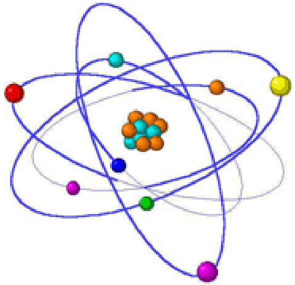
Radioisotope and Radiation Applications (FS2013)



Radiochemistry Applications (Week 7a)

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19.11. 2013

Radiochemistry Applications: Outline

Lecture 1

- ❑ Introduction
- ❑ Radionuclides are a Part of Nature
- ❑ Radioelements
- ❑ Radioanalysis
  - Analysis based on inherent activity
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  - Radiotracer applications:
    - Chemical equilibria and bonding
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- ❑ Emanation Techniques

Lecture 2

- ❑ Isotope Dilution Analysis (IDA)
  - Direct IDA
  - Variants of IDA
  - Radiometric methods
- ❑ Idea of the PROTRAC Facility at PSI
- ❑ Transuranium (TU) and (Superheavy) elements
  - Introduction
  - Production of TU elements
  - Production of superheavy elements
- ❑ Summary

Introduction

❑ **Nuclear and Radiochemistry** are the branches of chemistry dealing with the properties of radioactive matter:

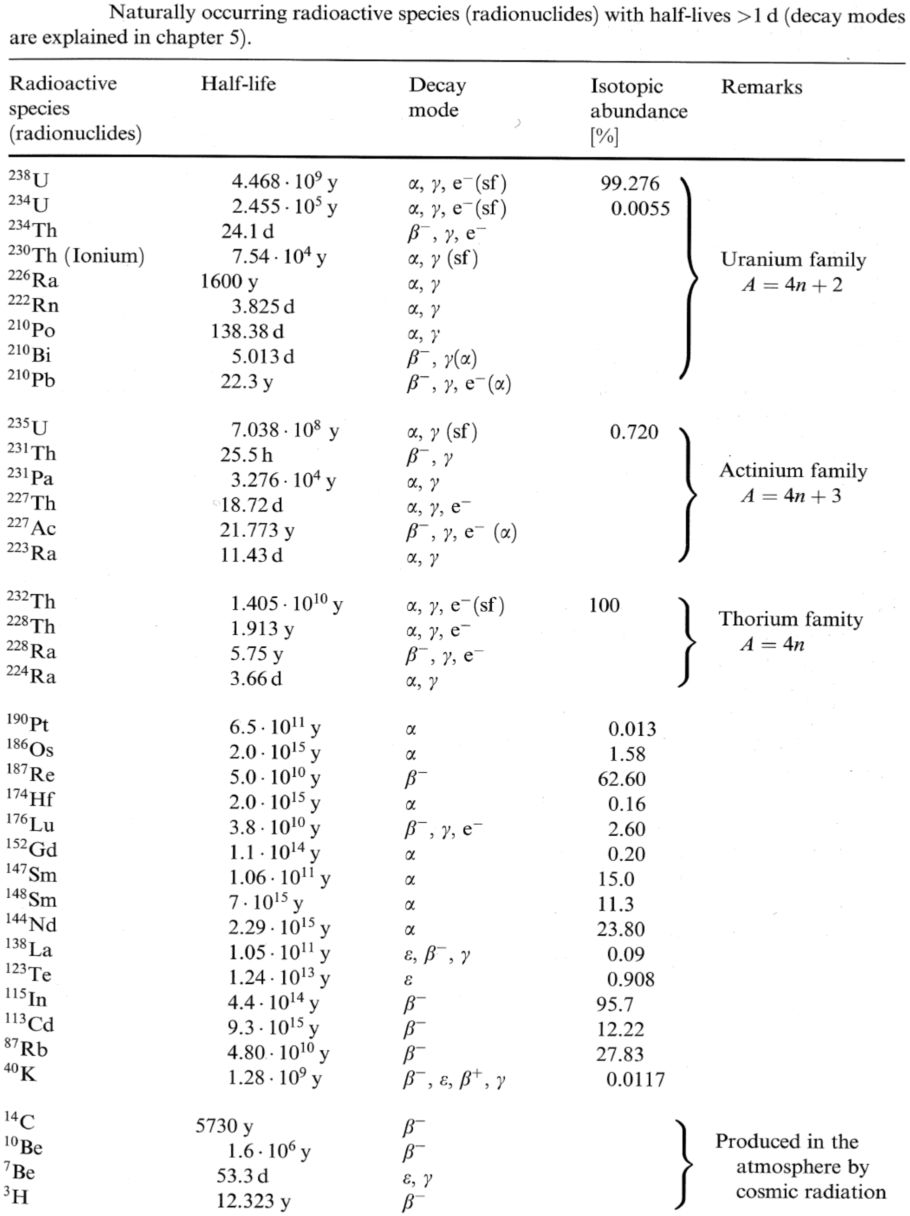
- **Nuclear Chemistry:** focus on chemical aspects of atomic nuclei and of nuclear reactions.
- **Radiochemistry:** focus on chemical properties, preparation and handling of radioactive substances.

❑ **Radiation Chemistry** deals with the chemical effects of radiation.

❑ **Research in nuclear and radiochemistry** comprises:

- Study of radioactive matter in nature.
- Investigation of radioactive transmutation and of nuclear reactions by chemical methods.
- Chemical effects of nuclear reactions (hot atom chemistry, $E=kT$, $1\,\mathrm{MeV} \leftrightarrow 1.16 \cdot 10^{10}\,\mathrm{K}$).
- Influence of chemical bonding on nuclear properties.
- Production of radionuclides and labelled compounds.
- Chemistry of radioelements (more than a quarter of all chemical elements).

Radionuclides are a Part of Nature !

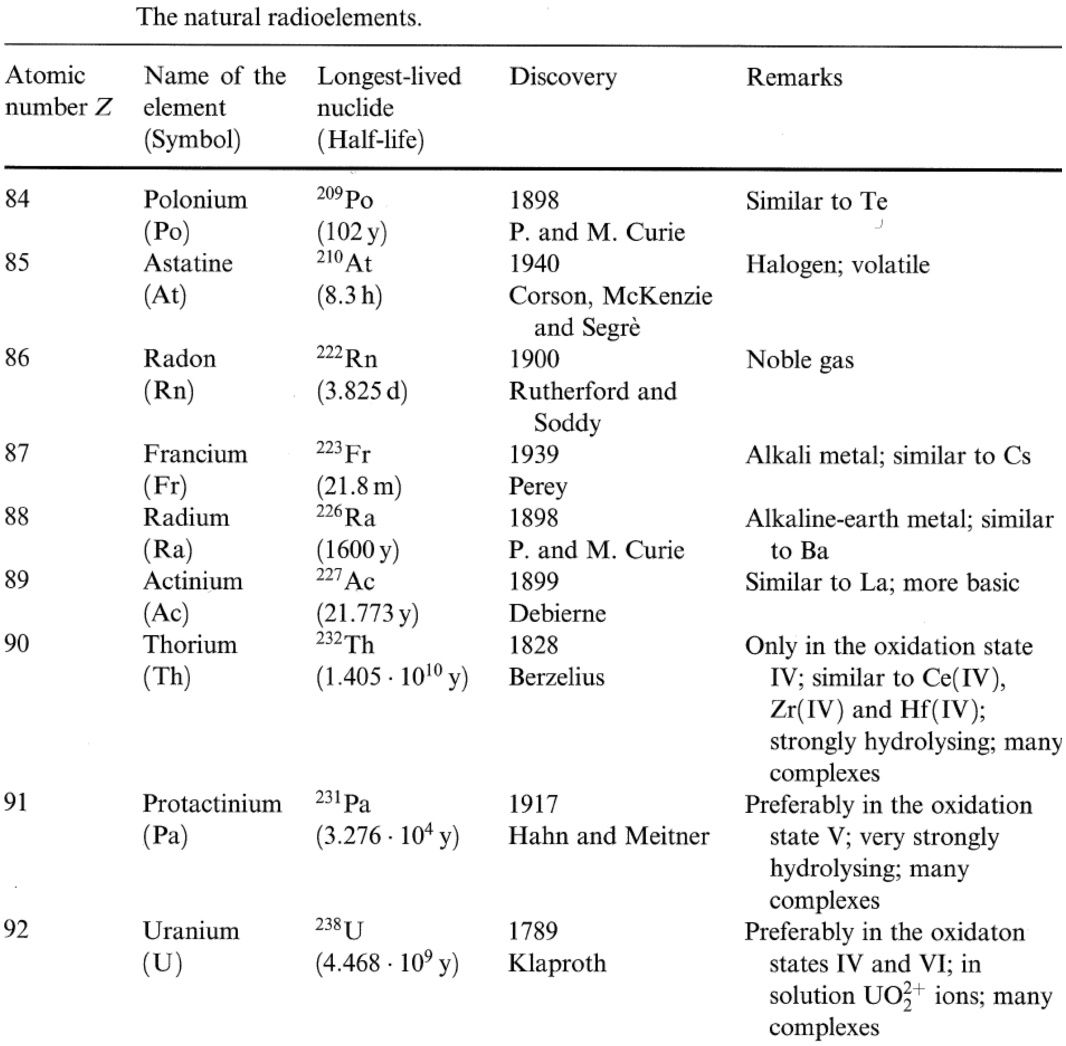


Naturally occurring radioactive species (radionuclides) with half-lives >1 d (decay modes are explained in chapter 5).

Radioactive species (radionuclides)	Half-life	Decay mode	Isotopic abundance [%]	Remarks
^{238}U	$4.468 \cdot 10^{9}$ y	α, γ, e^-(sf)	99.276	Uranium family $A = 4n + 2$
^{234}U	$2.455 \cdot 10^{5}$ y	α, γ, e^-(sf)	0.0055	
^{234}Th	24.1 d	β^-, γ, e^-		
^{230}Th (Ionium)	$7.54 \cdot 10^{4}$ y	α, γ (sf)		
^{226}Ra	1600 y	α, γ		
^{222}Rn	3.825 d	α, γ		
^{210}Po	138.38 d	α, γ		
^{210}Bi	5.013 d	$\beta^-, \gamma(\alpha)$		
^{210}Pb	22.3 y	$\beta^-, \gamma, e^-(\alpha)$		
^{235}U	$7.038 \cdot 10^{8}$ y	α, γ (sf)	0.720	Actinium family $A = 4n + 3$
^{231}Th	25.5 h	β^-, γ		
^{231}Pa	$3.276 \cdot 10^{4}$ y	α, γ		
^{227}Th	18.72 d	α, γ, e^-		
^{227}Ac	21.773 y	β^-, γ, e^- (α)		
^{223}Ra	11.43 d	α, γ		
^{232}Th	$1.405 \cdot 10^{10}$ y	α, γ, e^-(sf)	100	Thorium family $A = 4n$
^{228}Th	1.913 y	α, γ, e^-		
^{228}Ra	5.75 y	β^-, γ, e^-		
^{224}Ra	3.66 d	α, γ		
^{190}Pt	$6.5 \cdot 10^{11}$ y	α	0.013	
^{186}Os	$2.0 \cdot 10^{15}$ y	α	1.58	
^{187}Re	$5.0 \cdot 10^{10}$ y	β^-	62.60	
^{174}Hf	$2.0 \cdot 10^{15}$ y	α	0.16	
^{176}Lu	$3.8 \cdot 10^{10}$ y	β^-, γ, e^-	2.60	
^{152}Gd	$1.1 \cdot 10^{14}$ y	α	0.20	
^{147}Sm	$1.06 \cdot 10^{11}$ y	α	15.0	
^{148}Sm	$7 \cdot 10^{15}$ y	α	11.3	
^{144}Nd	$2.29 \cdot 10^{15}$ y	α	23.80	
^{138}La	$1.05 \cdot 10^{11}$ y	$\varepsilon, \beta^-, \gamma$	0.09	
^{123}Te	$1.24 \cdot 10^{13}$ y	ε	0.908	
^{115}In	$4.4 \cdot 10^{14}$ y	β^-	95.7	
^{113}Cd	$9.3 \cdot 10^{15}$ y	β^-	12.22	
^{87}Rb	$4.80 \cdot 10^{10}$ y	β^-	27.83	
^{40}K	$1.28 \cdot 10^{9}$ y	$\beta^-, \varepsilon, \beta^+, \gamma$	0.0117	
^{14}C	5730 y	β^-		Produced in the atmosphere by cosmic radiation
^{10}Be	$1.6 \cdot 10^{6}$ y	β^-		
^{7}Be	53.3 d	ε, γ		
^{3}H	12.323 y	β^-		

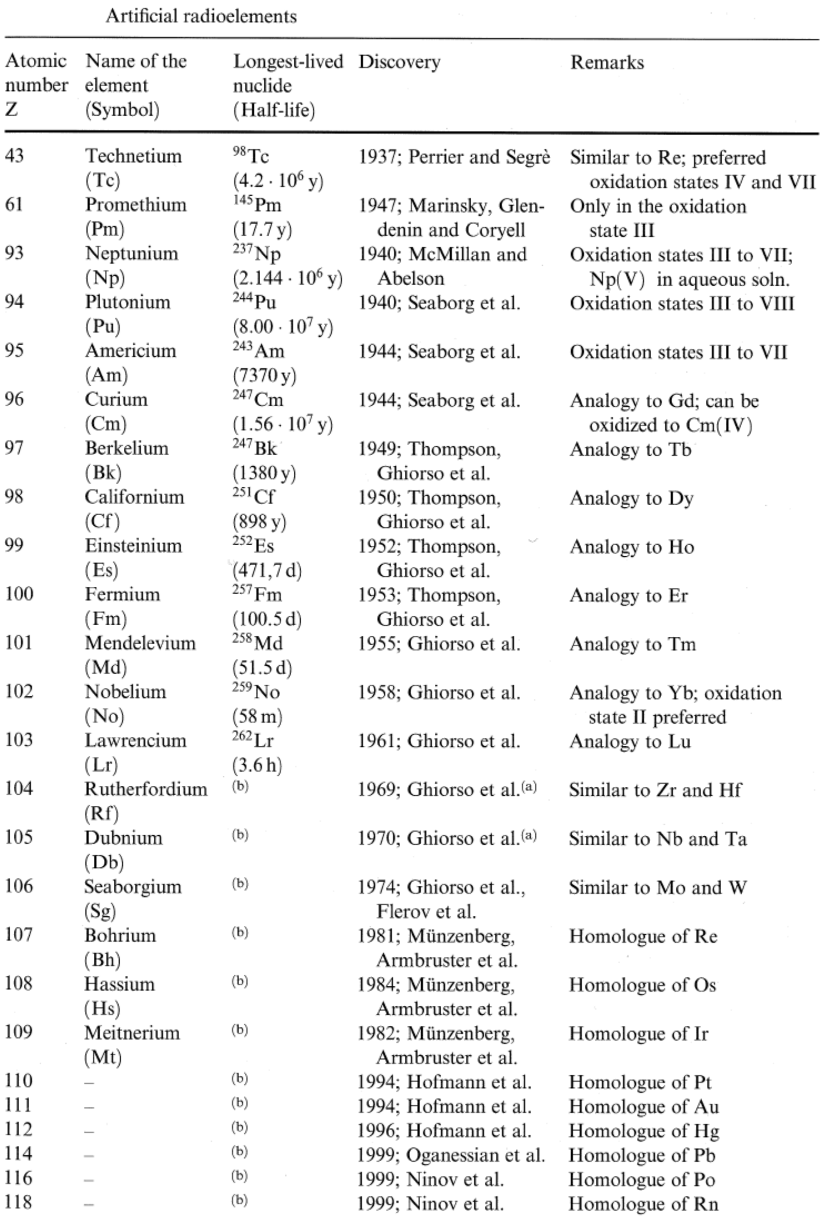
- Radioisotopes can be divided into two groups:
  - naturally occurring radioisotopes
  - man-made radioisotopes
- The naturally occurring radioactive substances are widely distributed on Earth, the major part can be found in the lithosphere.
- The natural radioisotopes can be classified according to their origin:
  - **Cosmogenic radionuclides.**
  - **Primordial radioisotopes:**
    - members of the natural decay series
    - terrestrial radionuclides

Radioelements: Elements that only exist as radionuclides



The natural radioelements.

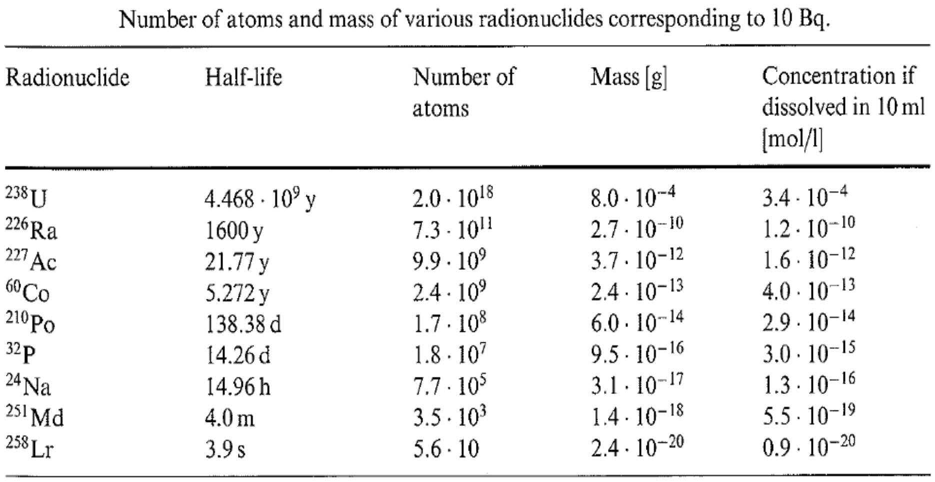
Atomic number Z	Name of the element (Symbol)	Longest-lived nuclide (Half-life)	Discovery	Remarks
84	Polonium (Po)	^{209}Po (102 y)	1898 P. and M. Curie	Similar to Te
85	Astatine (At)	^{210}At (8.3 h)	1940 Corson, McKenzie and Segrè	Halogen; volatile
86	Radon (Rn)	^{222}Rn (3.825 d)	1900 Rutherford and Soddy	Noble gas
87	Francium (Fr)	^{223}Fr (21.8 m)	1939 Perey	Alkali metal; similar to Cs
88	Radium (Ra)	^{226}Ra (1600 y)	1898 P. and M. Curie	Alkaline-earth metal; similar to Ba
89	Actinium (Ac)	^{227}Ac (21.773 y)	1899 Debierne	Similar to La; more basic
90	Thorium (Th)	^{232}Th ($1.405 \cdot 10^{10}$ y)	1828 Berzelius	Only in the oxidation state IV; similar to Ce(IV), Zr(IV) and Hf(IV); strongly hydrolysing; many complexes
91	Protactinium (Pa)	^{231}Pa ($3.276 \cdot 10^{4}$ y)	1917 Hahn and Meitner	Preferably in the oxidation state V; very strongly hydrolysing; many complexes
92	Uranium (U)	^{238}U ($4.468 \cdot 10^{9}$ y)	1789 Klaproth	Preferably in the oxidaton states IV and VI; in solution UO_2^{2+} ions; many complexes



Artificial radioelements

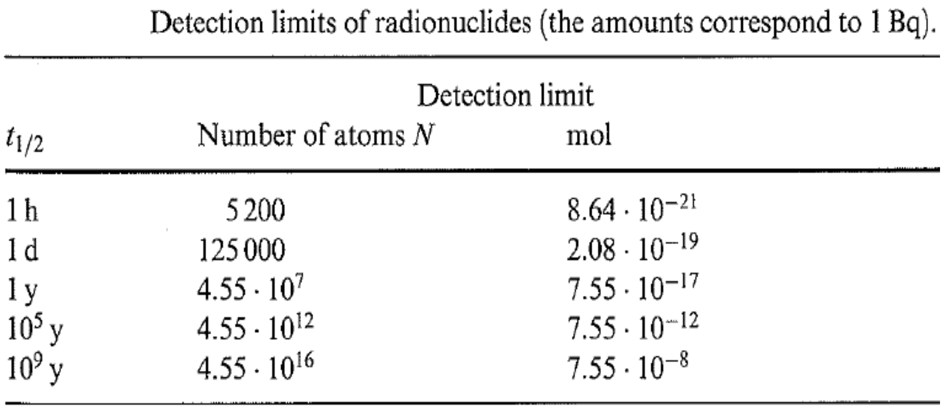
Atomic number Z	Name of the element (Symbol)	Longest-lived nuclide (Half-life)	Discovery	Remarks
43	Technetium (Tc)	^{98}Tc ($4.2 \cdot 10^{6}$ y)	1937; Perrier and Segrè	Similar to Re; preferred oxidation states IV and VII
61	Promethium (Pm)	^{145}Pm (17.7 y)	1947; Marinsky, Glendenin and Coryell	Only in the oxidation state III
93	Neptunium (Np)	^{237}Np ($2.144 \cdot 10^{6}$ y)	1940; McMillan and Abelson	Oxidation states III to VII; Np(V) in aqueous soln.
94	Plutonium (Pu)	^{244}Pu ($8.00 \cdot 10^{7}$ y)	1940; Seaborg et al.	Oxidation states III to VIII
95	Americium (Am)	^{243}Am (7370 y)	1944; Seaborg et al.	Oxidation states III to VII
96	Curium (Cm)	^{247}Cm ($1.56 \cdot 10^{7}$ y)	1944; Seaborg et al.	Analogy to Gd; can be oxidized to Cm(IV)
97	Berkelium (Bk)	^{247}Bk (1380 y)	1949; Thompson, Ghiorso et al.	Analogy to Tb
98	Californium (Cf)	^{251}Cf (898 y)	1950; Thompson, Ghiorso et al.	Analogy to Dy
99	Einsteinium (Es)	^{252}Es (471,7 d)	1952; Thompson, Ghiorso et al.	Analogy to Ho
100	Fermium (Fm)	^{257}Fm (100.5 d)	1953; Thompson, Ghiorso et al.	Analogy to Er
101	Mendelevium (Md)	^{258}Md (51.5 d)	1955; Ghiorso et al.	Analogy to Tm
102	Nobelium (No)	^{259}No (58 m)	1958; Ghiorso et al.	Analogy to Yb; oxidation state II preferred
103	Lawrencium (Lr)	^{262}Lr (3.6 h)	1961; Ghiorso et al.	Analogy to Lu
104	Rutherfordium (Rf)	(b)	1969; Ghiorso et al.(a)	Similar to Zr and Hf
105	Dubnium (Db)	(b)	1970; Ghiorso et al.(a)	Similar to Nb and Ta
106	Seaborgium (Sg)	(b)	1974; Ghiorso et al., Flerov et al.	Similar to Mo and W
107	Bohrium (Bh)	(b)	1981; Münzenberg, Armbruster et al.	Homologue of Re
108	Hassium (Hs)	(b)	1984; Münzenberg, Armbruster et al.	Homologue of Os
109	Meitnerium (Mt)	(b)	1982; Münzenberg, Armbruster et al.	Homologue of Ir
110	–	(b)	1994; Hofmann et al.	Homologue of Pt
111	–	(b)	1994; Hofmann et al.	Homologue of Au
112	–	(b)	1996; Hofmann et al.	Homologue of Hg
114	–	(b)	1999; Oganessian et al.	Homologue of Pb
116	–	(b)	1999; Ninov et al.	Homologue of Po
118	–	(b)	1999; Ninov et al.	Homologue of Rn

Advantage of Radionuclide Applications in Radioanalysis: High Sensitivity



Number of atoms and mass of various radionuclides corresponding to 10 Bq.

Radionuclide	Half-life	Number of atoms	Mass [g]	Concentration if dissolved in 10 ml [mol/l]
^{238}U	$4.468 \cdot 10^{9}$ y	$2.0 \cdot 10^{18}$	$8.0 \cdot 10^{-4}$	$3.4 \cdot 10^{-4}$
^{226}Ra	1600 y	$7.3 \cdot 10^{11}$	$2.7 \cdot 10^{-10}$	$1.2 \cdot 10^{-10}$
^{227}Ac	21.77 y	$9.9 \cdot 10^{9}$	$3.7 \cdot 10^{-12}$	$1.6 \cdot 10^{-12}$
^{60}Co	5.272 y	$2.4 \cdot 10^{9}$	$2.4 \cdot 10^{-13}$	$4.0 \cdot 10^{-13}$
^{210}Po	138.38 d	$1.7 \cdot 10^{8}$	$6.0 \cdot 10^{-14}$	$2.9 \cdot 10^{-14}$
^{32}P	14.26 d	$1.8 \cdot 10^{7}$	$9.5 \cdot 10^{-16}$	$3.0 \cdot 10^{-15}$
^{24}Na	14.96 h	$7.7 \cdot 10^{5}$	$3.1 \cdot 10^{-17}$	$1.3 \cdot 10^{-16}$
^{251}Md	4.0 m	$3.5 \cdot 10^{3}$	$1.4 \cdot 10^{-18}$	$5.5 \cdot 10^{-19}$
^{258}Lr	3.9 s	$5.6 \cdot 10$	$2.4 \cdot 10^{-20}$	$0.9 \cdot 10^{-20}$



Detection limits of radionuclides (the amounts correspond to 1 Bq).

$t_{1/2}$	Detection limit Number of atoms N	mol
1 h	5 200	$8.64 \cdot 10^{-21}$
1 d	125 000	$2.08 \cdot 10^{-19}$
1 y	$4.55 \cdot 10^{7}$	$7.55 \cdot 10^{-17}$
10^{5} y	$4.55 \cdot 10^{12}$	$7.55 \cdot 10^{-12}$
10^{9} y	$4.55 \cdot 10^{16}$	$7.55 \cdot 10^{-8}$

- In principle, a single radioactive atom can be detected (if measured at the moment of its decay).
- Mass m and activity A of a radionuclide are correlated by the half-life $T_{1/2}$ (M=atomic mass, N_{Av}=Avogadro's number):
  - $m = A\ M\ T_{1/2} / (\ln 2\ N_{Av})$ **(1)**
- Within 10 minutes and with an overall counting efficiency of 20% 10 Bq can be detected with a statistical error of ~3%.
- Especially short-lived radionuclides can be measured with extremely high sensitivity (extremely low detection limits).
- However, often microamounts of radioactive material must be handled swiftly.
- Especially NAA is a blank-free, non-destructive and multi-elemental method.

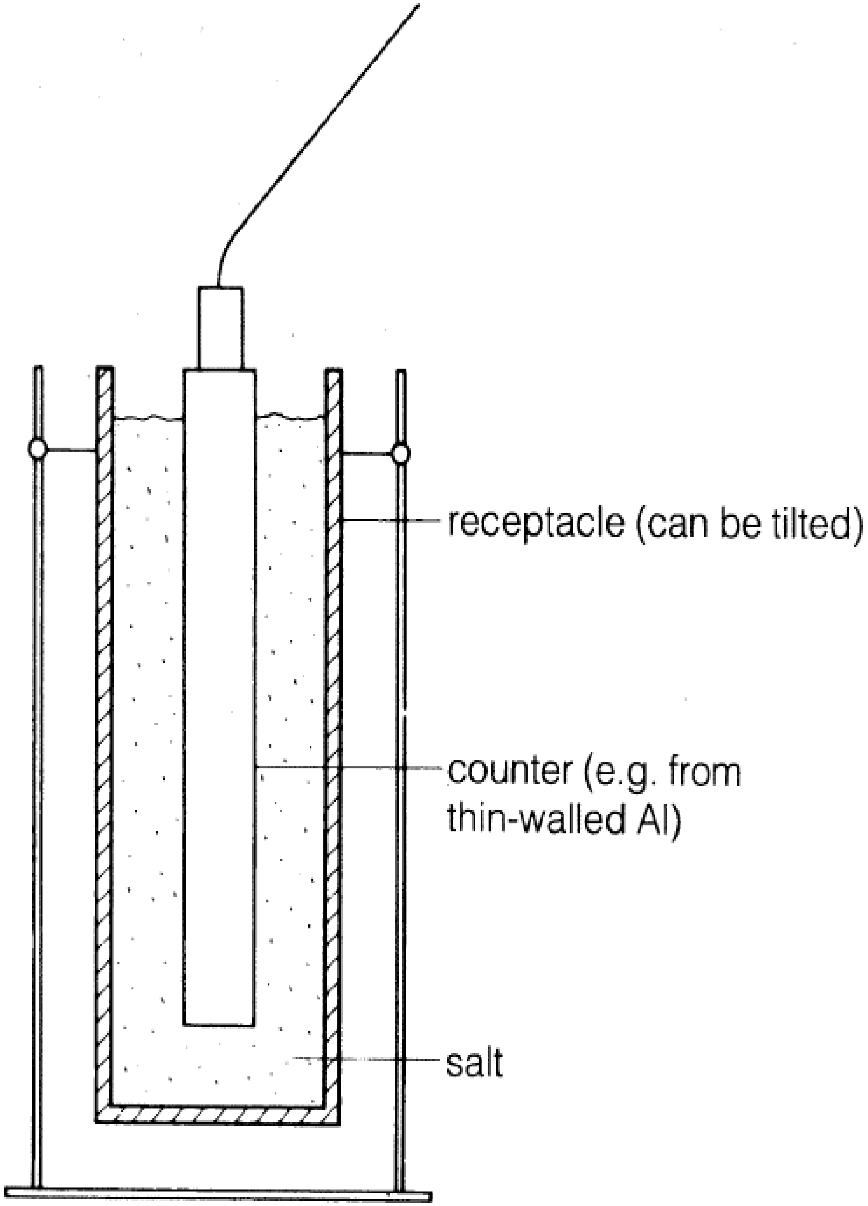
Overview: Fields in Radiochemistry

- ☐ **Radioanalysis** (analytical chemistry based on nuclear phenomena):
  - **Analysis on the basis of the inherent natural radioactivity** of the elements to be determined.
  - **Activation analysis.**
  - Analysis after addition of **radionuclides as tracers** (isotopic dilution and radiometric methods).
- ☐ Study of chemical and physical properties of the **transuranium and (super)heavy elements** including their radioactive decay.
- ☐ Study of macroscopic phenomena (where nuclear processes are involved) overlapping with other (applied) sciences:
  - Geo- and Cosmochemistry
  - Environmental and Biochemistry (surface chemical processes in the atmosphere)
  - Nuclear reactors, nuclear fuel and fuel cycles
- ☐ Synthesis and preparation of labelled compounds.
- ☐ Study of nuclear properties such as structure, reactions, radioactive decay.

Analysis Based on Inherent Radioactivity (1)

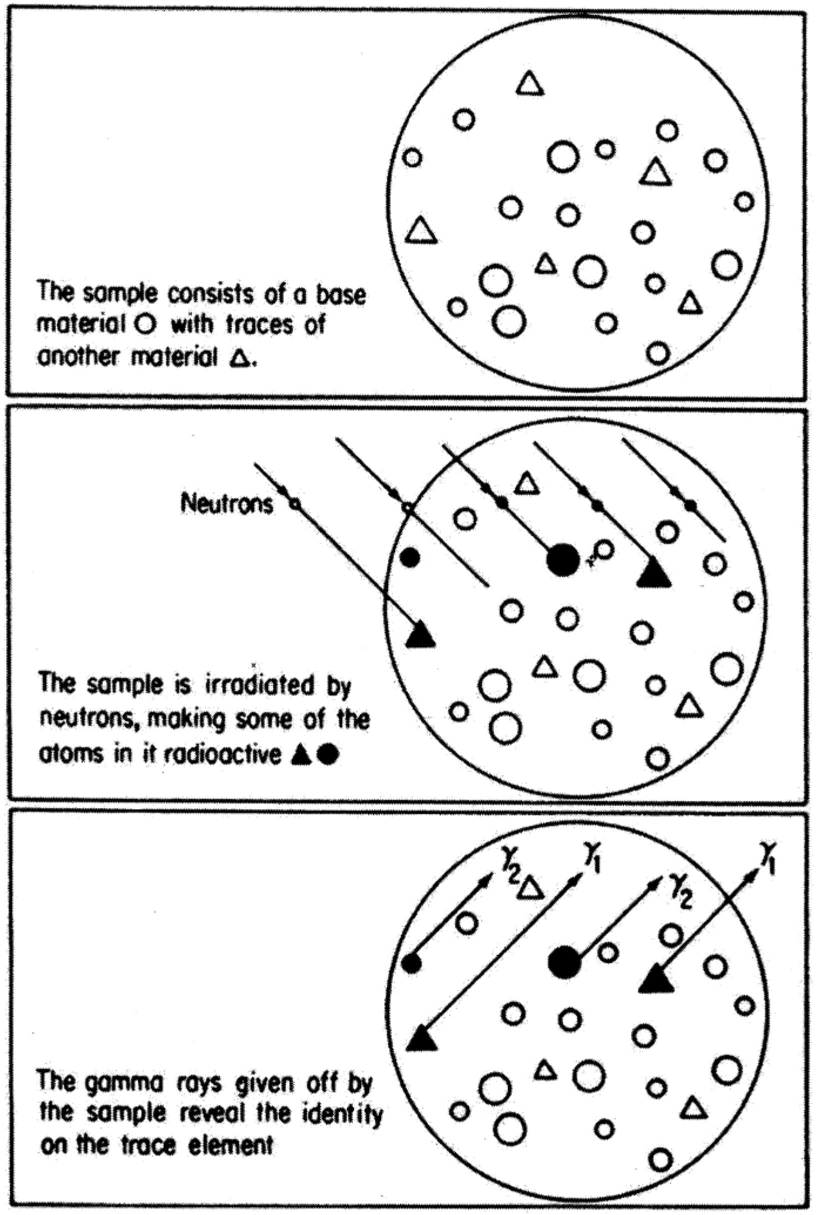
- ☐ **The activity of radioactive substances is a measure of their mass** (Eq.(1)), provided that the following conditions hold:
  - The isotopic composition of the element to be determined is constant.
  - There are no interfering radioactive impurities.
- ☐ If the daughter nuclei are also radioactive, either:
  - radioactive equilibrium must be established,
  - or the daughter nuclides must be separated off quantitatively.
- ☐ Interference with radioactive impurities can often be eliminated by measuring the α- or γ-spectrum of the radioisotopes.
- ☐ **Analytical determination based on natural radioactivity is often used for** the radionuclides **^{40}K, ^{238}U, ^{226}Ra** and **^{232}Th**.

Analysis Based on Inherent Radioactivity (2): Example



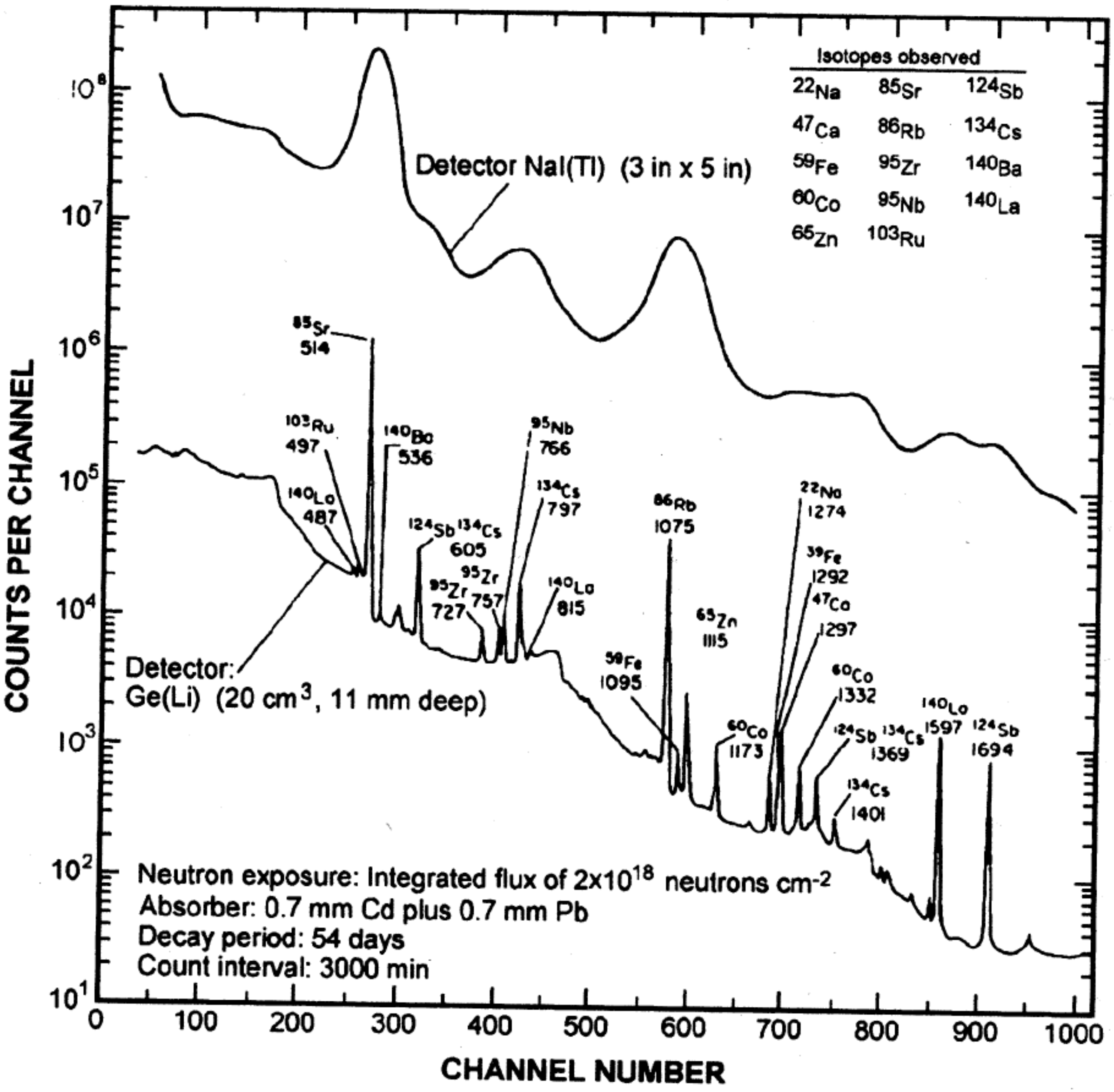
- ☐ Potassium contains 0.0117 % of the radionuclide ^{40}K ($T_{1/2}=1.28\cdot10^9$ a), and this atomic fraction is practically constant.
- ☐ The relatively high energetic β^--radiation (89.3 %, $E_\beta=1.31$ MeV) or γ-radiation ($E_\gamma=1.46$ MeV) after β^+-decay can be easily measured.
- ☐ The natural activity of 1kg of potassium is $3.13\cdot10^4$ Bq, which (assuming that 0.1 Bq can be measured) results in an detection limit of 3 mg.
- ☐ The figure shows a device applied to measure the K concentration in salts.

Activation Analysis in Radiochemistry (Supplement)



- ☐ Activation analysis induced by neutrons, charged particles or photons is widely used in radiochemistry. Often INAA (with HPGe-detectors and a multichannel analyzer) and RNAA (i.e., NAA with subsequent chemical purification) are applied.
- ☐ The activity of the radionuclide produced in the nuclear reaction T + x → P + y after an irradiation time t_i is given by: **$A = \lambda N_P = \sigma \Phi N_T \cdot (1 - \exp(-\lambda t_i))$**
- ☐ In NAA cases in which the neutrons induce a relatively high activity in the main material (m), the irradiation time t_i and decay time after irradiation t_d may be chosen to maximize the ratio:
  - **$A_x / A_m = \sigma_x N_T(x) \cdot (1 - \exp(-\lambda_x t_i)) \cdot \exp(-\lambda_x t_d)$ $/ \sigma_m N_T(m) \cdot (1 - \exp(-\lambda_m t_i)) \cdot \exp(-\lambda_m t_d)$**
- ☐ For short-lived radionuclides a fast transport system is needed, cf. **PROTRAC at PSI**.

Activation Analysis in Radiochemistry: Detectors/Example

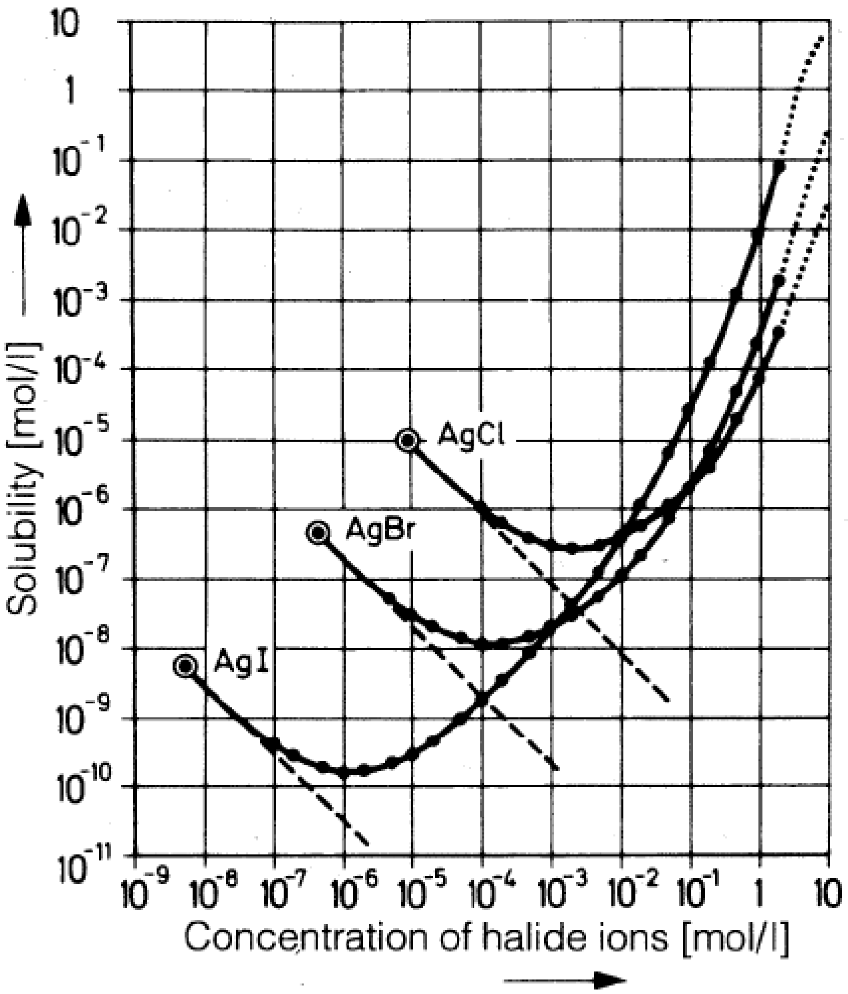


- ☐ To count γ-radiation, **scintillation and semiconductor detectors are mainly employed** often in combination with a multichannel analyzer operated by a computer and a program for peak search, energy calibration and radionuclide identification.
- ☐ The figure shows γ-ray spectra from a sample of neutron irradiated sea water obtained with a NaI(Tl) and a Ge(Li) detector.

Radiotracers in Chemistry: Introduction (Supplement)

- ❑ General prerequisite of tracer applications:
  - Tracers show the same behavior as the atoms or compounds to be investigated (same chemistry for isotopes usually given, isotope effects can be taken into account (H/T)).
  - Labelling of elements or chemical compounds must be possible.
- ❑ Radiotracer methods in chemistry allow investigation of the fate of the labelled elements and compounds in the course of a chemical reaction or a transport process. Thus radiotracer techniques offer unique possibilities for the study of reaction mechanisms in homogeneous and heterogeneous systems.
- ❑ Further Advantages:
  - Radionuclides can be measured accurately with **high sensitivity** at high dilution.
  - Often radiotracer techniques offer information that cannot be obtained by other means.
  - Radiotracer techniques have proved to be indispensable with respect to revealing the examination of individual steps of an analytical procedure, in particular with the aim of revealing the sources of systematic errors.
  - A wide variety of radionuclides and labelled compounds are available.
  - Radiation safety: The radiotracer method, if all necessary precautions are taken, is safe.
- ❑ In the following some **radiotracer applications in chemistry** will be described:
  - to measure chemical equilibria and elucidate chemical bonding
  - to study reactions mechanisms in homogeneous and heterogeneous systems
  - to investigate diffusion and transport processes

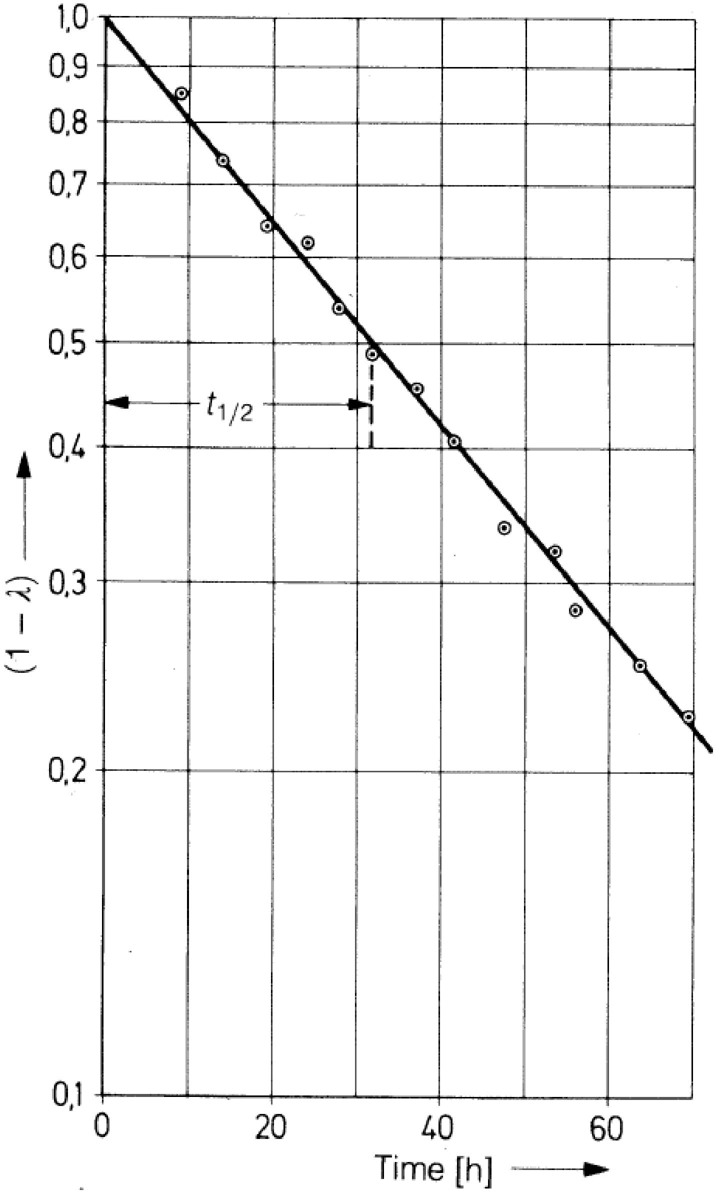
Chemical Equilibria (Example) and Chemical Bonding

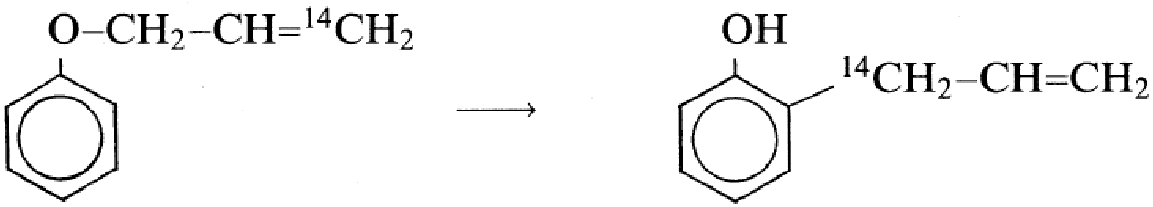


- The extraordinarily high sensitivity of radiochemical methods makes it possible to **measure solubility of sparingly soluble compounds or distribution equilibria in the range of very low concentrations**.
- Example: In the figure the concentration of Ag in the silver halides AgCl, AgBr, AgI is shown as a function of the concentration of the corresponding halides NaCl, NaBr and NaI. The fall is due to the solubility product, the subsequent rise due to complex formation. The minima cannot be found by electrochemical methods.
- **Radiotracer applications** were also used **to elucidate chemical bonding**. It could be shown, e.g., that the **Pb atoms in Pb_2O_3 are not equivalent, but exist in different oxidation states (II and IV)**.

Solubility equilibria of silver halides in water (⊙) and in sodium halide solutions. (According to K. H. Lieser, Z. Anorg. Allg. Chem., **229**, 97 (1957).)

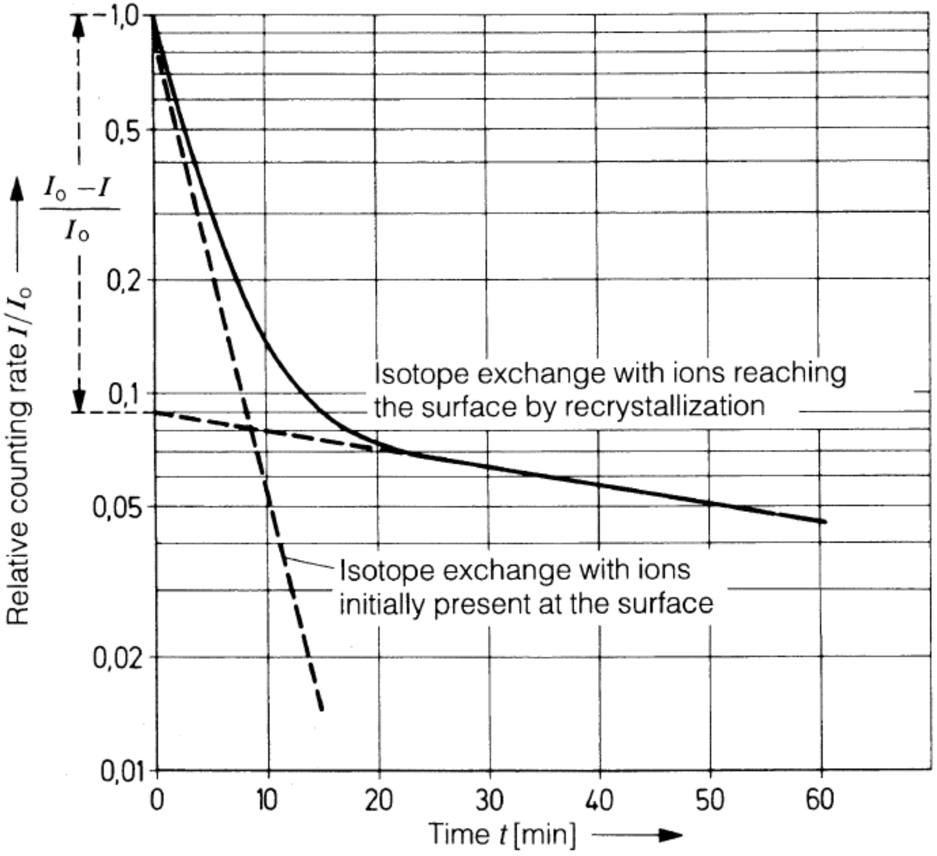
Reaction Mechanisms in Homogeneous Systems





- **The Claisen allyl rearrangement (on the top) could be elucidated by labelling with ^{14}C.** By investigation of the decomposition products is was proved that the terminal C atom of the allyl group forms a bond with the benzene ring.
- **Isotope exchange reactions can be studied with radiotracers: AX(1) + *AY(2) ↔ *AX(1) + AY(2)**
  - the rate of exchange is: $d^*c_1/dt = R\ (^*c_2/c_2 - {}^*c_1/c_1)$ **(2)**
  - with reaction rate:
    - $R = k_1(T)\ c_1$ (1st order reactions)
    - $R = k_2(T)\ c_1 c_2$ (2nd order reactions)
  - integration of Eq.(2) gives: $\ln(1-\lambda) = -R\ t\ (c_1+c_2)/(c_1 \cdot c_2)$ with
    $\lambda = (^*c_1 - {}^*c_1(0)) / (^*c_1(\infty) - {}^*c_1(0))$ (degree of exchange)
  - plotting $\ln(1-\lambda)$ versus time (see figure on the left) allows the determination of the reaction rate coefficients:
    - $k_1(T) = (\ln 2/T_{1/2}) \cdot (c_2/(c_1+c_2))$ (1st order reactions)
    - $k_2(T) = (\ln 2/T_{1/2})/(c_1+c_2)$ (2nd order reactions)

Reaction Mechanisms in Heterogeneous Systems



- Also in heterogeneous systems radiotracer techniques are used to clarify reactions mechanisms and to determine kinetic data.
- **In reactions between a solid and a gas or a solution, three steps are distinguished:**
  - transport of the reactant (in the gas phase or the solution) to the surface of the solid,
  - reaction at the surface of the solid
  - transport of the reaction products into the solid, the gas phase or the solution.
- Reactions at the solid/gas or solid/liquid interface comprise the following steps (which all can be described by reaction rates similar to $R=k(T)c_1c_2$):
  - adsorption of the reactant
  - reaction
  - desorption of the products
- The figure shows a typical result obtained in tracer experiments. By evaluation of such curves **the kinetics of the exchange reactions or the active surface area can be determined**.

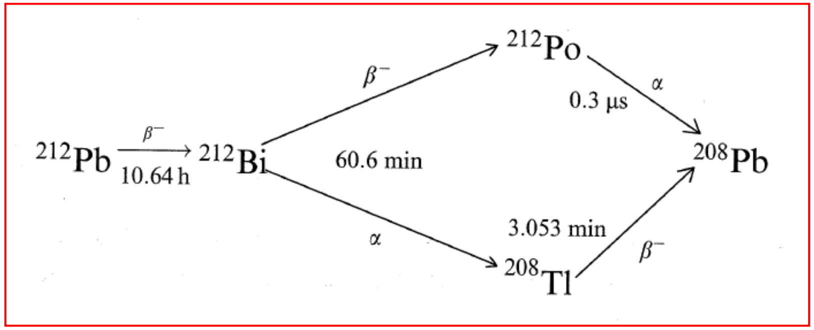
Diffusion and Transport Processes

- The high sensitivity of radiotracer methods makes them very attractive for the determination of diffusion coefficients (the latter relation holds if D is a constant):

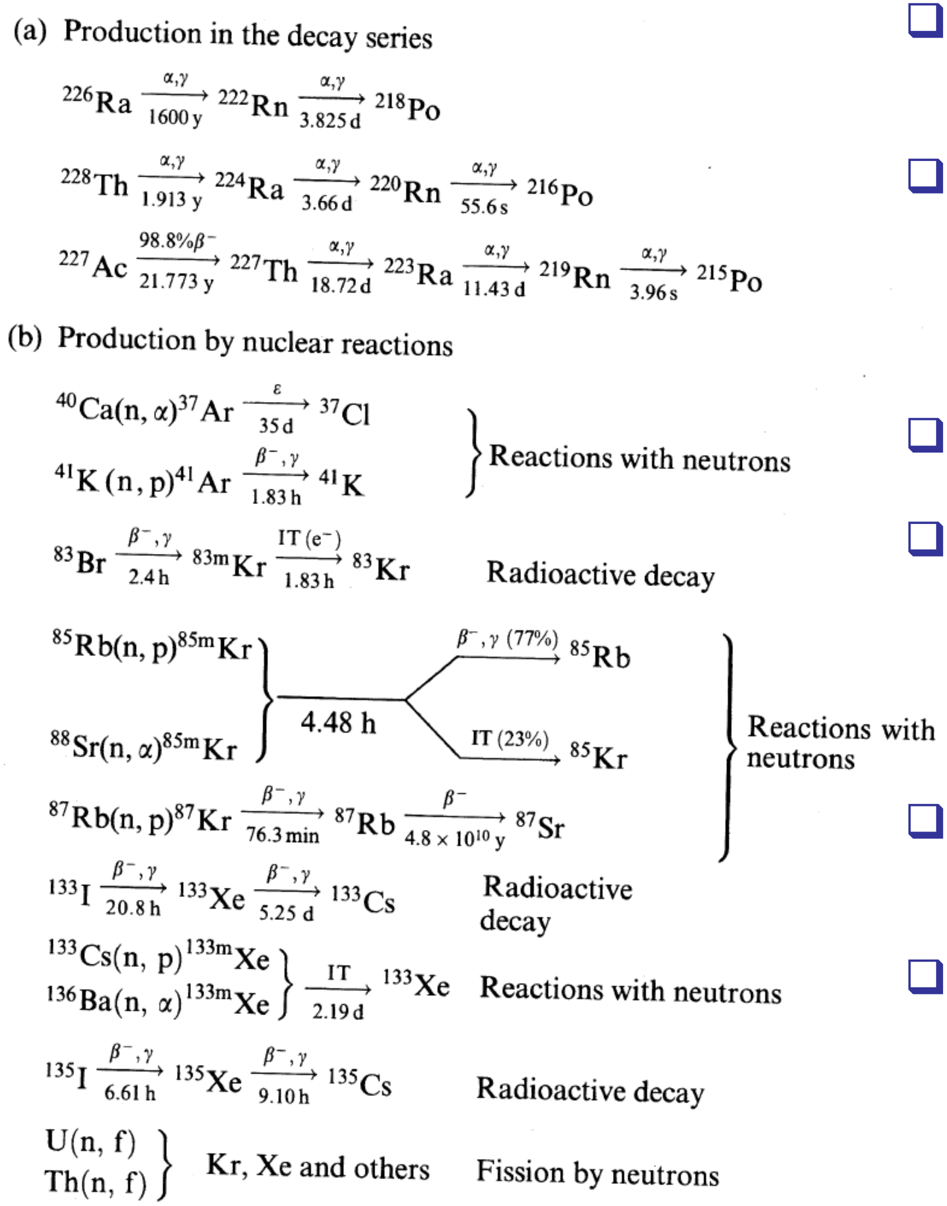
$$\frac{\partial\Phi(\vec{r},t)}{\partial t} = \nabla\cdot[D(\Phi,\vec{r})\nabla\Phi(\vec{r},t)] = D\nabla^2\Phi(\vec{r},t)$$

- **Self diffusion**, i.e. the diffusion of the intrinsic components of a substance, **can only be measured by indicator methods**.

- The following investigation methods may be distinguished:
  - **Radiation-absorption method**: the tracer is applied in form of an “infinitely thin” or “infinitely thick” layer and, at the end of the experiment, the sample is sliced into thin slices or dissolved stepwise. The mean penetration depth and D are calculated from the decrease in counting rate.
  - **Autoradiography**: Photographic emulsions provide qualitative information about diffusion (do the particle spread uniformly or along grain boundaries?).
  - **Recoil method**: A plane surface of lead is labelled with ^{212}Pb, the decay chain of which includes an α-decay of ^{212}Bi. The daughter ^{208}Tl receives a recoil, and depending on the penetration depth of ^{212}Pb, a greater or smaller fraction of recoiling ^{208}Tl atoms are sampled on a Cu-electrode (at potential -200V), and the β^- activity of ^{208}Tl is measured.



Emanation Techniques



(a) Production in the decay series

$^{226}\text{Ra} \xrightarrow[1600\,\text{y}]{\alpha,\gamma} {}^{222}\text{Rn} \xrightarrow[3.825\,\text{d}]{\alpha,\gamma} {}^{218}\text{Po}$

$^{228}\text{Th} \xrightarrow[1.913\,\text{y}]{\alpha,\gamma} {}^{224}\text{Ra} \xrightarrow[3.66\,\text{d}]{\alpha,\gamma} {}^{220}\text{Rn} \xrightarrow[55.6\,\text{s}]{\alpha,\gamma} {}^{216}\text{Po}$

$^{227}\text{Ac} \xrightarrow[21.773\,\text{y}]{98.8\%\beta^-} {}^{227}\text{Th} \xrightarrow[18.72\,\text{d}]{\alpha,\gamma} {}^{223}\text{Ra} \xrightarrow[11.43\,\text{d}]{\alpha,\gamma} {}^{219}\text{Rn} \xrightarrow[3.96\,\text{s}]{\alpha,\gamma} {}^{215}\text{Po}$

(b) Production by nuclear reactions

$^{40}\text{Ca}(n,\alpha)^{37}\text{Ar} \xrightarrow[35\,\text{d}]{\varepsilon} {}^{37}\text{Cl}$
$^{41}\text{K}(n,p)^{41}\text{Ar} \xrightarrow[1.83\,\text{h}]{\beta^-,\gamma} {}^{41}\text{K}$
Reactions with neutrons

$^{83}\text{Br} \xrightarrow[2.4\,\text{h}]{\beta^-,\gamma} {}^{83m}\text{Kr} \xrightarrow[1.83\,\text{h}]{\text{IT}\,(e^-)} {}^{83}\text{Kr}$ Radioactive decay

$^{85}\text{Rb}(n,p)^{85m}\text{Kr}$
$^{88}\text{Sr}(n,\alpha)^{85m}\text{Kr}$
4.48 h
$\xrightarrow{\beta^-,\gamma\,(77\%)} {}^{85}\text{Rb}$
$\xrightarrow{\text{IT}\,(23\%)} {}^{85}\text{Kr}$
$^{87}\text{Rb}(n,p)^{87}\text{Kr} \xrightarrow[76.3\,\text{min}]{\beta^-,\gamma} {}^{87}\text{Rb} \xrightarrow[4.8\times10^{10}\,\text{y}]{\beta^-} {}^{87}\text{Sr}$
Reactions with neutrons

$^{133}\text{I} \xrightarrow[20.8\,\text{h}]{\beta^-,\gamma} {}^{133}\text{Xe} \xrightarrow[5.25\,\text{d}]{\beta^-,\gamma} {}^{133}\text{Cs}$ Radioactive decay

$^{133}\text{Cs}(n,p)^{133m}\text{Xe}$
$^{136}\text{Ba}(n,\alpha)^{133m}\text{Xe}$
$\xrightarrow[2.19\,\text{d}]{\text{IT}} {}^{133}\text{Xe}$ Reactions with neutrons

$^{135}\text{I} \xrightarrow[6.61\,\text{h}]{\beta^-,\gamma} {}^{135}\text{Xe} \xrightarrow[9.10\,\text{h}]{\beta^-,\gamma} {}^{135}\text{Cs}$ Radioactive decay

U(n, f)
Th(n, f)
Kr, Xe and others Fission by neutrons

- ☐ Emanation techniques are based on the production of radioactive noble gases by decay of mother nuclides or by nuclear reactions.
- ☐ The **emanating power** is defined as the **fraction of radioactive noble gas escaping from a solid relative to the amount produced in the solid**. It is measured either by the activity of the noble gas itself or that of its daughter nuclides.
- ☐ The processes contributing to emanation are recoil and diffusion.
- ☐ The emanating power depends on various factors:
  - composition of the solid and reactions in it
  - lattice structure of the solid
  - specific surface area of the solid
  - temperature
  - $T_{1/2}$ of the noble gas radionuclide and its recoil energy
- ☐ The figure lists various possibilities of producing radioactive noble gases for application as emanating sources.
- ☐ Emanation measurements can be used to:
  - investigate the transformation, decomposition or other reactions in solids
  - study aging processes in precipitates
  - obtain information about surface areas
  - determine the density of porous substances

Isotope Dilution Analysis (1): Direct IDA

- In complex mixtures of components (e.g., biochemical systems) it may be quite difficult to ascertain the exact amount of a specific component.
- The basic idea of isotope dilution analysis (IDA) is to measure the changes in specific activity when a substance has been incorporated into a system containing an unknown amount of atoms or molecules of the same kind. Several types of IDA exist.
- In **direct IDA** an unknown amount x of some inactive material M in a system is determined by the following procedure:
  - We add y grams of active material M* of known activity A_0 to the system, thus the specific activity is: $\mathbf{S_0=A_0/y}$ **(3)**.
  - After complete mixing to obtain a homogenous distribution, a sample (of any size) is taken and (after purification, if needed) its specific activity S_1 is measured. Due to conservation of material we have $\mathbf{S_1=A_0/(x+y)}$.
  - By substituting $y=A_0/S_0$ (from Eq. (3)) we get $\mathbf{S_1=A_0/(x+(A_0/S_0))}$ and after rearrangement:

    $\mathbf{x} = A_0/S_1 - A_0/S_0 = (A_0/S_0)\cdot (S_0/S_1-1) = \mathbf{y\cdot(S_0/S_1-1)}$ **(4)**.
- **The same kind of equations hold if stable isotopes are applied** for labelling of the elements or compounds to be determined by isotope dilution analysis. In this case isotope ratios replace the specific activities and are measured by mass spectrometry.
- **Main advantage of the method: a quantitative separation of the element or compound to be determined is not necessary.** It is substituted by measuring any fraction.

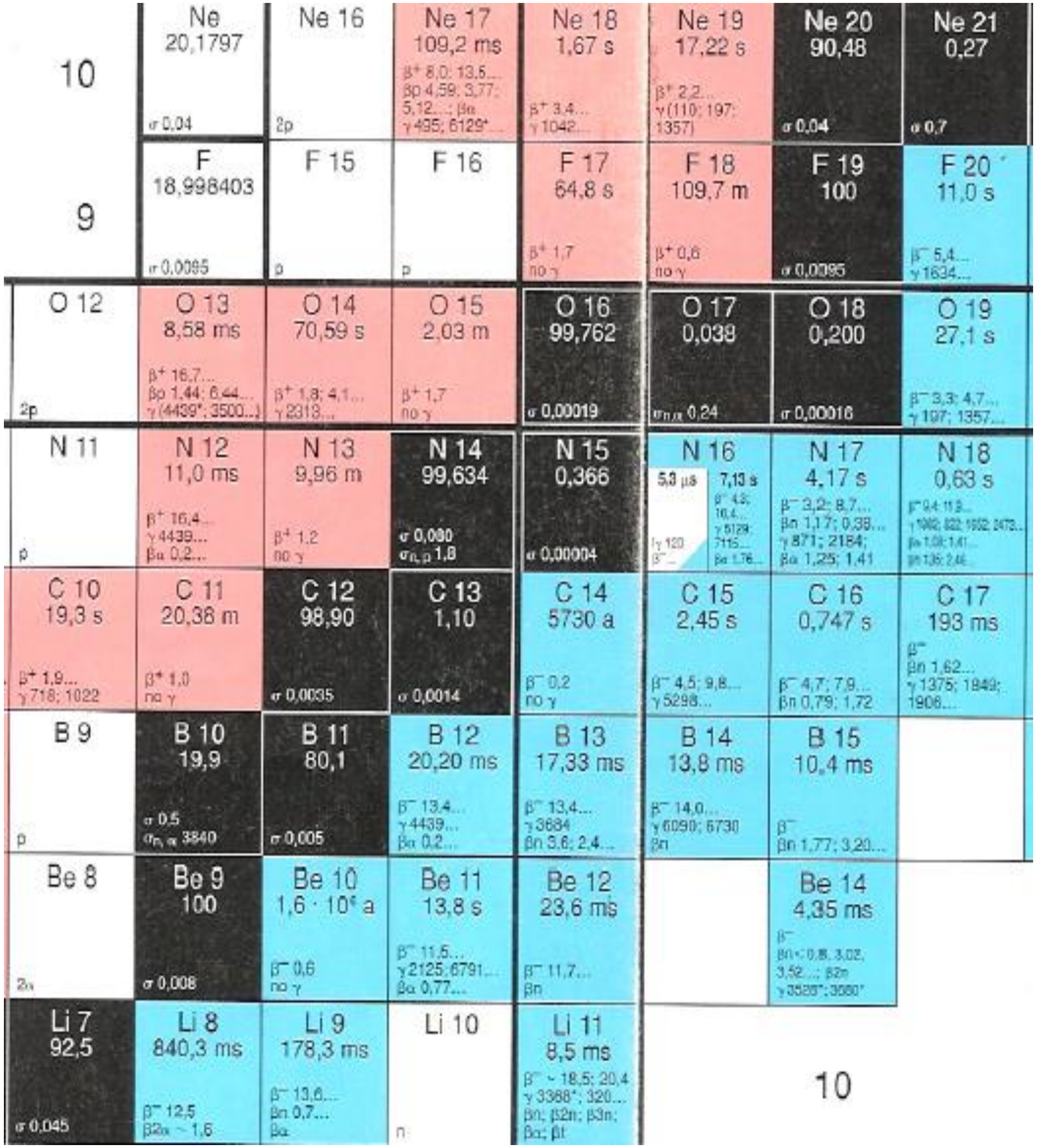
Isotope Dilution Analysis (2): Variants of IDA

- ☐ In **reverse or indirect IDA** an unknown amount q of radioactive material M*, whose specific activity $S_q = A/q$ is known, is determined by the following procedure:
  - We add r grams of inactive material M to the system.
  - After complete mixing to obtain a homogenous distribution, a sample (of any size) is taken and (after purification, if needed) its specific activity S_r is measured. Due to conservation of material we have $S_r=A/(q+r)=qS_q/(q+r)$ **(5)**.
  - By rearranging the terms we get $S_r(q+r) = qS_q$ **(6)** and $r/q = S_q/S_r-1$ and finally $q = r/(S_q/S_r-1)$ **(7)**.
- ☐ In **substoichiometric IDA** the IDA method is combined with substoichiometric analysis:
  - Two identical aliquots of the radiotracer solution are taken with mass y_0 and activity A_0.
  - One aliquot is added to the solution, and the other one is left as such.
  - Both aliquots (or the same amount **m** of them) react with a small amount of reagent, and the activities of the reaction products A_x and A_y is measured.
  - Since the mass **m** is the same, the specific activities in Eqs.(4),(7) can be replaced by the ratio of A_x, A_y.
  - Advantage of this method: the sometimes tricky task of measuring the specific activities is avoided.
- ☐ **Double dilution analysis** is used in reverse IDA, where the specific activity S_q cannot be measured. Adding r grams of inactive material to one aliquot and p grams to a second aliquot gives (Eq.(6)): $S_q= S_r+(r/q)S_r$ and $S_q= S_p+(p/q)S_p$, eliminating S_q leads to:
  - $q=(rS_r-pS_p)/(S_p-S_r)$.

Other Analytical Applications of Radiotracers & Radiation

- ☐ **Radiometric methods**: The principle in all radiometric techniques of analysis is to have a radioactive reagent R* of known activity to combine quantitatively with some unknown amount of material U to form a radioactive addition product R*U. By measuring the activity of the product R*U, the original amount of unknown material U is deduced.
  - The advantages of these methods are:
    - high sensitivity due to the use of radioactivity
    - the product R*U does not need to be chemically pure
  - The prerequisites for these methods are:
    - the product R*U must not contain any spurious radioactivity
    - the reaction between R*+U must be quantitative, no other species besides U is allowed to react with R*
- ☐ Techniques based on **absorption and scattering of radiation** (supplement):
  - Backscattering of β-radiation is also used as a basis for surface analysis.
  - Backscattering of γ- and X-rays is also applied (e.g., to determine the composition of ores).
  - Furthermore elastic scattering of γ-radiation.
  - Neutron backscattering is applied to measure hydrogen content.
  - Rutherford backscattering (i.e., elastic backscattering of α-particles) can be used for surface analysis.
- ☐ Finally **X-ray Fluorescence Analysis (XFA)** has been applied in radiation chemistry to analyze samples.

Seminar: PROTRAC facility at PSI



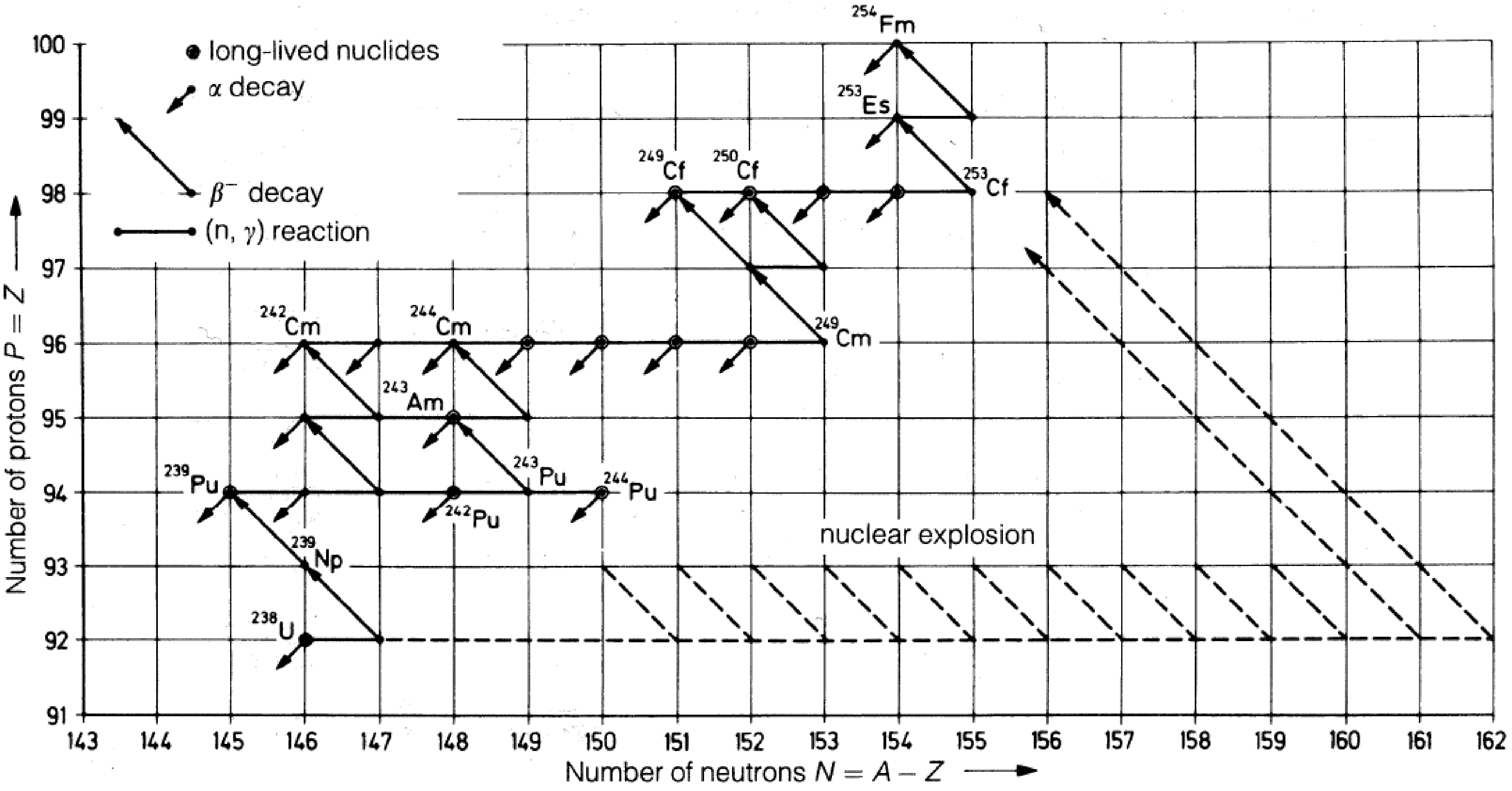
10	Ne 20,1797	Ne 16	Ne 17 109,2 ms	Ne 18 1,67 s	Ne 19 17,22 s	Ne 20 90,48	Ne 21 0,27
9	F 18,998403	F 15	F 16	F 17 64,8 s	F 18 109,7 m	F 19 100	F 20 11,0 s
O 12	O 13 8,58 ms	O 14 70,59 s	O 15 2,03 m	O 16 99,762	O 17 0,038	O 18 0,200	O 19 27,1 s
N 11	N 12 11,0 ms	N 13 9,96 m	N 14 99,634	N 15 0,366	N 16 5,3 µs 7,13 s	N 17 4,17 s	N 18 0,63 s
C 10 19,3 s	C 11 20,38 m	C 12 98,90	C 13 1,10	C 14 5730 a	C 15 2,45 s	C 16 0,747 s	C 17 193 ms
B 9	B 10 19,9	B 11 80,1	B 12 20,20 ms	B 13 17,33 ms	B 14 13,8 ms	B 15 10,4 ms	
Be 8	Be 9 100	Be 10 $1{,}6 \cdot 10^6$ a	Be 11 13,8 s	Be 12 23,6 ms		Be 14 4,35 ms	
Li 7 92,5	Li 8 840,3 ms	Li 9 178,3 ms	Li 10	Li 11 8,5 ms		10	

- PROTRAC stands for: **production of tracers for atmospheric chemistry.**
- The aim of the PROTRAC project is to provide the short-lived radioactive isotopes ^{13}N,^{11}C and ^{15}O to the PSI laboratories for experiments in atmospheric chemistry. To study interactions between gas molecules and surface highly sensitive techniques are used which employ radioactive-labelled molecules. The isotopes are produced by irradiation of a gas stream in a target by a proton beam.

Transuranium (TU) and Superheavy Elements: Introduction

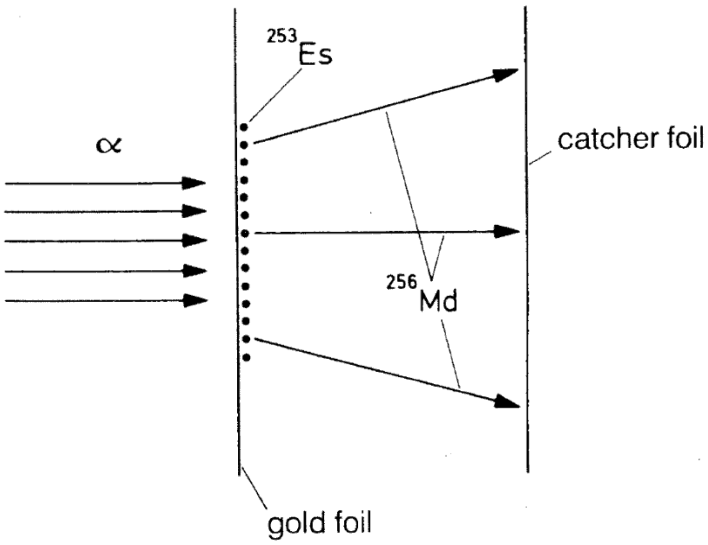
- ☐ The chemical behavior of the TU ($Z>92$) elements is of considerable interest because:
  - It is very complex and offers insights into the chemistry of the lighter elements.
  - It gives the unique opportunity to test periodic table predictions of chemical behavior **before** the relevant experiments are done.
  - Especially the environmental chemistry of the TU elements has become more important due to their large production in the recent decades by the nuclear power industry.
- ☐ To describe atomic orbitals of TU elements, relativistic quantum mechanics must be applied (instead of the Schrödinger- the Dirac-equation must be solved).
- ☐ In order to detect new (super)heavy elements often single atoms must be counted using radiochemical methods.
- ☐ In the recent decades there has been a scientific race to extend the periodic table and synthesize new elements. The various methods of production of TU elements are:
  1. Irradiation with neutrons: ${}^{A}Z(n,\gamma){}^{A+1}Z(\beta^{-})\,{}^{A+1}(Z+1)$
  2. Irradiation with deuterons or α –particles: ${}^{A}Z(d,n){}^{A+1}(Z+1)$ or ${}^{A}Z(\alpha,n){}^{A+3}(Z+2)$
  3. Irradiation with heavy ions: ${}^{A}Z + {}^{A'}Z' \rightarrow {}^{A+A'-x}(Z+Z') + xn$

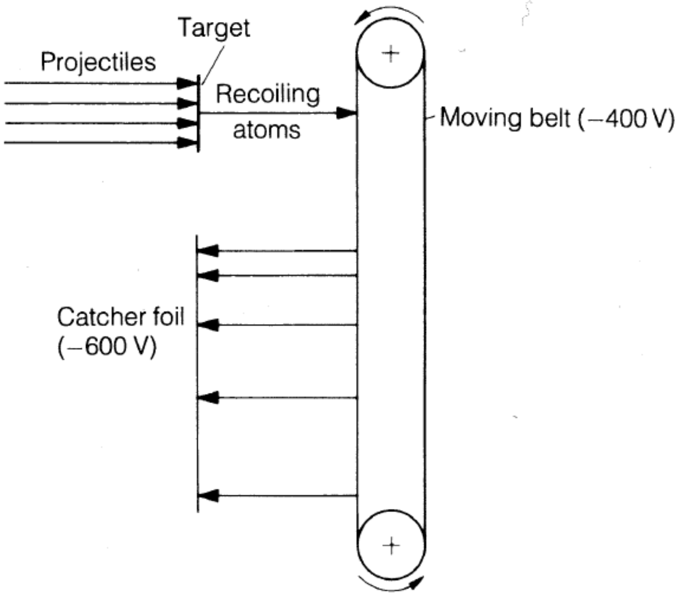
Production of TU elements by (n,γ)-Reactions and β-Decays (1)



Production of transuranium elements by neutron irradiation of ^{238}U.

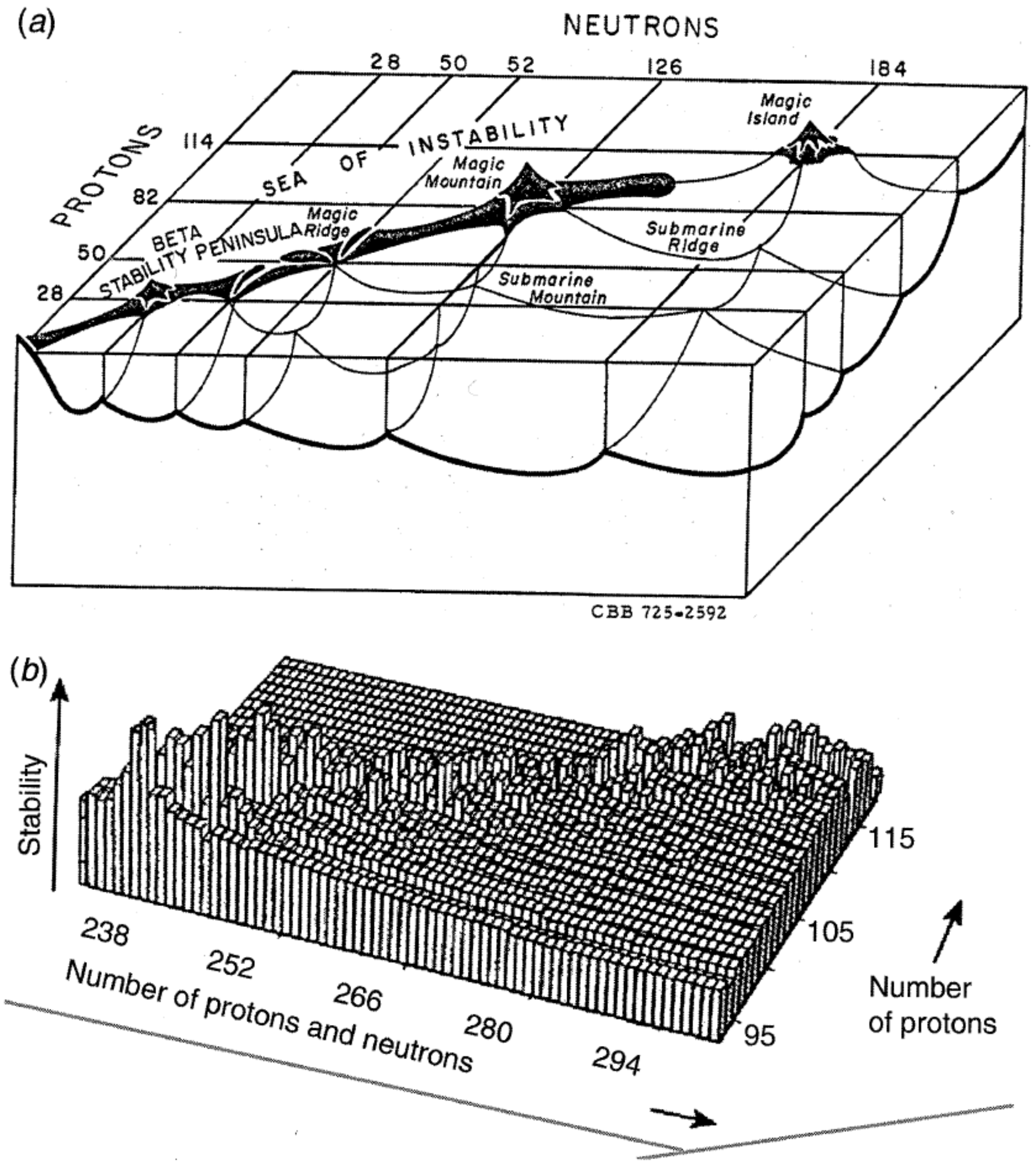
Production of TU Elements (2)





- The TU elements neptunium (Z=93), plutonium (Z=94), Americium (Z=95), Curium (Z=96), Berkelium (Z=97), Californium (Z=98), were synthesized between 1940-1950 by methods 1+2.
- Einsteinium (Z=99) and fermium (Z=100) were identified in the debris of the first thermonuclear explosion (i.e., were made via method 1) in 1952/53.
- Mendelevium (Z=101) was produced in 1955 by the reaction ^{253}Es(α,n)^{256}Md using the recoil technique for separation.
- For the production of elements with Z>101 heavy ion reactions with Z'>2 are necessary, because for irradiation with α-particles actinides with adequate $T_{½}$ as targets are not available. Two concepts for the synthesis of new, heavy nuclides are distinguished:
  - **hot fusion**: irradiation of actinides with ions of low atomic numbers (Z=5-16) leading to high excitation energies
  - **cold fusion**: irradiation of spherical closed-shell nuclei, like ^{208}Pb, with ions of medium Z (18-36) leading to low excited states
- Nobelium (Z=102) was synthesized in 1957 using a double recoil technique via the ^{246}Cm(^{12}C,4n)^{254}No(α)^{250}Fm reaction.

Production of TU and Superheavy Elements (3)



- Lawrencium(Z=103), rutherfordium (Z=104), dubnium (Z=105), seaborgium (Z=106) were produced via the hot fusion technique between 1961 and 1974.
- The concept of cold fusion was applied for the synthesis of the elements 107 to 112 (bohrium Z=107, hassium Z=108, meitnerium Z=109) in the years 1981-1996.
- Also using cold fusion the elements with Z=114,116,118 were made in 1999.
- In 2004 the synthesis of the superheavy elements with Z=113 and Z=115 was reported using cold fusion (PRC**69**,021601).
- Some nuclear structure calculations predicted an island of relative nuclear stability around Z=114 and N=184.

Summary

- ☐ **One of the main advantages of radionuclide applications in chemistry** is their generally **high sensitivity**.
- ☐ **Radiotracer methods** in chemistry allow investigation of the fate of the labelled elements and compounds in the course of chemical reactions or transport processes. Thus radiotracer techniques:
  - **offer unique possibilities for the study of reaction mechanisms in systems**
  - give often information that cannot be obtained by other means
  - have proved to be indispensable with respect to revealing the examination of individual steps of an analytical procedure, in particular with the aim of revealing the sources of systematic errors (**“referee method”, blank-free technique**).
- ☐ **Isotope dilution analysis is very powerful tool**, because:
  - It allows to determine the exact amount of a specific component, especially in complex mixtures of components (e.g., biochemical systems).
  - The main advantage of the method is that a quantitative separation of the element or compound to be determined is not necessary. This is substituted by measuring any fraction.
- ☐ **The chemical behavior of the TU (Z>92) elements is of considerable interest** because:
  - It is very complex and offers insights into the chemistry of the lighter elements.
  - It gives the unique opportunity to test periodic table predictions of chemical behavior **before** the relevant experiments are done.
- ☐ There is a strong radiochemistry group at PSI working in the fields of environmental chemistry (analytical and surface Chemistry) and heavy elements.

Literature / WWW-references

- ☐ K.H. Lieser, *“Nuclear and Radiochemistry”*, WILEY-VCH (2nd edition, 2001) **Chapters 17, 18**
- ☐ W. Loveland, D.J. Morrissey, G.T. Seaborg, “Modern Nuclear Chemistry”, WILEY (2006)
- ☐ G.C. Lowenthal, P.L. Airey, *“Practical Applications of Radioactivity and Nuclear Reactions”*, Cambridge University Press (2001) **Chapter 9**
- ☐ Home page of the *“Laboratory for Radiochemistry and Environmental Chemistry”* at PSI: **http://lch.web.psi.ch**