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Chemical behaviour of matter at very low concentration

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Introduction

The definition of a "very low" concentration is as fluctuant as subjective (1). It may apply to reagents in the micromolar range and as well to solutions with less than 100 species per unit volume. Today, with equipments based on tunable laser beams, even the ultimate conceivable case of a single atom detection is no more out of reach (2).

Historically, questions on the behaviour of matter in very small concentrations arose about a century ago with the discovery of the first short-lived natural radioelements. Later, radiochemists became used to dealing with "tracer" concentrations of artificial radioisotopes of most elements and "chemistry at the tracer scale" grew up as a specific topic of radiochemistry. The purity requirements to be met by materials for high technologies, such as semiconductors, the control of pollution in the environment and the recognition of the vital role of many elements in living organisms have prompted a wide development of "trace analysis".

The understanding of the terms "traces" and "low concentration" differs widely among chemists. Sometimes it is defined as the level at which the "trace" can influence the physical, chemical or biological properties of the host matrix. From the analytical point of view, traces are concentrations which are at the limit of detection by the most sensitive methods available. Because the sensitivity of analytical methods is continuously improving, this definition is not very reliable.

Alternatively, a trace can be defined on the basis of its physico-chemical behaviour (7). A species is considered as a trace when its behaviour differs from the behaviour as a macrocomponent. For aqueous solutions, peculiar and sometime erratic behaviour of traces include the adsorption on surfaces, coverage of surfaces less than a monomolecular layer, lack of formation of a visible solid phase by precipitation, irreproducible composition of solutions due to the presence of impurities. These phenomena may be encountered at concentrations below 10^{-5} to 10^{-7} M, which may be indicative of the upper limit of trace concentrations. This definition has the merit to give a practical concept of trace.

For radioactive matter, which is mostly the topic of this paper, a different terminology exists. It is necessary to make a distinction between a *radioactive tracer* and *species at the tracer level*, although both terms are often exchangeable. A radioactive tracer (or label) is a radioactive isotope of an element used for its convenience in following the behaviour of a (usually isotopic) stable or radioactive long-lived isotope. This practice does not necessarily imply a very low concentration. On the other hand, in many cases, traces at very low concentrations can only be followed because they are radioactive. Chemistry of Fr, At, Po, Rn etc and of most actinides is as well trace chemistry as chemistry at tracer concentration. In the present context, trace always applies to very low concentrations, easily detectable only via radioactivity and the discussion refers to "trace" chemistry rather than "tracer" chemistry.

The number of available species being measured is many orders of magnitude smaller than that corresponding to the limit mentioned earlier. This is easily inferred from the definitions of activity and the half-life. The number N of radionuclides with half-life T (in s) corresponding to an activity A (in Becquerels) is

$$N = 1.44 A T$$

It is not uncommon to use solutions in the laboratory with activities of the order of 10^5 Bq (3 μ Ci). For the natural isotope ^{212}Pb ($T = 10.6$ h) the initial number of nuclides would be 5×10^9 or, say, when dissolved in one mL, a 10^{-11} molar sample. With half-lives down to a few minutes and activities of about hundred Bq, conditions which are largely

compatible with radiochemists' savoir-faire, the detectable amounts are at least 5 orders of magnitude lower.

Still much smaller amounts of matter are encountered at the "sub-trace" scale. Here one deals at the most with a few hundred species and frequently much less. The average activity of ^{212}Pb in river water is of the order of 10^{-3} Bq per liter, which means less than 100 atoms per liter. In practice, such highly diluted matter is only revealed by its radioactivity. An example is radon and its short-lived daughters which are found near the surface of the earth at concentrations in the 1 atom per ml-range. This situation is not specific to natural radioactive species, but is also valid for anthropogenic matter, such as disseminated Pu and other actinides and fission products from the nuclear fuel cycle or from events like Chernobyl.

Of course, minute populations may also exist for stable elements and their species on earth and far beyond. For instance, in interstellar space, the density of matter, whether radioactive or not, may be as low as one atom per mL or even less.

In recent years, laser spectroscopic methods have witnessed remarkable achievements in the detection and speciation of a few elements, including actinides, in highly diluted systems (3,4). But it is radiochemistry which is the domain of chemistry at low and ultra-low concentrations. Indeed radiochemists are unwillingly (or unconsciously) confronted with single, or nearly single, atom chemistry. In any population of radioactive atoms there is a moment at which the last surviving atoms are present in strictly denumerable quantities. Likewise, in a radioactive filiation unavoidable transient situations exist in which only a few species of the nascent atoms are present.

Hence a rationale of chemistry at low and ultra-low concentrations relies mainly on radiochemistry. This is well exemplified in Starik's authoritative and encyclopaedic "Principles of Radiochemistry" published in 1959 (5) which is based on data accumulated since the early days of Radioactivity. More recent monographs on the chemistry and on the state of matter at very low concentrations, still in the radiochemist's spirit, include "Radiotracer Techniques and Applications" edited by Evans and Muramatsu (6), "Trace Chemistry of Aqueous Solutions" by Benes and Majer (7) and the two "environmental" oriented books by Das et al. (8-9).

The state of matter at very low concentration in natural aquatic systems

At the trace scale, the solution of a species is not necessarily truly homogeneous and thermodynamically stable, but rather represents a polydisperse system which contains not only simple and complexed ions, but also microparticles of variable dimension. Impurities which would be harmless under ordinary conditions can become overwhelmingly disturbing when their amount exceeds the tracer concentrations by many orders of magnitude. This may account for the erratic behaviour of many radioelements at very low concentration.

Substances at trace concentration can form colloids. This phenomenon was discovered by radiochemists but of course affects stable matter as well. The first mention of the existence of *radiocolloids* was made by Paneth (10) who found that in neutral solutions Bi and Po form colloids, but not Pb.

The presence of colloidal species in a solution of radionuclides is inferred from following observations:

- (i) the radioactive species can be separated from the solution by a physical method like filtration, ultrafiltration, centrifugation, ultracentrifugation.
- (ii) the species do not follow the laws of the behaviour of true solutions when a chemical gradient (diffusion, dialysis, isotopic exchange) or an electric gradient (electrophoresis, electrolysis, electro dialysis) is applied.
- (iii) the adsorption on solid surfaces and the spontaneous deposit differ from those in true solutions.
- (iv) autoradiography reveals the formation of aggregates.

The early work of Paneth was followed by numerous investigations and the introduction of still debated terminologies (7,11). The terms "real colloids" and "pseudocolloids" appeared in the literature. It can be argued that a "colloid is a colloid" and nothing else and is defined in IUPAC's "Compendium of Chemical Terminology" as a "state of subdivision implying that the molecules or polymolecular particles dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1 μm .

The behaviour of radiocolloids should only be discussed with respect to this definition of classical colloids. The microparticles are either inorganic, such as polysilicic acids and their

salts, very sparingly hydroxides like those of Fe^{3+} , aluminosilicates, or organic acids derived from vegetable matter, humic acids etc. which remain in suspension because of their large size. They are found in nearly neutral artificial aqueous solutions, but are much more abundant in natural aquatic systems. Colloids have no well defined absorption spectra.

As an important property, these particles bear "a superficial electric charge, which is often positive at $\text{pH} < 7$ and negative at $\text{pH} > 7$. OH groups and sites suitable for exchange are located at the surface.

With this definition, radioactive tracers have only two ways to achieve a colloidal state: by sorption on a pre-existing colloidal impurity in the solution or by polycondensation (or coprecipitation) of a radioactive monomeric species. It is this duality which lead to the definitions of *pseudo-radiocolloids* - the first type - and *true or real radiocolloids* - the second type. This point has been discussed by Lieser (12, 13) who proposed the more appropriate german (but untranslatable) expressions "Fremdkolloide" and "Eigenkolloide".

The formation of colloids of the first type obviously increases with the concentration of the supporting material. The fixation of a radionuclide on the colloidal support can proceed by physical adsorption, chemisorption or ion exchange. Of course, the observed behaviour represents the property of the support and not that of the radionuclide.

A strong correlation has been observed between the prevalence of radiocolloids and the hydrolysis of the element. Formation of colloids seems to be favoured for heavy elements in high oxidation states. Good examples are provided by polyhydro-xocomplexes and polyacids, which may condense by elimination of water molecules with the formation of oxo bridges, or alternately by electrostatic interactions due to the polarization of the OH bond. The self-condensation rate increases with a higher power of the concentration of the monomeric species (12).and the polymer grows until it reaches the typical colloid size.

For kinetic reasons, the self-condensation can hardly proceed in homogeneous conditions. The first step would involve the encounter of two hydrolyzed radioactive species or at least would require extremely long times, which is not supported by experiment. Hence it must be admitted that radiocolloids are generated in hetero-genous zones in which for some reason the concentration of the radioelements is much higher than in the bulk of the solution. This

could favour the kinetics of processes which may lead to the local supersaturation of some unknown solid phase.

Only hypotheses can be proposed for the origin of the heterogeneous zones. For example, radionuclides situated at the surface of a pseudocolloid could be detached by sputtering ensuing the radioactive recoil of atoms in underlying layers, or desorbed by some other mechanism.

The inevitable and sometimes not detected presence of colloids in trace and sub-trace chemistry explains why literature data are inconsistent and often contradictory. Theoretical analyses of the data are diverse as well. Therefore it is best appropriate, in a first instance, to make abstraction of colloids and to assess the basis of chemistry at very low concentration by considering truly homogeneous solutions. In practice these conditions are realized in a solution sufficiently acid or rich in complexing agents.

A word of caution concerns radionuclides in fission. The chemical effects of radioactive decays have been extensively investigated (e.g. ref. 14) but little attention has been paid to the behaviour of nucleogenic atoms at very low concentration. In the case of a decay, the prominent disintegration mode of many isotopes of heavy elements, including actinides, the main after-effect is the recoil energy of the daughter. It should not be overlooked that the chemical state of an atom projected in water with an initial kinetic energy of about 100 keV may be determined by redox processes at the end of the trajectory. The latter may involve reactive radiolytic species produced by the high-LET particle itself along its path (but the overall radiolysis of the system due to the emitted radiations is of course nil at the concentrations involved), α decay is inherently an oxidative process and one should not be too surprised to find transmutation after-effects in speciation experiments.

Speciation at low concentration

The term "speciation" is a relatively new-comer in the vocabulary of analytical chemistry. It applies to the determination of the chemical forms (species) in which an element is present. By extension it can include the physical support of the species, for instance an aerosol or a colloidal impurity. To underline the importance of speciation by just one example,

environmental plutonium in its oxidation states III and IV is generally retained in soils, while Pu(V) and Pu (VI) are transported by underground waters.

Speciation at low concentration is much more a challenge than elemental analysis which, as said, is feasible down to a few atoms (24). Most techniques employed for the direct characterization of species are limited to concentrations above 10^{-5} M with the notable exception of electrochemical and laser-based methods. The sensitivity of pulse electrochemical techniques for measurement of a multivalent element in a particular oxidation state may be quite acceptable, down to 10^{-8} M or possibly even 10^{-11} M in the case of pulse anodic redissolution. However, the analysis may be perturbed by secondary phenomena, such as redox waves, or the presence of O_2 . Pulsed laser spectroscopies yield useful informations, e.g. for curium in the 10^{-9} M range (3) or uranium in ng amounts (4). However, at the trace and subtrace levels to which the sole access is radioactivity, the emitted radiations do not carry informations on the atomic or molecular environment of the radionuclides. In-situ methods like Mossbauer emission spectroscopy, perturbed angular correlation, measurement of half-lives or $K\alpha/K\beta$ ratios are virtually ruled out for speciation at very low concentrations. Direct structural, thermodynamic and spectroscopic data are not available and the distinction of the various species of an element based on the radiation emitted by tracers is precluded. The methodology relies on the partition or transport methods which lead to the mutual separation of all or of part of the species. In practice, a second phase is opposed to the initial system and the distribution ratio of the sought species between the two phases is measured. This procedure which can no more be viewed as an in-situ technique represents a more or less strong perturbation of the initial system. Nevertheless, experience shows that the method gives satisfactory results in most cases.

As an alternative, a second phase (for example a solid) can be created inside the system. Of course at tracer scale and below, solubility products are no more attained, but they may still be meaningful since, for example, the propensity of an element to form colloids parallels its tendency to form sparingly soluble compounds. The practice of coprecipitating a trace element with a macroscopic support has been widely used as a separation technique since the early days of radiochemistry and general rules governing the incorporation of

radionuclides into carrier compounds have been established since a long time (e.g. ref. 2). More recently it has been proposed that syncrystallisation of a tracer with an isomorphous macroscopic carrier may lead to some information on the nature of a solid compound of the tracer (15).

The partition of a tracer between two phases may be realized in a static or in a dynamic experiment. In the first instance the phases are at rest, while in the second procedure one communicates a relative velocity to the phases. A dynamic partition can be viewed as a succession of many static separations. This is the principle of all chromatographic, thermochromatographic and electrophoretic techniques.

Partition experiments rely on the determination of the distribution coefficient

$$D = c_1 / c_2$$

of the tracer between the phases 1 and 2 and its variation with respect to the concentration of the macrocomponents which define the system. The limit of D is the equilibrium value D_e which is obtained when the chemical potential of the tracer is the same in the two phases. The value D_e contains information on the various species of the tracer in solution and on the equilibrium constant of all possible reactions in which they participate.

It can be shown that at tracer scale it is not necessary to measure equilibrium values of the distribution coefficient because the distribution coefficient D measured at any time t and the derivative dD/dt for time zero are univocally interrelated. An importance consequence is that thermodynamic properties at tracer scale can be obtained for systems which are not at equilibrium (16).

The nature of reactions

A discussion on chemical reactions at very low concentration is meaningful only in so far these reactions are observable. Radioactive matter with extremely short half-lives or reaction rates which would largely surpass the time span of geological events are irrelevant in the context. Thus when dealing with radionuclides, some critical values of radioactive half-life (T), half-time of chemical reaction (τ) and the time t for collecting data fix the range of reactions of interest.

In the following it is assumed that a system contains species at very low concentration and also matter in ponderable amounts. The two components are conveniently termed "microcomponent" and "macrocomponent". The frontier between both is somewhat arbitrarily fixed at $N = 10^{12}$ species per mL

On this basis, the reactions are classified into three types shown in Table 1.

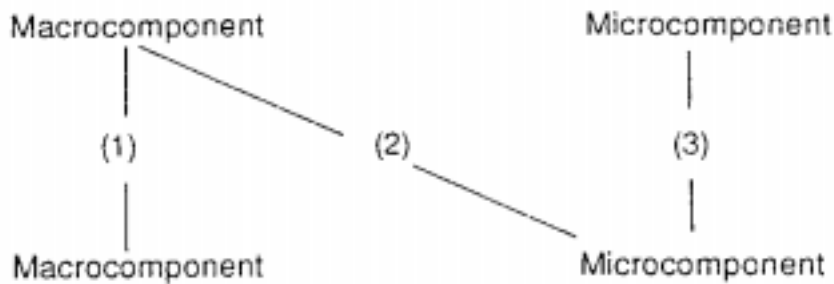


Table 1. Reaction pathways between macroreagents and tracers

- (1) : chemical reactions at ordinary concentrations
- (2) : trace chemistry (radiochemistry)
- (3) : trace and sub-trace chemistry (radiochemistry)

Reactions between macrocomponents (type 1) belong to chemistry at ordinary concentrations and are not further considered here. A reaction of type 3 between two microcomponents is the domain of trace chemistry. They are distinctive in the sense that they must proceed at very slow rates. The cross-combination reactions of type 2 between a macrocomponent and a trace species are not usually considered in traditional chemistry, but occur frequently in radiochemistry,

The reactions can be further classified into two classes, A and B, according to the reaction time available (Table 2).

Type	Reaction time	Examples
A	from a few hours to several years	chemistry in the laboratory naturally occurring reactions
B	from a few years to millions of years	geochemical reactions space chemistry

Table 2. Classification of reactions as a function of the reaction time available

Class A embraces the usual reactions performed in the laboratory for which the time t is typically between, say, a few minutes and several months, and the natural reactions which may occur over several years. In class B, the reactions extend over very large time scales, which may be millions of years. This case is met on geochemical processes on earth or in space and in interstellar chemistry.

With this classification it is possible to distinguish observable and observed reactions. The important parameters are the reaction time and the number of microcomponent species.

Reactions 3 A between radioactive microcomponents are generally not observable in the laboratory because of kinetic hindrance, despite the high sensitivity of radiation detection. Clearly, these reactions are still less amenable to observation when they concern stable elements.

On the other hand, 3 B reactions, when they are completed, can be observed since the reaction time (and necessarily the half-life of the tracers) are much in excess over the reaction half-time. When the microcomponents are radioactive, the observation during a time t (which can be rather long) can be performed on systems of limited spatial expansion, like natural ones.

The reactions 2 A and 2 B between a micro- and a macrocomponent are always kinetically allowed and are observable and observed. The progress of the reaction and the equilibrium state must be recorded from the change in the concentration of the radioactive microcomponent. These reactions are very numerous. All anthropogenic and natural reactions which control the behaviour of radionuclides, whether artificial or not, belong to this type. They intervene in the atmosphere, geosphere and in all living species.

Kinetics at tracer scale (17)

In a reaction between a macroreagent and a trace species, the consumption of the former is negligible; hence its concentration is constant and equal to the analytical concentration. In addition, all reactions of the trace species are of pseudo-first order with respect to the macrocomponent. The advancement of the reaction must be followed by measuring the

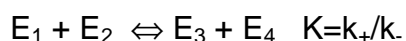
change of the concentration of the microreagent, which is easily achieved if the latter is radioactive. This practice is typical of trace chemistry.

Reactions between microcomponents at the trace level are kinetically hindered because the probability of encounter between two microspecies is low. Intuitively, there should exist some limiting concentration below which such reactions are no more observed in the laboratory where experiments are seldom conducted on time scales exceeding one year. On the other hand, on the very long time scales prevailing in geochemistry or in interstellar space, reactions between microcomponents are no more necessarily precluded. The advancement of reactions of this type depend more on the concentration of the reacting species than on the chemical half-time. Reactions of natural or artificial radionuclides which have developed over a long time may be observable (however, the available reaction time for the latter does not exceed 50 years, i.e. the historical age of nuclear industry) .

The mechanisms of reactions, with a given stoichiometry, are rarely known at ordinary concentrations. When the reagents are at tracer concentration, the discussion of the kinetics is even more difficult.

It is assumed that the mechanism involves one slow rate-determining step. If the latter is of first-order, the microcomponent disappears at the same rate whatever its concentration, and the overall rate does not change in the course of the reaction.

The case of a second-order determining step is much more relevant in the present context. Let us consider two trace species E_1 and E_2 which participate in a process for which all stoichiometric coefficients are equal to one:



With decreasing concentrations, the probability of encounter between E_1 and E_2 decreases, and accordingly also the velocity of the reaction. This can be expressed more precisely by calculating the half-time of the reaction as a function of the initial concentrations E_1^0 and E_2^0 . The general expression of 1: is rather complicated. Here we consider only the very simple case corresponding to following conditions:

$E_1^0 = E_2^0 = C_0$ and k_+ (forward reaction) $\gg k_-$ which leads to

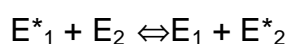
$$T \approx 1/(k_+ \times C_0)$$

The half-time of the reaction increases rapidly when the concentration E_1 and E_2 decrease. The diminution of E_1^0 and E_2^0 by a factor 10^n leads to a 10^n -fold increase of τ . A decrease from 10^{-12} M to 10^{-16} M increases the half-time by a factor 10^4 , e.g. from one hour to more than one year. It follows that

- (i) the slow rate-determining step can prevent the reaction if the value of n is high enough
- (ii) a reaction which is fast at ordinary concentrations may become very slow at the trace level.
- (iii) the reactions (type 3 A) between two radionuclides at trace level or between a trace and a microcomponent impurity, in general, cannot be observed in ordinary laboratory conditions. Hence the reagents coexist in the form in which they have been introduced in the solutions. However, 3 B reactions, can be observed, provided the half-lives are sufficiently long.
- (iv) all non-colloidal species containing radionuclides at trace level are monomeric, with the possible exception of natural species of very long-lived radionuclides

Two specific cases will be considered: an isotopic exchange reaction and the disproportionation of a multivalent element.

a) The kinetic of an isotope exchange reaction (neglecting isotope effects) between two species such as

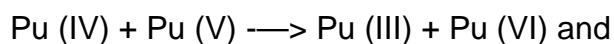


where $*$ denotes a radionuclide, is often a second order process and the half-time of the exchange is given by

$$t = \ln 2 / (c_1^0 + c_2^0)k$$

It follows that an isotope exchange reaction of type 3A between the species e^- and Eg at trace level is not observable; equilibrium may possibly be established over geological times only (reaction 3B). This conclusion is relevant in particular to actinide elements: the exchange between $Np(IV)$ and $Np(V)$ which is observed at ordinary concentration ceases at trace level..

b) Another case of interest are the redox or self-redox reactions of heavy elements such as



This latter disproportionation reaction is a special case of a reaction between microcomponents, with $E_1 = E_2$. The derivation of x is somewhat complicated; it is found to be proportional to c^{-1} .

Hence disproportionation of a radioelement is excluded for traces. Oxidation states which are unstable with weighable amounts of radioelements can exist at very low concentration.

Finally, the only kinetic data available at tracer scale are those related to the reaction of the tracer with a macrocompound.

Thermodynamics at the trace scale

Thermodynamics of trace chemistry does not pose a particular problem. At concentrations down to 10^{-16} M the law of mass action can be derived and applied without restriction in reactions involving trace concentrations (provided, of course, the reactions be kinetically allowed). The partition function of a species can still be expressed with the Stirling approximation and the free enthalpy and chemical potentials describing the equilibrium state are established in the usual way.

Chemistry at the sub-trace level.

A peculiar situation arises at the extreme dilutions when the number of available species decreases below one hundred. As indicated previously, this is not a purely intellectual game because such extremely low concentrations are encountered. Probably no more than a few papers have previously dealt with this question (18-19). However, in relation to the discharge of actinides in the environment, the chemical behaviour of matter in such exceptional conditions has been reconsidered and the validity of the usual chemical concepts has been questioned

Sub-trace chemistry deals at the most with only several hundred species and frequently with much less, the ultimate limit being one single atom.

The thermodynamics at sub-trace scale haven been developed recently (20-23). It can be shown that when the Stirling approximation fails (in other words, when the population of

species can no longer be treated as a continuous variable, a situation prevailing for less than about 100 items) the law of mass action must be expressed in terms of the average number N' of reacting species. The latter is calculated

from the canonic probability P for realizing the microstates of the system, set up in terms of the exact, but strictly limited, values N :

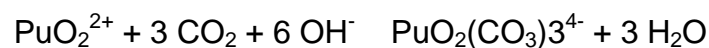
$$N' = \sum PN$$

the summation being performed over all possible discrete values of N . With increasing number of species, the equilibrium constant K computed with the average populations tends toward equality with the constant K calculated in the classical way. Hence the peculiar behaviour of the species at sub-tracer scale can be expressed by the ratio

$$\rho = K' / K$$

which becomes equal to unity when the classical description applies.

This scheme had been applied to a variety of reactions described in reference 22. It is found that for all reactions between a microcomponent at sub-tracer level and a macrocomponent, the ratio $\rho = 1$, whatever the number of reacting species, provided all stoichiometric coefficients of the microcomponent are equal to one. Hence the behaviour of a few Pu atoms with respect to complexation, e.g. by carbonate, is on the average the same at sub-trace level. A typical reaction is



For all other reactions, including dimerisation or disproportionation, the ratio ρ is a function of the reacting species and must be calculated for each specific case.

The experimental verification of the theoretical predictions lies still very far ahead. The number of radionuclides required for registering an activity of one disintegration per min. is related to the half-life T (in s) by $T = 42 N$. This figure corresponds, for

instance, to 1.8×10^{10} atoms of ^{239}Pu , 9 orders of magnitude above sub-trace populations.

A one hundred population would be available for a half-life of one hour, which is by far too short to allow the completion of the equilibrium.

It must be concluded that at the present time, the sub-trace behaviour of matter is still speculative. But at least it has the merit to pose the problem of chemistry at the single atom level.

In conclusion, it must be emphasized that with its specific methodology and the unique sensitivity of nuclear detection, radiochemistry is particularly suited as a tool for chemistry at very low concentrations. In addition, the concepts of radiochemistry are not restricted to radioactive species, but apply as well to micro-amounts and sub-micro-amounts of stable matter.

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