

Radioactivity
Applied to Chemistry

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PREFACE

During and after World War II an increasingly large number of chemists were becoming interested in the applications of radioactivity to chemistry. Many of them probably felt, as did the contributors to this book, that they were unfamiliar with much of the earlier work extending back to the discovery of radioactivity. For some phases there existed excellent reviews and collections, including G. Seaborg's (S18) review of the applications of artificial radioactivity up to 1940, O. Hahn's (H3) discussion of work with naturally occurring radioactive substances carried out in the Kaiser Wilhelm Institute for Chemistry in Berlin-Dahlem up to 1934, and still earlier monographs by K. Fajans (F5) and F. Paneth (P4). However, these were all of limited scope, and much information remained uncollected and, in 1947, unknown to us. In an effort to correct this situation, an exhaustive literature search was undertaken.

Our purpose in writing this book has been to make the results of our literature search available to others. In an effort to accomplish this purpose effectively, we have divided the book into two parts. In Part I, consisting of ten chapters, we have tried to acquaint the reader with the nature of the contributions that have been made to various branches of chemistry through the application of radioactivity. Numerous illustrative examples from the literature are included, and we have pointed out both the possibilities and the limitations of the various applications. In Part II, consisting of eighteen extensive tables arranged according to subject, we have furnished the reader with a summary of and a key to the literature concerning these applications. Most of the summary tables list data that are representative of information reported in designated publications. A few tables, for practical reasons, merely indicate the nature of the work reported. The order, subject matter, and numbers of the tables correspond to those of the chapters. No table corresponding to Chapter 7, "Radioactivity Applied to the Discovery and Investigation of the Newer Elements," is included in Part II because it was considered more convenient, for both reader and author, to include the results of the literature search in the text of that chapter.

Except for a few minor limitations stated in the introductions to several tables in Part II and in the discussions of neptunium and plu-

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onium chemistry in Chapter 7, we have attempted to include summaries of and references to all applications of radioactivity to chemistry published and available by January, 1950. We have not summarized other aspects of radiochemistry, radiochemistry being defined as chemical work with radioactive materials. Thus, we have excluded topics such as radiochemical techniques, the preparation of tagged compounds, and the isolation of radioactive nuclides by use of isotopic carriers (either for use as tracers or for the determination of radioactivity in connection with studies of nuclear reactions). Radiation chemistry and the isotope effect are discussed briefly, but the literature on these subjects is not summarized. As the title of this book indicates, applications of stable tracers are not included. (Table 4A, the summary of self-diffusion coefficients, is an exception.) We regret this rather arbitrary omission of much useful tracer data, but some limit on the scope of the book had to be set. As it is, the preparation of the book has required several years more than was originally anticipated.

The search of the literature was conducted essentially independently by each compiler. In general, references were first obtained from reviews and compilations in existence at the time and from Chemical Abstracts and Abstracts of Declassified Documents. Papers located by these means were abstracted, and any additional references found in the papers were looked up. In this way work on a specific subject was followed back to its origin. Later, when P. Süe's (S101) listing of papers concerned with applications of artificial radioactivity (1934-1947) and the United Nations' (U6) bibliography of the applications of radioactive tracers in the non-biological sciences (1923-1948) became available, these compilations were checked against our bibliography. The few additional articles thus found were abstracted. During the years the book was being written and edited, we attempted to keep the material up to date by following the current issues of Chemical Abstracts, Abstracts of Declassified Documents, or Nuclear Science Abstracts, and a number of the more common chemical journals. Journals concerned principally with biochemistry, biology, geology, metallurgy, engineering, physics, and other fields related to chemistry were not followed. As a result we may have overlooked chemical tracer studies reported in such journals, particularly when the tracer study was not a main topic of an article. The inclusion or omission of work lying near the diffuse boundary between these fields and chemistry has necessarily been somewhat arbitrary. Abstracting was discontinued in January, 1950, after the December, 1949, issues of the American journals had been examined. (At this time the late 1949 issues of foreign journals were not available.)

Some information that became available later is included, but no attempt has been made to include all or even most of such material.

This book has been written for the reader with a good knowledge of chemistry but not necessarily more than an elementary knowledge of radioactivity. It is intended primarily as a reference book, but can be used, as it is at Washington University, as the text for graduate and senior undergraduate courses in applied radiochemistry. The material supplements that presented in Friedlander and Kennedy's *Introduction to Radiochemistry*; it emphasizes the chemical rather than the nuclear aspects of the subject. Washington University offers two radiochemistry courses, an introductory course in which the Friedlander-Kennedy book is used as the text, and a seminar-type course in which this book is the text. Neither course is a prerequisite for the other, although radiochemistry majors, who take both courses, normally take the introductory course first. It may be of interest to note that this book had its beginning in the first such seminar, conducted in 1947 at Washington University, in which all the contributors except Professors Bonner and Garner were participants.

Considerable effort has been directed towards the preparation of an integrated book with reasonably uniform organization, terminology, and general style. The presence of most of the contributors at Washington University during the literature search and preparation of the first rough manuscript was a great help because information could be integrated and discrepancies resolved through personal discussions. We have attempted to use a self-consistent set of symbols and abbreviations throughout, and these are listed at the front of the book. We have tried also to be consistent in the use of half-life values. These values, as well as other nuclear properties of a number of useful radioactive tracers, including those used in researches summarized in this book, are given in Appendix VI. All references to the literature are denoted by numbers keyed to the bibliography. The index is for the material in Part I, and only the general topics summarized in the tables in Part II are listed.

I gratefully acknowledge the whole-hearted cooperation of the contributors not only in making their own contributions but also in discussing the contributions of others. I am deeply indebted to Professor Norman Bonner, the assistant editor, for his invaluable assistance and advice. I thank Adela Bonner, Mary Wahl, and the wives of the contributors for their aid in preparing the manuscript and in proof-reading. I should also like to express my appreciation to Dr. G. Friedlander and Professors J. W. Kennedy, C. D. Coryell, J. W. Irvine, Jr., and M. D. Kamen for examining the manuscript and offering many

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ARTHUR C. WAHL

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SYMBOLS AND ABBREVIATIONS

A	Amount of radioactivity.	en	Ethylenediamine.
A	Mass number;	equil.	Equilibrium.
	Arrhenius constant.	equiv.	Equivalent.
a	Constant.	erf	Error function
Å	Angstrom (10^{-8} cm).		$\left(\operatorname{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-t^2} dt \right)$
Ac⁻	Acetate ion ($C_2H_3O_2^-$).		
ads.	Adsorb, (ed), adsorption.		
a.l.	Atomic or molecular layers.	ev	Electron volt (1 absolute-ev/molecule = 23,052 g-cal/mole).
alk.	Alkaline.		
amt.	Amount.	evap.	Evaporat(e), (ed), (ion).
(aq)	Aqueous phase.	ext.	Extract, (ed), (ion).
aq.	Aqueous.	F	Fraction exchange;
at.	Atomic.		Faraday constant (96,487 absolute coulombs/g-equiv.);
A.W.	Atomic weight.		Magnitude and direction of diffusional flow.
b	Constant.		
C	Concentration.	F	Free energy;
c	Velocity of light (2.998×10^{10} cm/s).		Partition function.
cal	Gram calorie.	f	Gram formula weight per liter.
c.d.p.	Critical deposition potential.		
conc.	Concentration;	Fis.	Fission.
	Concentrated.	G	Constant;
coppt.	Coprecipitat(e), (ed), (ion).		Number of molecules reacted or produced per 100 ev.
D	Homogeneous distribution coefficient of tracer between solid and solution.	(g)	Gas phase.
D	Diffusion coefficient.	H	Heat content.
D	H ² atom (deuterium).	h	Planck's constant (6.624×10^{-27} erg second).
d	H ² nucleus (deuteron).		
d	Day.	h	Hour.
daut.	Daughter, (s), [radioactive decay product, (s)].	IT	Isomeric transition.
		K	Equilibrium constant;
dil.	Dilute.		K-electron or other orbital-electron capture.
dipy	α, α' -dipyridyl.	k	Boltzmann's constant (1.3805×10^{-16} erg/degree).
dis.	Dissolve, (d).		
dist.	Distill, (ed), (ation).	k	Specific rate constant.
E	Oxidation potential;		Thousand electron volts.
	Emanating power.	kev	
E	Energy.	l	Length.
e⁻	Electron.		
e	Electronic charge (1.602×10^{-10} absolute coulomb).	(l)	Liquid phase.
		ln	Natural logarithm.

log	Common logarithm.	S	Entropy;
M	Number of molecules.		Area.
M	Mass of atom or molecule.	s	Atomic stopping power relative to air.
m	Electron mass (5.486×10^{-4} atomic weight units).	s	Second.
m	Mass of a particle (p , n , etc.).	(s)	Solid phase.
m	Minute.	sat.	Saturat(e), (ed), (ion).
ma	Milliampere.	sens.	Sensitivity.
meas.	Measurable.	soln.	Solution.
Mev	Million electron volts.	supersat.	Supersaturat(e), (ed), (ion).
mmole	Millimole.	supnt.	Supernatant solution.
mole	Gram molecular weight (6.023×10^{23} molecules).	T	Absolute temperature.
$M.W.$	Molecular weight	T	H^3 atom (tritium).
N	Avogadro's number (6.023×10^{23} molecules/mole).	t	Time.
N	Number of atoms, molecules, or ions.	$t_{\frac{1}{2}}$	Half-time;
n	Mole fraction	temp.	Half-life.
n	Number of equivalents.	TTA ⁻	Temperature.
n	Neutron;	u	Thenoyltrifluoroacetone ion.
	Force index.		Electrical mobility of an ion.
Nat.	Occurs in nature.	V	Volume.
no.	Number.	v	Velocity.
P	Probability factor.	v	Volt.
p	Proton;	vol.	Volume.
	Pressure.	W	Total energy (includes rest mass).
p_i	Momentum of particle i .	wf	Gram formula weight per 1000 g of water.
pn	Propylenediamine.	wt.	Weight.
ppt.	Precipitat(e), (ed), (ion).	x	Variable.
prefd.	Preformed.	y	Variable.
py	Pyridine.	y	Year.
ppm	Parts per million.	Z	Collision number.
Q	Heat of nuclear reaction.	Z	Atomic number.
Q	In the expression	\underline{Z}	Charge on an ion.
	$E = E^0 - \frac{RT}{nF} \ln Q.$	z	Variable.
		α	Alpha particle;
R	Reaction rate;		Fine structure constant.
	Range of alpha particle or recoil atom.	β	Beta particle (β^- or β^+).
R	Gas constant (1.9864 g-cal degree ⁻¹ mole ⁻¹).	γ	Gamma ray.
r	Radius vector.	Δ	Heat.
r	Radius.	δ	Energy of pairing nuclear spins.
red.	Reduc(e), (ed), (tion), (ing).	ϵ	Energy.
ref.	Reference.	ζ	Bond energy.
r.h.	Relative humidity.	η	Coefficient of viscosity.
rm.	Room (used as rm. temp.).	θ	Angle.
S	Specific activity.	λ	Decay constant;
			Equivalent conductance of an ion.

λ	Logarithmic distribution coefficient of tracer between solid and solution.	ϕ	Phenyl radical.
		ω	Initial velocity of separation.
		$?$	Uncertain.
μ	Micro-;	$*$	An asterisk after the symbol of an element indicates the element is tagged (i.e., some of the atoms are radioactive).
	Micron;		
	Reduced mass, $(M_1 \times M_2)/(M_1 + M_2)$.		
μ	Absorption coefficient.		
ν	Frequency.	$'$	A prime after the symbol of an element indicates all the atoms of that element are radioactive.
π	3.1416.		
ρ	Density.		
σ	Electrical conductivity.		
σ	Cross section for a nuclear reaction;	\sim	Approximately.
	Mean collision diameter.	(A) or [A]	Concentration of A in moles or equivalents per liter.

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PART I

INTRODUCTION

Survey of Applications of Radioactivity. Most of the applications of radioactivity to chemistry are based on two characteristics of radioactive atoms. (1) *Before a radioactive atom decays its chemical behavior is essentially the same as that of other atoms isotopic with it.* (2) *When a radioactive atom does decay it emits energetic radiation that may be detected.* Thus the fate of radioactive atoms in a chemical reaction may be determined by radioactivity measurements. Because of the essential identity in the chemical behavior of isotopes,¹ it may be quite accurately inferred that other isotopic atoms originally in the same chemical form as the radioactive atoms suffered the same fate. This *tracer* (or *indicator*) *method* is probably the most widely used application of radioactivity to chemistry. The tracer method as applied to isotopic exchange reactions, chemical kinetics, structural chemistry, self-diffusion studies, and analytical chemistry is discussed in Chapters 1 through 5.

The very high efficiency with which the energetic radiations emitted by radioactive atoms may be detected makes possible the estimation of very small amounts of radioactive material. For example, as little as 10^{-16} gram of 8.0-day I^{131} may be easily detected with a Geiger counter. This high sensitivity makes possible the study of extremely small amounts of material (Chapter 6) and has led to the discovery of fifteen previously unknown elements (Chapter 7).

Newly formed products of nuclear reactions are usually in highly excited chemical states. If the products are radioactive, information concerning their behavior may be obtained even though the amounts of such products are too small for detection by chemical or spectrographic methods. This subject is discussed in Chapter 8. If the radioactive product of a nuclear reaction is an inert gas, so that there is little doubt about its chemical form, information concerning the solid material in which the nuclear reaction occurred may be obtained from studies

¹ As originally defined, **isotopes** are atomic species of the same atomic number but different mass numbers. The word *isotope* is also commonly used in a broader sense to designate a particular atomic (or nuclear) species. T. Kohman (K87) has suggested the word **nuclide** for this latter usage.

of the escape of the inert gas from the solid (Chapter 9). The estimation of the extent of the solid surface by this emanation method and by tracer adsorption methods is discussed in Chapter 10.

Two general limitations on the applications of radioactivity to chemistry should be considered, though for most work they are unimportant. The limitations are: (1) The energetic radiation emitted by radioactive atoms may appreciably alter the system under study. (2) The difference in the chemical behavior of isotopes may be sufficiently great to affect the experimental results.

In passing through matter the radiation emitted by a radioactive substance dissipates most of its energy by exciting and ionizing molecules along its path. These excited molecules and ions may participate in reactions that are not possible for unexcited molecules in the system. The study of these radiation-induced reactions is called *radiation chemistry*. Although a detailed discussion of this interesting and important field is beyond the scope of this book, a brief discussion is included at the end of Chapter 8 because of the possible importance of radiation chemistry in any chemical study involving radioactive atoms. In general, experiments at low levels of activity (~ 1 microcurie) are relatively free from radiation-induced side reactions because of the low efficiency with which the energy is normally utilized (~ 1 reaction per 100 ev absorbed). However, when high levels of activity are employed the radiation-induced reactions may become important not only in the system under study but also in the experimenter studying the system. Under such conditions the experimenter must make allowances for these radiation effects and take precautions to safeguard his own health. Some useful references concerning health protection are N30, T17, M67, L54.

The Isotope Effect. It is well known that there are no qualitative differences in the chemical behavior of isotopes. Also for most purposes quantitative differences may be ignored. The almost constant isotopic composition of the elements in the earth's crust and the difficulty of isotope separation by chemical methods indicate the smallness of the isotope effect. However, isotopes of the lightest elements have been at least partially separated by chemical methods, and the isotope effects have been measured for various reactions of these elements. Therefore the isotope effect should be considered when radioactive isotopes of the lightest elements are used as tracers.

Differences in the chemical behavior of isotopes due to differences in mass are predicted from quantum theory, and for a number of reactions these theoretically predicted differences have been checked by experiment. The mass of the atoms in a molecule should affect both the

velocity and vibrational energy of the molecule. If isotopic molecules² at the same temperature are considered, the heavier molecules have the lower velocity and therefore suffer fewer collisions. This effect is proportional to the square root of the ratio of the masses of the molecules. The heavier molecules also have less vibrational energy than the light molecules, and therefore require more energy for dissociation. Except for the hydrogen isotopes, these energy differences are small, and if only the equilibrium distribution of isotopes between several molecular species is of interest even the small energy differences are partially canceled because they are operative in the same direction in all molecules. Therefore the equilibrium distribution of isotopes (other than those of hydrogen) among several molecular species is nearly random. Table 1 shows for several exchange reactions how far the true equilibrium distribution deviates from a purely random one.

TABLE 1
EQUILIBRIUM DISTRIBUTION OF ISOTOPES

Exchange Reaction	$(K/K')_{298.1}^a$
$\text{HT} + \text{H}_2\text{O} = \text{H}_2 + \text{HTO}$	6.194
$\text{HD} + \text{H}_2\text{O} = \text{H}_2 + \text{HDO}$	3.703
$\text{HCl} + \text{DI} = \text{DCl} + \text{HI}$	1.527
$\text{C}^{13}\text{O}_2 + \text{C}^{12}\text{O}_3 = \text{C}^{12}\text{O}_2 + \text{C}^{13}\text{O}_3$	1.012
$\text{HCN}^{15} + \text{N}^{14}\text{H}_4^+ = \text{HCN}^{14} + \text{N}^{15}\text{H}_4^+$	1.038
$\text{CO}^{16} + \text{H}_2\text{O}^{18} = \text{CO}^{18} + \text{H}_2\text{O}^{16}$	1.036
$\text{Cl}^{35}\text{Cl}^{37} + \text{Cl}^{35}\text{O}_3^- = \text{Cl}_2^{35} + \text{Cl}^{37}\text{O}_3^-$	1.04
$\text{Br}^{79}\text{Br}^{81} + \text{Br}^{79}\text{O}_3^- = \text{Br}_2^{79} + \text{Br}^{81}\text{O}_3^-$	1.008
$\text{I}^{127}\text{I}^{129} + \text{I}^{127}\text{O}_3^- = \text{I}_2^{127} + \text{I}^{129}\text{O}_3^-$	1.002

^a K is the true equilibrium constant calculated from Urey's (U1) summary of partition functions. K' is the equilibrium constant calculated for random distribution of the isotopes.

Isotopic molecules are also expected to undergo chemical transformations at different rates. Nearly always the heavier molecule will react more slowly than the light molecule, partly because it undergoes fewer collisions and partly because more energy is required to excite it to the activated transition state. The atoms in an activated transition state are less tightly bound than those in the reactants, and the differences between the energy levels of the heavy and the light molecules are smaller. In the limit, when the atoms are free, there are no energy differences. Therefore the maximum isotope effect in rate processes will be observed when the tracer atom is firmly bound in the reactant molecule and is free in the transition state (B84). J. Bigeleisen (B79,

² Isotopic molecules are molecules that are identical in chemical and structural formulas but differ in their isotopic composition.