the experiment without any spurious spikes.

Therefore the overall picture which emerges does not seem to fit a single interpretation which can satisfactorily account for all the experimental data. However, on balancing the various arguments presented, it must be noted that the stronger evidence observed, i.e. the correlation between helium and neon, favours the occurrence of air contamination, although the increase in the He/Ne ratio with He suggests the concurrent air contamination and helium release.

4. Conclusions

Even if clear-cut evidence for air contamination or a quantitative estimate of the influence of the contamination on our helium data could not be attained, we believe that we have shown how these measurements can be performed with a non-dedicated instrument and have identified the type of controls that are necessary. Relatively simple, although expensive, modifications of the collecting lines which are under way are expected to cure the air contamination problem. Some further comments regarding the neon measurements may be of general interest. We measured the amount of neon by detecting Ne^+ at nominal mass 20 because as a rule, our resolving power allowed us to do so and also because a substantial amount of data have been al-

ready accumulated when extreme experimental conditions such as that of the inset to Fig. 6 have been encountered. However, by using mass spectrometers of lower resolution power neon concentrations can be measured by examining the doubly ionized Ne^{2+} ion at nominal mass 10. Indeed, if it depends on the specific experimental conditions and the mass spectrometer background, many fewer problems due to the superimposition of masses are likely to be encountered at such a mass number. The resulting improvement of the measurement should compensate the reduced sensitivity caused by the lower electron impact cross-section for the double-ionization process.

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