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Abstract

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PHYSICAL CHEMISTRY

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IN THE TRACER-ATOM METHOD

It is known that, for the study of isotopic exchange and of the mechanism of certain chemical reactions, the method of “labeled” atoms is at present widely used (¹). Both radioactive and stable isotopes are used as “labeled” atoms, and the analysis of the presence of an isotope in a given compound is carried out by means of radiometric methods of investigation, or by means of mass-spectrometric methods or IR spectra. In all cases, in order to study the mechanism of formation of various products of chemical reactions, it is necessary to separate these products from the reaction mixture and to establish in which of the products the “labeled” atoms are contained.

The Mössbauer effect opens up a new possibility—to use Mössbauer isotopes as “labeled atoms” for studying the mechanism of the course of various chemical reactions, for isotopic analysis of reaction products, and also for other investigations (²), while the effect of resonance scattering or absorption of gamma quanta without recoil is used as the analyzer. In this case, in a number of instances the tasks listed can be solved even without isolating the compounds from the reaction mixture, since the NGR spectrum carries not only quantitative but also qualitative information, i.e., it indicates how much of the Mössbauer isotope is contained and in which compound.

The basic idea of the method consists in the fact that, in succession, each of the components interacting with one another in the complex system under investigation (i.e., a system multifunctional with respect to the element being studied) is enriched beforehand with the “Mössbauer” isotope of the element contained in it (for example, Fe⁵⁷, Sn¹¹⁹), introduced in this way into the system in a specified chemical state, and then the change in the NGR spectrum of the products of the interaction, caused by such enrichment, is studied in comparison with the analogous spectrum for the natural isotopic composition of the initial components.

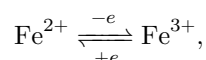
Figure 1

Figure 1: Figure 1

The proposed technique, in its various variants, may prove especially fruitful in the study of rapid oxidation-reduction processes or isotopic exchange, and also for investigations of chemical processes at low temperatures. Let us give several examples of possible application of this technique.

The possibility arises of studying electron exchange in systems containing iron. The simplest such reaction is the reaction of electron exchange between Fe^{2+} and Fe^{3+} ions. In the works of Siborg (³), rapid electron exchange between Fe^{2+} and Fe^{3+} ions was detected; however, when a chemical method for separating the products was used, the actual results could have been distorted (⁴).

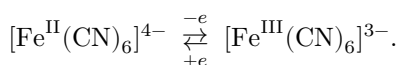
Van Alten and Rice (⁵), studying electron exchange



used a diffusion separation technique based on a very small difference in the diffusion rates of Fe^{2+} and Fe^{3+} ions. They succeeded in detecting slow electron exchange in a 3 N HClO_4 solution.

Meanwhile, owing to the strong difference between the nuclear gamma-resonance (NGR) spectra for Fe^{2+} and Fe^{3+} ions (²), the proposed method makes it possible easily to observe the weakening of the singlet line of Fe^{3+} and the growth of the intensity of the doublet spectrum of Fe^{2+} , if Fe^{3+} ions enriched in Fe^{57} are taken as the initial ions. In this case this process can be studied over a broad temperature range, including in the solid frozen state.

In (^{6,7}) electron exchange in the following systems was investigated:



Chemical methods of investigation make it possible to carry out separation in a time of ~ 2 min, but in doing so they themselves can induce electron exchange. Physical methods, for example diffusion or electrophoresis, require a much longer separation time (10–15 min). The authors of (^{6,7}) found that electron exchange occurs rapidly, but quantitative information could not be obtained. The use of the Mössbauer method, which makes it possible to dispense with ion separation, would provide substantial assistance in this case as well.

Fig. 1. *a*—velocity spectra of a solution containing Fe^{3+} ions enriched in Fe^{57} ; *b*—velocity spectrum of a solution containing Fe^{2+} ions with the natural content of Fe^{57} ; *c*—velocity spectrum of a solution obtained by mixing solutions (*a* and

b), frozen a few minutes after mixing; *d*—velocity spectrum of a solution obtained by mixing solutions (*a* and *b*), frozen 12 h after mixing.

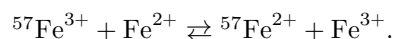
As an example demonstrating the application of the proposed method, we carried out qualitative experiments to investigate electron exchange between Fe^{2+} and Fe^{3+} ions in a medium containing Cl^- and SO_4^{2-} ions at $\text{pH} \sim 1$.

The NGR spectra of the samples studied were recorded on a 500-channel gamma-resonance spectrometer of electrodynamic type ⁽⁸⁾. Co^{57} , diffused into chromium, served as the source of resonant quanta. All spectra were recorded at the temperature of liquid nitrogen. The data are given in Fig. 1 and in Table 1.

The initial systems were a solution containing 8 mg of Fe^{3+} ions enriched to 60% with the isotope Fe^{57} (the spectrum of Fe^{3+} ions in solution is shown in Fig. 1a), and a solution containing 12 mg of Fe^{2+} ions with the natural content of Fe^{57} (Fig. 1b). The initial solutions were then poured together into one cuvette, thoroughly mixed, and frozen at 80°K. The whole procedure took several minutes.

The spectrum of the mixture of divalent and trivalent iron in solution is shown in Fig. 1c. We see that the spectral parameters are characteristic of Fe^{2+} ions; moreover, the intensity of the lines in the spectrum is much greater than for the initial

solution of Fe^{2+} . This indicates an increase in the number of Fe^{57} atoms in the form of Fe^{2+} ions owing to the occurrence of the electron-exchange reaction



The Fe^{3+} line is very weakly visible in the spectrum because of the small *f* for the Fe^{3+} ion in solution and the great extent of electron exchange.

Figure 1e shows the spectrum obtained after the solution had been kept for 12 hours. A certain additional increase in the intensity of the Fe^{2+} lines indicates that in the first case exchange had occurred, although to a great extent, but not to completion.

Table 1

Parameters of the NGR spectra

No.	Sample	δ (mm/sec)	$\Delta\xi$ (mm/sec)	<i>f</i> (rel. units)
1a	$^{57}\text{Fe}^{3+}$ in solution	0.76	0	1
1b	Fe^{2+} in solution	1.58	3.09	2.7

No.	Sample	δ (mm/sec)	$\Delta\xi$ (mm/sec)	f (rel. units)
1c	$^{57}\text{Fe}^{3+} \xrightleftharpoons[-e]{+e}$ Fe ²⁺ in solution	1.58	3.0	1.6
1d	$^{57}\text{Fe}^{3+} \xrightleftharpoons[-e]{+e}$ Fe ²⁺ in solution	1.58	3.09	1.8

The NGR line of the Fe³⁺ ion lies to the right of the left-hand line of the Fe²⁺ ion doublet, partially overlapping it; therefore the shape of the left-hand peak may be substantially distorted by the admixture of the Fe³⁺ line.

The spectrum was recorded over two hours, and in the case of 1c the shape of the left-hand line of the doublet, when observed on the oscilloscope 15 min after the start of the run, was strongly distorted; on the right a noticeable admixture line was observed, whose relative contribution had decreased substantially by the end of the experiment. This apparently indicates the occurrence of electron exchange in the frozen solution at 80° K.

To study such processes it is necessary to increase substantially the speed with which the spectrum is obtained; this can be achieved by increasing the intensity of the source and improving the geometry of the setup. The use of more intense sources and spectrometers with constant velocities, and the carrying out of measurements at the 10-20 points of the NGR spectrum most important for the study of the process, will apparently make it possible to perform the necessary measurements within several minutes.

The experiments carried out confirm the high effectiveness of the proposed method for investigations of electron- and isotope-exchange reactions. They show that, in the system considered, electron exchange between Fe²⁺ and Fe³⁺ ions proceeds rapidly, but at a fully measurable rate.

In the future we intend to use the method described above for a quantitative study of the kinetics and mechanism of reactions involving Fe²⁺ and Fe³⁺ ions, and complex and organometallic compounds of iron.

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