

We would like to express our appreciation to Professor Felix Bloch for his continued interest in our work. Thanks are also due Mr. William S. Gorton Jr. of the Department of Chemistry for preparing the liquid ammonia sample.

\* Assisted by the Joint Program of the AEC and the ONR.

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<sup>11</sup>F. Bitter, *Phys. Rev.* **75**, 1326 (1949).  
<sup>12</sup>This figure is that given by Bloch, Levinthal, and Packard, *Phys. Rev.* **72**, 1125 (1947), rounded to six places.

### The Dependence of a Nuclear Magnetic Resonance Frequency upon Chemical Compound\*

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January 18, 1950

IN the course of measurements on  $N^{14}$ , mentioned in the previous letter, we made the surprising observation that its frequency of resonance, in liquid samples, depended strongly upon the chemical compound in which it was contained.<sup>1,2</sup> This effect is strikingly demonstrated by the appearance of two resonances, separated by 1.6 kc in the neighborhood of 3300 kc, corresponding to a field of 10,500 gauss, using a solution of  $NH_4NO_3$  in 2.0-molar  $MnSO_4$  as a sample. These resonances presumably arise from the  $NH_4^+$  and  $NO_3^-$  complexes, since samples of  $NH_4C_2H_3O_2$  and  $HNO_3$  separately give rise to two different resonances whose frequencies approximate those from the above sample. The separation is four times greater than the line widths measured between points of maximum slope.

We have observed, within a resolution of 0.1 kc, that the  $N^{14}$  resonances from the ion  $NH_4^+$  from the compounds  $NH_4NO_3$ ,  $NH_4C_2H_3O_2$ , and  $MH_4Cl$  coincide at one frequency, while those from the ion  $NO_3^-$  from the compounds  $NH_4NO_3$ ,  $HNO_3$ , and  $Cu(NO_3)_2$  coincide at another frequency. Measuring the  $N^{14}$  resonances from other molecules relative to that arising from the ion  $NO_3^-$  from  $HNO_3$  or  $NH_4NO_3$ , we have obtained the results given in Table I. All such frequency shifts have been in the direction of lower frequency.

The separations of resonances from four pairs of compounds were also measured at 6700 gauss, corresponding to a frequency of 2100 kc, to determine whether or not the frequency separations were independent of the field intensity. They are apparently proportional to it, for the ratios of the separations are in agreement

TABLE I. Frequency shifts relative to the resonance from the ion  $NO_3^-$  at 10,500 gauss.

Compound observed	Frequency shift (kc)
$NH_4^+$ from $NH_4NO_3$ , $NH_4C_2H_3O_2$ , $NH_4Cl$	-1.0
Liquid $NH_3$ , containing 0.6-molar $Cr(NO_3)_3$ ; $NH_4OH$	-1.2
$(NH_2)_2CO$	-1.0
KCN	-0.2

TABLE II. Resonance frequency separations with different compounds and field intensities.

Compounds compared	Separation (kc) at		Ratio
	10,500 gauss	6700 gauss	
$NH_4^+$ and $NO_3^-$ from 7.5-molar $NH_4NO_3$ in 2.0-molar $MnSO_4$	1.6	0.9	0.58
$HNO_3$ and $NH_4C_2H_3O_2$	1.0	0.7	0.70
$HNO_3$ and $(NH_2)_2CO$	1.0	0.6	0.60
$NH_3$ , containing 0.6-molar $Cr(NO_3)_3$ and $NO_3^-$ , from $NH_4NO_3$	1.2	0.7	0.58

with the ratio  $6700/10,500=0.64$ , within our experimental resolution. (See Table II.)

We further made the observation that the separation of the two resonances arising from  $NH_4NO_3$  was dependent on the concentration of the paramagnetic salt  $MnCl_2$  added to it. A 7.5-molar solution of this salt without  $MnCl_2$  shows two resonances separated by 1.0 kc, as given in Table I, but with 1.0- and 2.0-molar concentrations of  $MnCl_2$  the separations become 1.4 kc and 1.6 kc, respectively.

We shall continue to investigate this phenomenon because of its direct significance for the interpretation of nuclear magnetic resonance frequencies in terms of nuclear moments, as well as to obtain an insight into its origin. With the largest observed line shift amounting to about 5 parts in  $10^4$ , this effect is almost twice as large as the total diamagnetic correction calculated for the atom. These calculations, however, do not hold for the polyatomic molecules which we have studied and appreciable modification of the diamagnetism, as well as terms due to induced paramagnetism (high frequency matrix elements) can be expected, particularly in cases where three out of seven electrons may be strongly influenced by the chemical bond. The fact that the shifts are of the same order of magnitude as the diamagnetic correction and exhibit likewise proportionality to the applied field suggests a similar origin, although we have not been able to explain satisfactorily the observed magnitude of the effect. Until it is clearly understood, the accuracy of magnetic moments determined under certain chemical conditions remains somewhat in doubt.

We should like to express our appreciation to Professor Felix Bloch for stimulating discussions about this work.

\* Assisted by the Joint Program of the AEC and the ONR.

<sup>1</sup>W. C. Dickinson, at M. I. T., has also observed similar shifts for  $F^{19}$  in different compounds. We are grateful to Professor F. Bitter for communicating this information to us.

<sup>2</sup>W. D. Knight, *Phys. Rev.* **76**, 1259 (1949), has observed a large frequency difference between the nuclear magnetic resonance frequency of a metal and its salt. The satisfactory explanation which he has given for this difference does not apply, however, to our case.

### Spallation Products of Arsenic with 190-Mev Deuterons\*

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January 5, 1950

RECENT investigations<sup>1</sup> of the nuclei formed when arsenic is bombarded with 190-Mev deuterons in the 184-in. cyclotron have been extended.

The target material consisted of twice sublimed arsenic. Spectrographic analysis<sup>2</sup> showed no impurity in sufficient quantity to account for the formation of any of the isotopes reported here with the observed yield.

The use of improved chemical separations and counting techniques has enabled the identification of 38 nuclear species among the elements from chromium through selenium. Table I lists the isotopes identified, the observed and the "nominal" half-lives as reported in the literature,<sup>3</sup> and the yields relative to that of  $As^{72}$  taken as 1.00.

In calculating yields, the extent of electron capture has been taken from the data collected in reference 3. For  $Se^{73}$ ,  $Ge^{69}$ , and  $Ga^{66}$ , crude absorption measurements indicated that approximately two-thirds of the decays are by electron capture. The yield of  $As^{72}$  is based on the count of beta-particles, as no x-rays were observed (< 50 percent of the disintegrations). The yields reported here should all be accurate to within a factor of two and many accurate to within 20 percent, depending on the certainty with which electron-capturing ratios and counting efficiencies of x-rays are known.

Table I contains two changes in isotope assignment differing from those previously reported.<sup>1</sup> The 44-min. selenium and 52-min.

arsenic daughter are placed at mass 70 since careful separations revealed no active germanium daughter. The 40-hr. germanium cannot be found when germanium is chemically separated from the 60-hr. As<sup>71</sup>, so the former is assigned to mass 69, in agreement with the work of McCown, Woodward, and Pool.<sup>4</sup>

It is reasonable to assume that stable nuclei are formed in the spallation process with yields of the same order of magnitude as those of the adjacent isotopes. On this basis we assign a yield to each isotope which we cannot observe, following the trends

TABLE I. Isotopes produced by <sup>32</sup>As<sup>76</sup>+D<sup>+</sup> (190 Mev).

Isotope	Radiation type <sup>a</sup>	Nem. half-life <sup>a</sup>	Obs. half-life	Yield rel. As <sup>72b</sup>
<sup>68</sup> Se <sup>75</sup>	K	127 days	120 days	0.14
<sup>69</sup> Se <sup>72</sup>	β <sup>+</sup> , K	6.7 hr.	6.7 hr.	0.3
<sup>70</sup> Se <sup>72</sup>	K	9.5 days	9.7 days	0.008 <sup>c</sup>
<sup>70</sup> Se	β <sup>+</sup>	44 min.	~44 min.	0.004 <sup>c</sup>
<sup>74</sup> As <sup>74</sup>	β <sup>+</sup> , β <sup>-</sup>	17.5 days	19 days	1.25
<sup>75</sup> As <sup>73</sup>	K	90 days	(long)	2
<sup>76</sup> As <sup>72</sup>	β <sup>+</sup>	26 hr.	26.7 hr.	1.00 <sup>b</sup>
<sup>77</sup> As <sup>71</sup>	K	60 hr.	60 hr.	0.7 <sup>c</sup>
<sup>78</sup> As <sup>70</sup>	β <sup>+</sup>	52 min.	52 min.	0.1
<sup>71</sup> Ge <sup>71</sup>	K	11 days	11 days	2.0
<sup>72</sup> Ge <sup>69</sup>	β <sup>+</sup> , K	39.7 hr.	40 hr.	0.9
<sup>73</sup> Ge <sup>68</sup>	K	250 days	250 days	0.3 <sup>c</sup>
<sup>74</sup> Ge <sup>67</sup>	β <sup>+</sup>	23 min.	21 min.	0.1 <sup>c</sup>
<sup>75</sup> Ge <sup>66</sup>	β <sup>+</sup> (?)	140 min.	~150 min.	0.008 <sup>c</sup>
<sup>70</sup> Ga <sup>70</sup>	β <sup>-</sup>	20.3 min.	20 min.	0.018
<sup>71</sup> Ga <sup>68</sup>	β <sup>-</sup>	68 min.	70 min.	0.56
<sup>72</sup> Ga <sup>67</sup>	K	78.3 hr.	80 hr.	1.0
<sup>73</sup> Ga <sup>66</sup>	β <sup>+</sup> , K	9.4 hr.	9 hr.	0.6
<sup>72</sup> Zn <sup>72</sup>	β <sup>-</sup>	49 hr.	~50 hr.	0.0002
<sup>73</sup> Zn <sup>69m</sup>	I.T.	13.8 hr.	13.5 hr.	0.015
<sup>74</sup> Zn <sup>65</sup>	β <sup>+</sup> , K	250 days	(long)	0.2
<sup>75</sup> Zn <sup>64</sup>	β <sup>+</sup> , K	38 min.	39 min.	0.02
<sup>76</sup> Zn <sup>62</sup>	K	9.5 hr.	10 hr.	0.002 <sup>c</sup>
<sup>67</sup> Cu <sup>67</sup>	β <sup>-</sup>	56 hr.	61 hr.	0.013
<sup>68</sup> Cu <sup>64</sup>	β <sup>+</sup> , β <sup>-</sup> , K	12.8 hr.	12.8 hr.	0.20
<sup>69</sup> Cu <sup>65</sup>	β <sup>+</sup>	10.5 min.	10 min.	0.10
<sup>70</sup> Cu <sup>61</sup>	β <sup>+</sup> , K	3.4 hr.	3.3 hr.	0.03
<sup>66</sup> Ni <sup>66</sup>	β <sup>-</sup>	56 hr.	56 hr.	0.0006 <sup>c</sup>
<sup>67</sup> Ni <sup>65</sup>	β <sup>-</sup>	2.6 hr.	2.6 hr.	0.003
<sup>68</sup> Ni <sup>57</sup>	β <sup>+</sup>	36 hr.	34 hr.	0.00003
<sup>61</sup> Co <sup>61</sup>	β <sup>-</sup>	1.75 hr.	1.83 hr.	0.014
<sup>62</sup> Co <sup>58</sup>	β <sup>+</sup> , K	72 days	~100 days	0.006
<sup>63</sup> Co <sup>55</sup>	β <sup>+</sup>	18.2 hr.	~18 hr.	0.0002
<sup>59</sup> Fe <sup>59</sup>	β <sup>-</sup>	46.3 days	46 days	0.005
<sup>56</sup> Mn <sup>56</sup>	β <sup>-</sup>	2.59 hr.	2.6 hr.	0.0026
<sup>57</sup> Mn <sup>52</sup>	β <sup>+</sup> , K	5.8 days	6.2 days	0.0003
<sup>61</sup> Cr <sup>61</sup>	K	26.5 days	25 days	0.002
<sup>62</sup> Cr <sup>49</sup>	β <sup>+</sup>	41.9 min.	40 min.	0.00006

<sup>a</sup> See reference 3.

<sup>b</sup> Absolute yield of As<sup>72</sup>: 0.02 barn.

<sup>c</sup> Determined from measurement of daughter activity.

apparent among the observed isotopes. The resultant yield pattern can be described as follows: (1) For each element below arsenic, the yields of the isotopes increase towards the line of nuclear stability. (2) For each mass number the yields of isobars increase towards the line of stability. (3) The lower the atomic number, the lower becomes the total yield of a given element.

From a consideration of the *Q*-values of the reactions and the energy necessary for Coulombic barrier penetrations, we conclude: (1) Reactions leading to arsenic, germanium, and gallium isotopes are mostly non-capture excitation reactions, in which only a fraction of the deuteron's energy is imparted to the nucleus. These comprise more than 90 percent of all the reactions. (2) Less likely processes involving preliminary capture of the deuteron lead to isotopes of lower lying elements. (3) The formation of nuclear species lower than Fe<sup>59</sup> involves the emission of one or more alpha-particles. Such reactions occur approximately one percent of the time.

The author wishes to thank Mr. James Vale and the members of the 184-in. cyclotron group for performing the many bombard-

ments. He acknowledges the helpful advice of Professors B. B. Cunningham and G. T. Seaborg.

\* This work was performed under the auspices of the AEC.

<sup>1</sup> H. H. Hopkins, Jr. and B. B. Cunningham, Phys. Rev. **73**, 1406 (1948).

<sup>2</sup> Analysis performed by Mr. John Conway.

<sup>3</sup> Table of Isotopes from G. T. Seaborg and I. Perlman, Rev. Mod. Phys. **20**, 585 (1948).

<sup>4</sup> McCown, Woodward, and Pool, Phys. Rev. **74**, 1311 (1948).

## Electron Recombination in Helium

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January 18, 1950

RECENTLY, Biondi and Brown<sup>1</sup> have applied microwave techniques to the study of the rate of decay of ionization in helium. Their main object was the investigation of ambipolar diffusion, but they also took the opportunity of measuring the effective electron recombination coefficient,  $\alpha$ , under the following conditions: mean electron energy, 0.039 eV; electron concentration from  $8 \times 10^9$  to  $3 \times 10^{10}$ /cm<sup>3</sup>; gas pressure from 20 to 30 mm Hg. They found it to be  $1.7 \times 10^{-8}$  cm<sup>3</sup>/sec.

With ions of an *atomic* nature only three types of mechanism seem possible, either (a) that the excess energy of the recombining electrons appears as radiation, (b) that it is given up to some third body, or (c) that the electrons disappear through attachment to impurities. We will consider these separately.

(a) Goldberg<sup>2</sup> and Huang<sup>3</sup> have computed the relevant matrix elements associated with direct radiative recombination to the 1<sup>1</sup>S, 2<sup>1</sup>S, 2<sup>3</sup>S, 2<sup>1</sup>P and 2<sup>3</sup>P levels; those for the remaining levels can be taken as hydrogenic.<sup>4</sup> An elementary calculation shows that the total contribution to  $\alpha$  is only about  $4 \times 10^{-12}$  cm<sup>3</sup>/sec.

In the case of helium there are no suitably located doubly excited states so that dielectronic recombination<sup>5</sup> can be ignored.

(b) A slow electron can lose only about  $10^{-3}$  to  $10^{-4}$  of its kinetic energy in a single collision with a helium atom.<sup>6</sup> Very many collisions are therefore required to bring about any considerable reduction. When allowance is made for this in the well-known Thomson theory<sup>7</sup> of three-body recombination, it appears that the process,  $\text{He}^+ + e + \text{He} \rightarrow 2\text{He}$ , is negligible. Other electrons may be more important as third bodies. The necessary formulation of the problem has not yet been developed in detail. However, the cross section for the energy-loss collisions is likely to be less than  $\pi r^2$ , where  $r$  is the distance such that  $e^2/r$  is equal to the mean energy of the electrons; and this yields an  $\alpha$  which is too small by more than an order of magnitude.

(c) If  $\eta$  is the coefficient associated with the postulated attachment process,  $n(x)$  is the concentration of foreign molecules, and  $n(e)$  is the concentration of electrons, then  $\eta n(x)/n(e)$  is the maximum possible contribution to  $\alpha$ . It appears that  $n(x)$  is perhaps  $10^{13}$ /cm<sup>3</sup> at a pressure of 25 mm Hg. Thus,  $\eta$  would have to be some  $2 \times 10^{-11}$  cm<sup>3</sup>/sec. to account for an  $\alpha$  of  $1.7 \times 10^{-8}$  cm<sup>3</sup>/sec. when  $n(e)$  is, say,  $10^{10}$ /cm<sup>3</sup>. This is improbably high.<sup>8</sup> Furthermore,  $\alpha$  would only be independent of  $n(e)$  if detachment was also rapid so that a quasi-equilibrium could be established between it and attachment;<sup>5</sup> and in this case a still greater  $\eta$  is needed.

It would seem, therefore, that the recombination measurements of Biondi and Brown are difficult to reconcile with the assumption that the ions involved were He<sup>+</sup>. If, instead, they were He<sub>2</sub><sup>+</sup>, the position would be quite different for dissociative recombination,  $\text{He}_2^+ + e \rightarrow 2\text{He}$ , could occur and quantum considerations indicate that this may well be of the required rapidity. It is perhaps relevant to mention that Bates and Massey<sup>9</sup> have suggested that reactions of this type may be mainly responsible for recombination in the ionosphere. Their hypothesis demands that the associated coefficient be of the order  $10^{-8}$  cm<sup>3</sup>/sec. The ions concerned are of course different, and  $\alpha$  may vary greatly from gas to gas.

He<sub>2</sub><sup>+</sup> is known to be stable and has been observed in the laboratory.<sup>10</sup> It may be formed from He<sup>+</sup> through the three-body