

A Rapid Electrical Method of Separating CarrierFree Radioactivities

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Citation: [The Journal of Chemical Physics](#) **17**, 665 (1949); doi: 10.1063/1.1747358

View online: <http://dx.doi.org/10.1063/1.1747358>

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In our experiments thus far, either *n*-propyl alcohol, *n*-butyl alcohol or *n*-propyl ether served as solvent for the first step and for the second, pairs of the following hydrocarbons in various proportions—methane, propane, propene, butene-1, and isopentane. A number of combinations proved to be homogeneous and fluid at the temperature of liquid nitrogen.

One of the above combined solvents was tested and found to remain fluid at about five degrees below the freezing point of nitrogen. Its composition was 1 part by volume of *n*-propyl alcohol, 4.5-parts liquid propane, and 4.5-parts liquid propene.

A number of hexahydrated rare earth bromides and nitrates were dissolved in such solvents, and absorption spectra were taken at the temperatures of liquid nitrogen. Solubilities of some of the rare earths were sufficient at 77°K for obtaining spectra in a path length of 25 cm. At a given concentration of a rare earth, (neodymium nitrate hexahydrate) the solution kept at 77°K for nine days remained clear and continued to give the same spectrum. When somewhat more was dissolved at about 175°K, a reduction in temperature to 77°K brought a quick appearance of turbidity, indicating that transformations were occurring at the low temperatures. The spectra of some of the dissolved salts became comparable in sharpness with those from their crystals at the low temperature. Bands arising at higher temperatures became resolved into lines at 77°K.

The line widths in the spectra of neodymium and samarium salts ranged from about one to five angstroms. The dissolved praseodymium and thulium salts gave more diffuse lines. The bromide and nitrate of neodymium showed strikingly different structures within corresponding groups, both in the spacings and numbers of component lines, indicating different symmetries of the fields about the positive ions. There were marked changes in the spectra on reducing the temperature from that of dry ice to that of liquid nitrogen. The refinement in the spectrum of samarium bromide hexahydrate was especially great on lowering the temperature.

Electrical conductances were measured over a range of temperatures and were found to drop rapidly at the lowest temperature, finally reaching in one solution 2×10^{-11} mhos for the specific conductance at 77°K.

Detailed descriptions of methods and results will be given in full detail in future papers.

We wish to express our indebtedness to Dr. Fred J. Leitz for his collaboration in the early stages of this work.

This contract is based on work performed under Contract Number W-7405 eng. 26 for the Atomic Energy Project at Oak Ridge National Laboratory.

milligram amounts, was evaporated onto a circular filter paper and placed in the center of the stack which had been previously moistened with a suitable electrolyte. A direct current of 0.04 ampere/cm² for a half hour was sufficient to move ions through about 15 layers of filter paper. By a proper choice of complexing ions and pH, the desired activity could be moved to either one of the electrodes or retained at the initial position in the center of the stack. In some mixtures, one activity migrated to one of the electrodes, milligram amounts of non-isotopic elements to the other, while impurity activities remained at the initial position. Recovery of the desired fraction consisted simply of removing filter papers from the appropriate region of the stack. The activity was usually concentrated in less than five adjacent papers.

In each of the separations described below, 0.20 ampere was passed for one half hour through a stack of 30 filter papers, 2.6 cm in diameter.

(1) Separation of carrier-free radio-columbium from manganese dioxide precipitate: A solution of the precipitate in 5 percent oxalic acid was evaporated onto a filter paper and placed in the middle of the stack which had been saturated with 1*m* ammonium oxalate solution. Under these conditions, columbium migrated to the anode region and manganous ions migrated to the cathode.

Another sample of precipitate was dissolved in concentrated hydrochloric acid and was placed in a stack saturated with 3*N* hydrochloric acid. The columbium activity remained on the original papers and the manganous ions migrated to the cathode.

(2) Separation of carrier-free radio-columbium and radio-zirconium from radio-yttrium and rare earth activities: A sample of solution was electrolyzed in a stack saturated with 1*m* ammonium oxalate. Columbium and zirconium were recovered in the anode papers. Yttrium and rare earth activities (Eu, Nd, and Pr) remained on the original paper.

(3) Separation of carrier-free radio-arsenic from milligram amounts of copper hydroxide carrier: The precipitate was dissolved and electrolyzed in 3*N* hydrochloric acid. The arsenic activity remained in original position. Cupric ions migrated to the cathode.

The technique has also been used as a rapid preliminary test in establishing the chemical identity of carrier-free radio-isotopes. For example, an activity which is found to migrate in dilute hydrochloric acid cannot be radio-arsenic.

Other applications of this type are obvious.

We are grateful to Dr. J. G. Hamilton for his interest in this problem.

* Lieutenant Colonel, U. S. Army.

† This work was performed under the auspices of the U. S. AEC, contract W-7405-eng-48A-1.

¹ Kendall and Crittenden, *Proc. Nat. Acad. Sci.* **9**, 75 (1923).

² Kendall and Clarke, *Proc. Nat. Acad. Sci.* **11**, 393 (1925).

³ Kendall and West, *J. Am. Chem. Soc.* **48**, 2619 (1926).

A Rapid Electrical Method of Separating Carrier-Free Radioactivities

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May 3, 1949

ELEMENTS with similar chemical properties may be separated by electrical transference methods as shown by the work of Kendall and co-workers.¹⁻³ We have found a modification of their technique to be of value for rapid separations of carrier-free radioisotopes from other activities and from milligram amounts of non-isotopic carriers.

Our apparatus consists of a stack of filter papers moistened with electrolyte and placed between two platinum electrodes. In a typical separation, a sample of solution containing one or more carrier-free radio-elements, and possibly other stable elements in

Selection Rules for Singlet-Triplet Perturbations in Polyatomic Molecules

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May 13, 1949

IN a recent paper¹ Shull has shown that the triplet-singlet emission band of benzene has the vibrational structure of a ¹B_{1u}—¹A_{1g} transition thus showing that the perturbing singlet state is a ¹B_{1u} state. The question of the symmetry of the triplet state required by this observation was not definitely decided, although by analogy with the rule for diatomic molecules that ³Σ⁺ states perturb ¹Σ⁻ states, Shull tentatively concluded that

TABLE I. Spin-orbit perturbations in polyatomic molecules.

The + signs mean that all components of the spin-orbit operator connect the states shown. σ means that the principle axis component and π that the perpendicular components connect the states. x , y , and z mean that these particular Cartesian components of the spin-orbit operator connect the states shown.

$C_{\infty v}$	Σ^+	Σ^-	π	Δ	T_d	A_1	A_2	E	F_2	F_1
Σ^+	0	σ	π	0		0	A_1	A_2	E	F_1
Σ^-	σ	0	π	0	A_1	A_1	0	0	0	+
π	π	π	σ	π	A_2	A_2	0	0	0	+
Δ	0	0	π	σ	E	E	0	0	0	+
					F_2	F_1	+	0	+	+
					F_1	F_2	0	+	+	+

D_6	A_1	A_2	B_1	B_2	E_1	E_2	D_4	A_1	A_2	B_1	B_2	E
A_1	0	σ	0	0	π	0	A_1	0	σ	0	0	π
A_2	σ	0	0	0	π	0	A_2	σ	0	0	0	π
B_1	0	0	0	σ	0	π	B_1	0	0	0	σ	π
B_2	0	0	σ	0	0	π	B_2	0	0	σ	0	π
E_1	π	π	0	0	σ	π	E	π	π	π	π	σ
E_2	0	0	π	π	π	σ						

C_{2v}	A_1	A_2	B_1	B_2
	D_2	A_1	B_1	B_2
A_1	A_1	0	z	y
A_2	B_1	z	0	x
B_1	B_2	y	x	0
B_2	B_3	x	y	z

the triplet state must be $^3B_{2u}$. A closer study of the selection rules has verified this conclusion.

The simplest way to derive the selection rules is to consider the group properties of the spin-orbit interaction operator. This is the part of the Hamiltonian principally responsible for mixing singlet and triplet states. For a system of n electrons (n even in our case) and m nuclei, the spin-orbit operator can be written:

$$H' = \sum_i A_i (l_{xi}s_{xi} + l_{yi}s_{yi} + l_{zi}s_{zi}),$$

with

$$A_i = \sum_k \frac{1}{r_{ik}^3} \frac{V(r_{ik})}{r_{ik}}.$$

In this formula, l_{xi} is the operator for the x component of the orbital angular momentum for electron i and s_{xi} is the operator for the x component of the spin angular momentum for electron i . r_{ik} is the distance of electron i from nucleus k , and $V(r_{ik})$ is the potential at the position of electron i due to nucleus k .

H' may be separated into sums whose orbital and spin factors are separately symmetric or antisymmetric under the operation of electron interchange. One component would be:

$$H'_x = \frac{1}{2n} \sum_{i=1}^n \sum_{j=1}^n (A_i l_{xi} + A_j l_{xj})(s_{xi} + s_{xj}) + \frac{1}{2n} \sum_{i=1}^n \sum_{j=1}^n (A_i l_{xi} - A_j l_{xj})(s_{xi} - s_{xj})(i \neq j).$$

The first (symmetric) part splits the degenerate triplet level, and the second (antisymmetric) part mixes singlet and triplet states. We shall be interested in the second part.

Assuming now that we have product type spin-orbit functions, the matrix elements of the spin-orbit operator split up into separate integrals over orbital and spin coordinates. The orbital and spin wave functions are assumed to transform properly under the operations of the symmetry group of the molecule. We will consider only the selection rules for the orbital part of the wave function, at present. Presumably, at least one of the triplet components may be perturbed by a singlet state.

The integral over space coordinates will be non-zero when the product of the representation of the wave functions contains the

representation of the significant part of the spin-orbit operator, viz. $A_i l_{xi} - A_j l_{xj}$ etc. Since the A_i remain unchanged by symmetry operations, the l_i determine the symmetry properties of the spin-orbit operator. The angular momentum operators have the symmetry properties of rotation operators. Hence with the help of character tables the selection rules may be written down. The rules $g \leftrightarrow g$, $u \leftrightarrow u$, $g \leftrightarrow u$ and $+\leftrightarrow -$ are found directly, and agree with what is known from atomic and diatomic molecular spectra. Analogous to the latter rule in D_{6h} is the rule $B_{1u} \leftrightarrow B_{2u}$ which confirms Shull's tentative conclusion. Selection rules for the more important symmetry groups are given in the tables. The rules for D_{6h} etc., may be derived from those given for D_6 by applying the $g \leftrightarrow g$, $u \leftrightarrow u$ rule.

Many of these same results can be obtained from the correlation between the continuous rotation groups and the point groups, established by Bethe.² The method used here seems simpler and more direct.

¹ H. Shull, J. Chem. Phys. 17, 295 (1949).

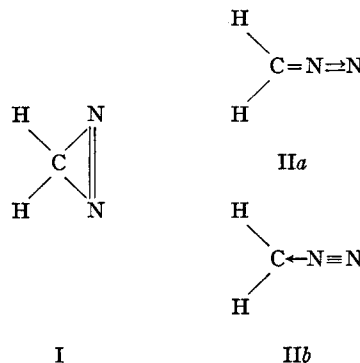
² H. Bethe, Ann. d. Physik 3, 133 (1929).

The Infra-Red Spectrum and Structure of Diazomethane*

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April 26, 1949

THE structure of diazomethane¹ has been represented by a cyclic formula I and by the straight chain formulas IIa and IIb. Measurements



of the ultraviolet absorption spectrum² were interpreted in favor of the cyclic structure but electron diffraction investigations³ subsequently provided strong evidence for a straight chain structure. The low dipole moment⁴ of the diazo group however excludes either of the straight chain structures separately, but is consistent with a resonance hybrid of the two structures.

The infra-red spectrum of diazomethane vapor has been measured with a Perkin-Elmer Model 12B infra-red spectrometer and shows a very close similarity to the infra-red spectrum of ketene.⁵ Strong "parallel" type bands were observed at 3074, 2103, 1416, and 852 cm^{-1} with PR separations of $\sim 27 \text{ cm}^{-1}$ (cf. the ketene bands at 3066, 2153, 1386, and 1120 cm^{-1} with PR spacings of $\sim 25 \text{ cm}^{-1}$). These bands may be assigned to the four totally symmetric vibrations of the straight chain structure. Several perpendicular type bands were resolved and showed the intensity alternation associated with a twofold axis of symmetry.⁶ A weak perpendicular type band was observed in the region of 3150 cm^{-1} with a spacing of $\sim 18 \text{ cm}^{-1}$ but only three Q branches were free from overlapping by neighboring absorption bands. A complex