

## The Isotope Effect in the Evaporation of Lithium, Potassium and Rubidium Ions

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extreme curvature required by the experimental points but can only be shifted parallel to itself because of the uncertainty in  $\Delta E_0^\circ$ . The slight curvature in Fig. 2, mentioned above is probably due to the anharmonic terms and the rotational stretching terms in the energy expression for HI which also explains why Fig. 1 is a straight line since these quantities are nearly negligible for a heavy molecule like iodine.

*Note added in proof:* Further consideration shows that the attempted correction of Bodenstein's temperatures may not be justified as his experimental temperatures with the sulfur baths fit the theoretical curve as well as the corrected ones. However, this does not affect any of the calculations made above since either set of temperatures will give the same  $\Delta E_0^\circ$  within the probable error stated. The doubtful points are thus the ones at the lowest and highest temperatures which may be explained by errors in analysis or what is more likely some further uncertainty in the experiments.

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## The Isotope Effect in the Evaporation of Lithium, Potassium and Rubidium Ions

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(Received April 8, 1936)

Abundance ratio measurements are necessarily complicated by the possibility of an isotope effect at the source. In the emission of positive thermions of lithium, potassium and rubidium the extent to which the ion ratio represents the atom ratio within the source can be estimated by observing the change in the abundance ratio as a function of the percent of alkali evaporated. In the case of lithium an initial ratio of  $\text{Li}^7/\text{Li}^6 = 11.60$  was observed; the abundance ratio followed the computed ratio for ideal evapora-

tion until the lithium was 40 percent exhausted, beyond which it fell below the ideal value. The abundance ratios of  $\text{K}^{39}/\text{K}^{41} = 14.22$  and  $\text{Rb}^{85}/\text{Rb}^{87} = 2.59$  remained almost unchanged during the process of exhaustion. It is apparent therefore that a correction factor needs to be applied to the ion abundance ratio for lithium, but is unnecessary for potassium and for rubidium. The atomic weights computed from the abundance ratios are  $\text{Li} = 6.939$ ,  $\text{K} = 39.094$  and  $\text{Rb} = 85.46$ .

AN accurate estimation of isotope abundance ratios from mass-spectrographic measurements necessarily involves the question of an isotope effect at the positive ion source. The extent to which the ion ratio represents the true abundance ratio is amenable to a comparatively simple test in the case where positive thermions are used as the ion source.

In the mass spectrograph which was described recently,<sup>1</sup> heated platinum disks impregnated with alkali were used as the source of positive ions. These ion emitters were prepared by coating the platinum with a water paste made from the salt to be tested. These coated disks can be used directly as positive ion emitters, although platinum impregnated with alkali is in general the more satisfactory source. This impregnation is readily accomplished by heating the disk to dull redness in contact with the adhering coating for about half an hour; the coating is then removed by scraping and washing with distilled water.

During the heating process the platinum dissolves sufficient alkali to become an excellent emitter of positive ions.

The test for a preferential isotope effect in the emission of alkali ions was made by observing the changes in the abundance ratio as a function of the fraction of the alkali evaporated. This fraction was obtained from a determination of the time and current necessary for the complete exhaustion of the less abundant isotope; the abundance ratio was measured at regular intervals during the exhaustion period.

### RESULTS

The procedure just described yields the abundance ratio as a function of the less abundant isotope evaporated from the platinum. Curve A, Fig. 1 shows a representative run obtained with lithium. The initial abundance ratio,  $\text{Li}^7/\text{Li}^6 = 11.6$ , is the same as that reported previously.<sup>2</sup> During the exhaustion period it was necessary

<sup>1</sup> A. Keith Brewer, *J. Am. Chem. Soc.* **58**, 365 (1936).

<sup>2</sup> A. Keith Brewer, *Phys. Rev.* **47**, 571 (1935).

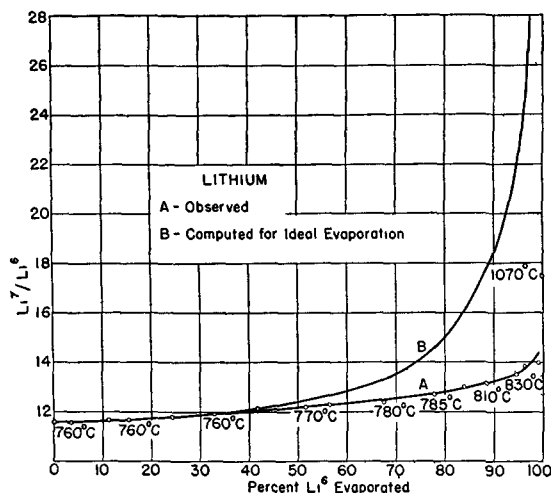


FIG. 1.

to raise the disk temperature to obtain sufficient current to measure the abundance ratio; the approximate temperatures at which the ratios were determined are shown accompanying the points. Temperature, in itself, appears to have little effect on the abundance ratio since it remained the same over the range of positive ion currents that could be investigated.

The results obtained with potassium are shown in line A, Fig. 2. The abundance ratio,  $K^{39}/K^{41} = 14.22$ , is essentially the same as that obtained from most mineral sources. This ratio remained almost unchanged throughout the evaporation period, dropping to 14.1 for about 90 percent emitted, and to 13.8 for the last traces of potassium left in the platinum.

The initial abundance ratio obtained from rubidium is  $Rb^{85}/Rb^{87} = 2.59 \pm 0.01$ . This is essentially the same as  $2.59 \pm 0.04$  obtained previously<sup>3</sup> but is lower than the value of  $Rb^{85}/Rb^{87} = 2.68 \pm 0.02$  recently reported by Nier,<sup>4</sup> using a different type of ion source. Since the previous value was obtained with an entirely different spectrograph and rubidium salt, it seems definite that the abundance ratio from this type of source is very close to  $Rb^{85}/Rb^{87} = 2.59$ .

The abundance ratio as a function of the percent of  $Rb^{87}$  evaporated is shown in Fig. 3. No measurable change was observed during the

<sup>3</sup> A. Keith Brewer and P. D. Kueck, Phys. Rev. **46**, 894 (1934).

<sup>4</sup> A. O. Nier, Phys. Rev. **49**, 272 (1936).

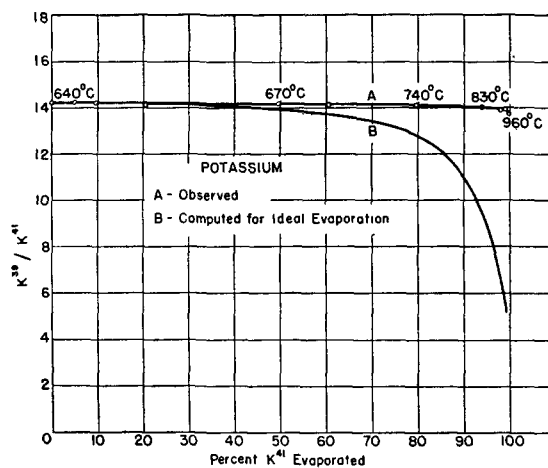


FIG. 2.

exhaustion period. The conspicuous fact to be observed in the above results is that potassium and rubidium show almost no isotope effect while lithium shows a marked shift in the abundance ratio during the evaporation period.

#### DISCUSSION OF RESULTS

The thermionic emission of positive ions from platinum impregnated with alkali offers two possibilities for the exhibition of an isotope effect: First, through a difference in the rate of diffusion to the surface, and second, through a difference in the rate of escape from the surface as positive ions.

Assuming that the alkali atoms are at liberty to diffuse freely through the platinum, the number  $N$  of atoms striking unit area of the bounding surface in unit time with a velocity component between  $u$  and  $u+du$  normal to the surface is

$$N(u)du = n(m/2\pi kT)^{1/2} u e^{-mu^2/2kT} du, \quad (1)$$

where  $n$  is the concentration of alkali atoms per unit volume of platinum and  $m$  is their mass.<sup>5</sup>

The total number of atoms striking the bounding surface is the integral of the above expression from 0 to  $\infty$  while the number escaping as ions is the integral between  $u_0$  and  $\infty$  where  $u_0$  is the minimum velocity for escape. Thus  $N^+$ , the number of positive ions escaping per second per sq. cm is

<sup>5</sup> L. B. Loeb, *Kinetic Theory of Gases* (McGraw-Hill).

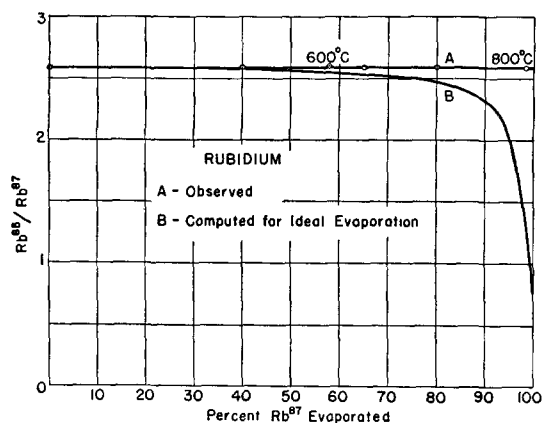


FIG. 3.

$$N^+ = n(kT/2\pi m)^{1/2} e^{-m u_0^2/2kT}. \quad (2)$$

This equation can be applied directly to the case of lithium, a similar equation being written for each isotope. This gives

$$n_7/n_6 = N_7^+/N_6^+ (m_7/m_6)^{1/2} e^{-(m_6 u_0^2 - m_7 u_7^2)/2kT} \quad (3)$$

for the abundance ratio of the isotopes in the metal ( $n_7/n_6$ ) as a function of the ratio of the positive ion currents ( $N_7^+/N_6^+$ ).

From this expression it will be seen that if perfect mixing of the lithium atoms takes place within the platinum the observed ion ratio must be multiplied by the square root of the ratio of the isotope masses to correct for the difference in the collision frequency with the bounding surface, and also by an exponential factor to correct for a possible difference in the work functions.

While it cannot be stated with certainty that the work function for the two isotopes is the same, the difference must be negligible since the ionization potential is the same for each to within one-millionth of a volt. This being the case the exponential factor becomes equal to one and can be neglected. In consequence it seems apparent that the ratio of the isotope atoms leaving the surface as positive ions is proportional to the concentration at the bounding surface. Any isotope effect that may exist, therefore, comes from the difference in the collision frequency with the surface.

Assuming the exponential factor in Eq. (3) is equal to unity and that perfect mixing takes place in the platinum disk used in these experi-

ments it is possible to compute the abundance ratio that should exist for the escaping ions at different stages of the evaporation of the alkali. Lines *B* in Figs. 1, 2 and 3 are so computed for various percentages of the lesser isotopes evaporated. A comparison of the observed *A* lines with the computed *B* lines gives, in consequence, the extent to which perfect mixing and ideal diffusion take place within the platinum source.

A possible explanation of the fact that lithium exhibits an isotope effect while potassium and rubidium do not may be found in the dimensions involved. The radius of the lithium ion is 0.6Å, potassium is 1.33Å, and rubidium is 1.48Å; the radius of the platinum atom in the metal is 1.39Å. A solid solution of potassium or rubidium in platinum, since the dimensions are essentially the same, will, therefore, be of the replacement type in which the alkali atom replaces a platinum atom in the metal lattice. In this case diffusion takes place step by step from lattice to lattice with little or no opportunity for mixing; an isotope effect, in consequence, is not to be expected. The lithium atom, on the other hand is small compared to the separation of the platinum atoms; here interstitial solution is possible in which the lithium atoms do not enter into the metal structure but actually penetrate the platinum lattice. The lithium atoms are in this case free to move more or less at random through the platinum mass, thus permitting a more ideal mixing than is possible in a replacement solution where the dissolved atoms are confined to fixed positions. This mixing is not perfect, however, since Fig. 1 shows that the computed and observed curves begin to diverge before the alkali is half exhausted. It has been pointed out that not all atoms colliding with the bounding surface will escape as positive ions, but only those of high energy content. This means that lithium atoms will tend to concentrate in the surface region thus congesting the interstitial space and obstructing the freedom of collision.

Results obtained with coated lithium aluminum silicate emitters lead to a conclusion of similar character. The abundance ratio remained constant at 11.60 for some time, then rose to a final value of 13.88 after prolonged heating above the fusion point.

The various methods that have been employed for the separation of isotopes have been discussed by Aston.<sup>6</sup> The present results suggest some of the conditions under which thermionic emission can be utilized for this purpose. It is evident that when the atoms to be emitted as thermions do not have to conform to any definite lattice structure within the emitter conditions approaching ideal evaporation may be realized. Emission from fused salts show an appreciable isotope effect. In the case of metallic emitters the positive ions which have been held in interstitial solution exhibit a preferential emission of the light isotope ions while those held in replacement solution show little if any effect.

The values for the abundance ratios which have just been presented may now be employed in estimating the atomic weights of these elements by the method recently described in detail for potassium.<sup>7</sup> The atomic weight of 39.094 obtained for potassium remains un-

changed. With 1.00027 for the conversion factor from the physical to the chemical scale and  $-8.2$  for the packing fraction, the atomic weight of rubidium comes out to be 85.46. This value compares favorably with 85.44 accepted by the committee on atomic weights and 85.48 recently obtained by Archibald, Hooley and Phillips.<sup>8</sup>

In estimating the atomic weight of lithium it is necessary to apply a correction for the isotope effect of free evaporation to the abundance ratio obtained from fresh filaments. Assuming this correction is initially that for ideal evaporation the abundance ratio becomes  $11.60\sqrt{7/6} = 12.52$ . With this corrected value for the abundance ratio and 7.0146 and 6.0146 obtained by Bainbridge<sup>9</sup> for the isotope masses the atomic weight comes out to be 6.939. The most recent values for the isotope masses<sup>10</sup> of  $\text{Li}^6 = 7.0180$  and  $\text{Li}^7 = 6.0167$  lead to 6.942 for the atomic weight. Both these values are in close agreement with the accepted value of 6.940.

<sup>6</sup> F. W. Aston, *Mass-Spectra and Isotopes* (Edward Arnold & Co., London, 1933).

<sup>7</sup> A. Keith Brewer, *J. Am. Chem. Soc.* **58**, 370 (1936).

<sup>8</sup> Archibald, Hooley and Phillips, *J. Am. Chem. Soc.* **58**, 70 (1936).

<sup>9</sup> K. T. Bainbridge, *Phys. Rev.* **44**, 56 (1933).

<sup>10</sup> M. L. Oliphant, *Nature* **137**, 396 (1936).

## Quantum-Mechanical Treatment of Helium Hydride Molecule-Ion $\text{HeH}^+$

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(Received March 23, 1936)

Helium hydride molecule-ion has been treated by the variation method, including ionic and polarization terms in the variation function and varying the effective nuclear charge. The equilibrium internuclear distance is found to be  $1.57a_0$ . Fitting a parabola to the lower part of the best potential energy curve leads to a value of 0.43 megadyne/cm for the force constant and a value of  $2800\text{ cm}^{-1}$  for the

fundamental vibration frequency. The minimum energy obtained for the system is  $-5.844W_H$ , which, when subtracted from the best value for the energy of the helium atom using the same type of variation function, gives a value for the dissociation energy of 2.02 ev. The doubly charged ion,  $\text{HeH}^{++}$ , is found to be unstable.

**S**INGLY charged helium hydride molecule-ion has been known<sup>1</sup> for many years from mass spectroscopic investigations of helium hydrogen mixtures. Its position with respect to that of  $\text{H}^2\text{H}^2\text{H}^{1+}$  in the mass spectrograph has been used to determine accurately the mass of the deuteron.<sup>2</sup> Spectroscopic work has not shown the existence of this ion.

The only previous quantum-mechanical discussion of  $\text{HeH}^+$  is a variation treatment made by Glockler and Fuller.<sup>3</sup> They consider two problems: (1) The interaction of a proton with an excited helium atom, the wave function for the electrons being  $\psi_1 = ae^{-\alpha r_1}$  and  $\psi_2 = (b + cr_2)e^{-\beta r_2}$ ; and (2) the interaction of a hydrogen atom with a singly ionized helium atom, the wave functions

<sup>1</sup> F. W. Aston, *Isotopes*, Both editions; T. R. Hogness and E. C. Lunn, *Phys. Rev.* **26**, 44 (1925).

<sup>2</sup> K. T. Bainbridge, *Phys. Rev.* **44**, 57 (1933).

<sup>3</sup> G. Glockler and D. L. Fuller, *J. Chem. Phys.* **1**, 886 (1933).