

Das gleiche gilt für die Umladung auf  $\text{SO}_2^-$ . Ähnliche Verhältnisse liegen bei den  $\text{PH}_2^-$ - und  $\text{PH}^-$ -Ionen vor. Da ein solcher Vorgang nur möglich ist, wenn die EA des stoßenden Ions kleiner ist als die des gestoßenen Moleküls, muß gelten:

$$\text{EA} \begin{matrix} (\text{PH}_2) \\ (\text{PH}) \\ (\text{AsH}_2) \\ (\text{AsH}) \end{matrix} < \text{EA} \begin{matrix} (\text{CS}_2) \\ (\text{SO}_2) \end{matrix}$$

Nach früheren Untersuchungen<sup>6</sup> besitzen  $\text{CS}_2$  und  $\text{SO}_2$  EA-Werte von weniger als 1,1 eV, also sind auch die EA der hier gefundenen negativen Elektronen kleiner als 1,1 eV.

Dem Institut für anorganische Chemie der hiesigen Universität danken wir für die Herstellung der verwendeten Gase. Dem Bundesministerium für wissenschaftliche Forschung sprechen wir für die Überlassung von Geräten unseren Dank aus.

<sup>6</sup> K. KRAUS, W. MÜLLER-DUYSING u. H. NEUERT, Z. Naturforschg. **16a**, 1385 [1961].

## Isotopic Effects in Single Filament Thermal Ion Sources

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Isotopic effects occurring during the evaporation of microgram quantities of chemically pure rubidium, potassium and lithium compounds are studied. The measured isotopic ratios show a time dependent variation corresponding to a RAYLEIGH distillation. The fractionation factor is equal to the square root of the ratio of the masses. The highest observed enrichments are 45% for lithium, 10% for potassium and 5% for rubidium. The measured isotopic ratio depends also on the filament material and on the chemical composition of the sample. The discriminations are of the order of the square root of the ratio of the masses.

On several occasions it has been observed that isotopic abundance ratios from mass-spectrometric measurements show a drift over the course of the measurement, reflecting an enrichment of the heavier isotopes on the filament (e.g. BREWER<sup>1</sup>; REUTERSWÄRD<sup>2</sup>; ORDZHONIKIDZE and SHIUTTSE<sup>3</sup>; SHIELDS et al.<sup>4</sup> etc.). This trend occurs mainly in single filament ion sources and is most pronounced during the measurement of light elements, such as lithium and potassium (HABFAST<sup>5</sup>, BENTLEY et al.<sup>6</sup>, HOFF<sup>7</sup> etc.).

We have attempted to study systematically the time variation of the measured isotopic ratios. For this purpose we chose lithium, potassium and rubidium. Furthermore, we made some comparisons between single and double filament ion sources and studied the dependence of the measured isotopic ratios on filament material and on the chemical composition of the sample. We did not try to obtain absolute figures for isotopic ratios which would have

required a calibration of the other discrimination factors of the mass-spectrometer. Our studies were also not aimed at measuring differences in natural isotopic abundances.

### I. Time Variations

The drift of the isotopic ratio with time may be realized if we assume, that during the evaporation of the alkali, the reservoir (or the material on the filament) undergoes continuous and complete mixing. The observed isotopic ratio should then vary according to the RAYLEIGH distillation formula (COHEN<sup>8</sup>):

$$\left(\frac{[m_2]}{[m_1]}\right)_t = \frac{1}{\alpha} \left(\frac{[m_2]}{[m_1]}\right)_0 \left(\frac{[m_2]}{[m_1]}\right)^{\alpha-1}, \quad m_2 > m_1. \quad (1)$$

$([m_2]/[m_1])_t$  is the isotopic abundance ratio in the vapor at time  $t$ , and  $([m_2]/[m_1])_0$  is the ratio in the reservoir at the beginning of the distillation.  $[m_2]_0$  and  $[m_2]_t$  are the amounts of the isotope  $m_2$  in the

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<sup>1</sup> A. K. BREWER, J. Chem. Phys. **4**, 350 [1936].

<sup>2</sup> C. REUTERSWÄRD, Ark. Fys. **11**, 1 [1956].

<sup>3</sup> K. ORDZHONIKIDZE and V. SHIUTTSE, Sov. Phys.-JETP **2**, 396 [1956]. Translation Theoret. Phys. USSR **29**, 479.

<sup>4</sup> W. R. SHIELDS, E. L. GARNER, C. E. HEDGE, and S. S. GOLDICH, J. Geophys. Res. **68**, (No. 8) 2331 [1963].

<sup>5</sup> K. HABFAST, Z. Naturforschg. **15a**, 273 [1960].

<sup>6</sup> P. G. BENTLEY, J. BISHOP, D. F. DAVIDSON, and P. B. F. EVANS, J. Sci. Instrum. **36**, 32 [1959].

<sup>7</sup> L. HOFF, Phys. Rev. **53**, 845 [1938].

<sup>8</sup> K. COHEN, The Theory of Isotope Separation, McGraw-Hill Book Company, Inc., New York 1951.



reservoir at the beginning and at time  $t$  respectively. The fractionation factor  $\alpha$  is equal to  $\sqrt{m_2/m_1}$ , if the vapor pressures and the accommodation coefficients of the isotopes are the same.

For the study of time variations an amount of 0.1 to 0.5  $\mu\text{g}$  of the respective alkali chloride was placed in the center of a tantalum filament and transformed into the sulphate by adding a droplet of sulphuric acid. Great care was taken to prevent the

spreading of the sample over the whole filament. Sometimes, a V-type indentation in the center of the ribbon was made. In order to avoid crusting on the surface, chemically pure reagents were used throughout.

The temperature of the filament was raised slowly until a satisfactory ion current was detected. Subsequently, the temperature was held constant and the decline of the ion intensity was followed over a

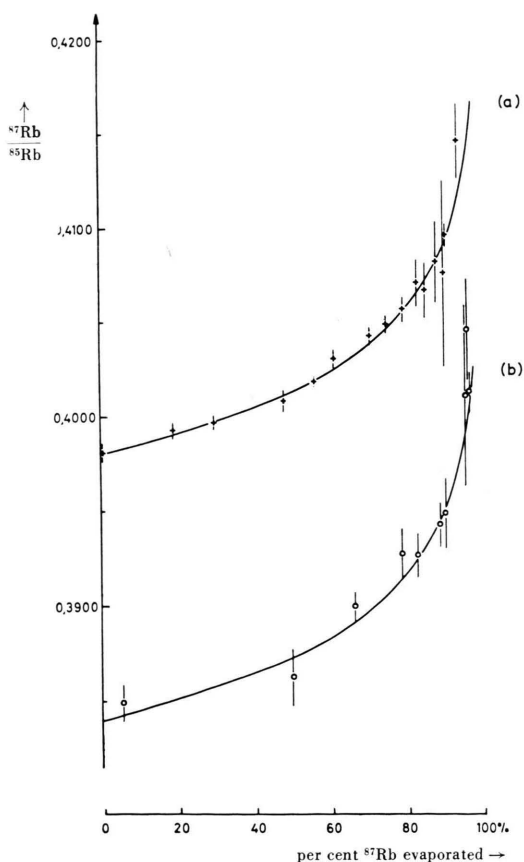


Fig. 1. Time variation of the observed isotopic abundance ratio of rubidium during the course of a measurement ( $\text{Rb}_2\text{SO}_4$  on tantalum filament). Curve (a) and curve (b) represent double and single collector measurements taken during the same run. Solid lines are RAYLEIGH curves.

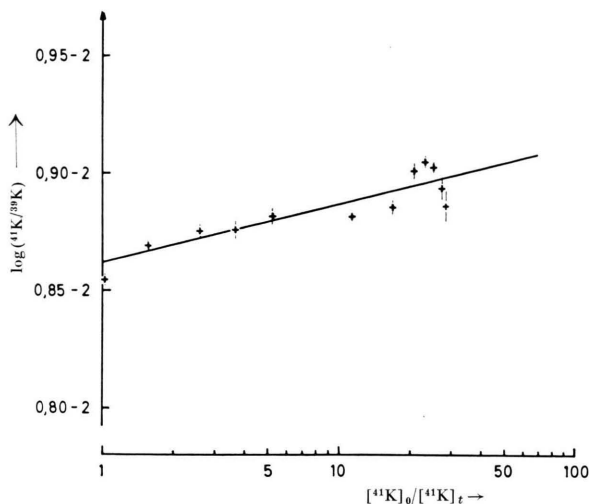


Fig. 2. Time variation of the isotopic abundance ratio of potassium ( $\text{K}_2\text{SO}_4$  on tantalum filament). The solid line represents the RAYLEIGH curve.

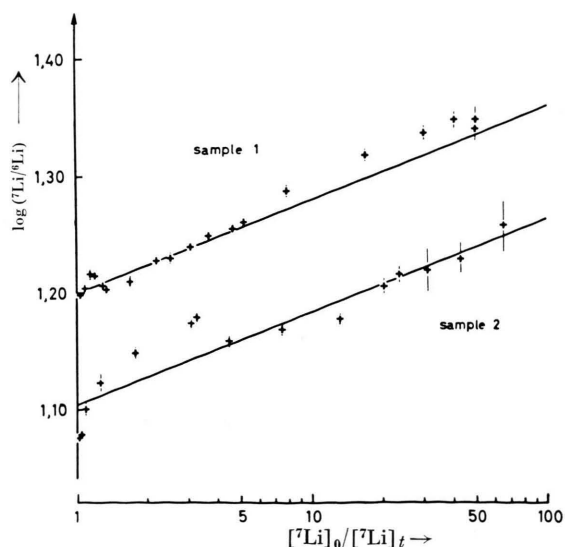


Fig. 3. Time variation of the isotopic abundance ratio of lithium ( $\text{Li}_2\text{SO}_4$  on tantalum filament). The solid lines represent the RAYLEIGH curve. Samples 1 and 2 have different initial isotopic compositions.

period of 10 to 38 hours until the evaporation was complete. This was assured by raising the temperature of the filament at the end of the run.

Investigations were carried out on two mass-spectrometers in order to ascertain that the observed effect was not limited to one instrument. Ions were detected with a single ion collector, without electron multiplier. The rubidium measurements were done both with a single and a double collector, the latter permitting a higher relative accuracy.

Fig. 1 shows the results of one of the rubidium runs. The per cent figures along the abscissa were obtained from the time integral,  $\int I dt$ , of the ion intensity. The curves were calculated from equation (1) with  $\alpha = \sqrt{87/85}$ . Within the experimental errors the measured points fall on the RAYLEIGH distillation curves. The observed enrichment of the heavier isotope near the end of the run amounts to 5%. The points along curve (a) and (b) are of the same run and were taken alternately with a double and a single collector respectively. The double collector balancing panel was not calibrated absolutely, thus absolute ratios cannot be read from curve (a). The curve only demonstrates the time variation in the measured  $^{87}\text{Rb}/^{85}\text{Rb}$  ratio. Fig. 1 shows that the RAYLEIGH effect may be observed with both single and double collectors, the latter giving a higher relative accuracy.

Figs. 2 and 3 show log-log plots of a potassium and two lithium runs. The solid lines again represent the RAYLEIGH curves with  $\alpha = \sqrt{m_2/m_1}$ . The highest observed enrichments for potassium and lithium are 10 and 45 per cent respectively. Two different salts

were used for the lithium analyses. Sample (1) was purchased in 1960 and may have been enriched artificially. For all three elements the time variation of the isotopic ratio is in agreement with a RAYLEIGH distillation curve, indicating that the mixing time in the reservoir on the filament is short compared with the duration of the mass-spectrometric measurement (several hours to more than a day). Many runs on several mass-spectrometers proved, that this behavior is not accidental and the fractionation factor is indeed equal to the square root of the mass ratio. This result agrees essentially with the results of REUTERSWÄRD<sup>2</sup> on potassium. BREWER<sup>1</sup> found smaller fractionation factors, but he used an entirely different loading technique.

Our measurements with a double filament ion source showed smaller enrichments, in accord with the results of HABFAST<sup>5</sup>.

A deviation from this regular RAYLEIGH fractionation was often observed at the beginning of the measurements. At values  $\int I dt < 5$  per cent the measured isotopic ratios consistently appeared below the RAYLEIGH curve. Fig. 4 shows the beginning of a rubidium measurement where this initial sharp rise of the observed ratio is clearly visible. This observation is contrary to that of RIJK and SHUKOLIUKOV<sup>9</sup> who found an initial decrease of the  $^{41}\text{K}/^{39}\text{K}$  ratio.

If the ratio between the ordinate intercept of the RAYLEIGH curve and the first measurable isotopic ratio is formed, a figure of the order of the fractionation factor  $\alpha$  of that element is obtained. The

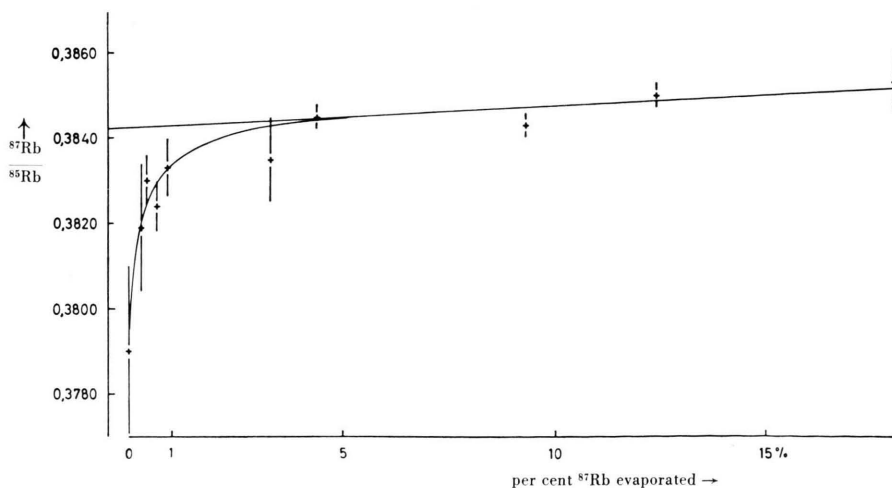


Fig. 4. Initial steep rise of the isotopic ratio and subsequent shallow RAYLEIGH distillation ( $\text{Rb}_2\text{SO}_4$  on tantalum filament).

<sup>9</sup> G. R. RIJK and Y. A. SHUKOLIUKOV, Dokl. Akad. Nauk, SSSR **94**, 667 [1954].

same behaviour was observed in potassium and lithium runs. We have not made further experiments to study the cause of this effect. However, since it is not reproduced quantitatively in every run, it may cause an appreciable error not only for absolute but also for relative measurements.

Fig. 5 shows the two principle time variation effects. If the temperature is not kept constant, more irregular variations are observed.

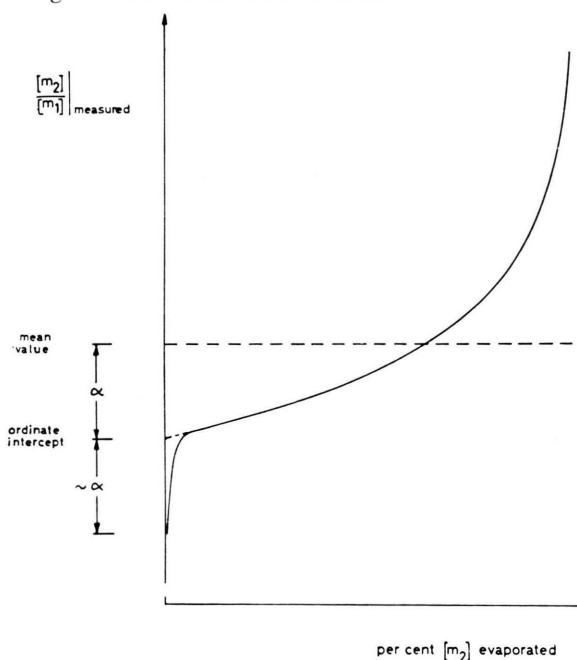


Fig. 5. General pattern of the time variation during the course of a measurement.

## II. Chemical Effects

We have investigated the dependence of the measured isotopic ratio of the three alkalis on the chemical composition of the sample and on the filament material used. To guard against spurious results these investigations were carried out on three dif-

ferent mass-spectrometers. In all cases curves of the type shown in Fig. 5 were obtained, with a RAYLEIGH fractionation factor of  $\sqrt{m_2/m_1}$ . However, different chemical compounds and different filament materials yielded differences in the absolute isotopic composition. These differences were entirely reproducible and are summarized below:

1) The  $[m_2]/[m_1]$  ratios ( $m_2 > m_1$ ) on tungsten filaments were consistently lower than those on tantalum for the three alkalis, the deviation being of the order of  $\sqrt{m_2/m_1}$  (Tab. 1). Studies of the same substance on tantalum and tungsten actually gave parallel RAYLEIGH curves.

2) No significant differences in absolute ratio were observed between  $\text{Rb}_2\text{SO}_4$  and  $\text{RbNO}_3$  when investigated on the same filament material. However,  $\text{RbCl}$  yielded higher  $^{87}\text{Rb}/^{85}\text{Rb}$  values than the two other compounds. As can be seen from Tab. 2 these differences are again of the order of  $\sqrt{m_2/m_1}$ .

Thus the measured isotopic composition of rubidium increased in the following order: sulphate on tungsten — sulphate on tantalum — chloride on tungsten — chloride on tantalum. These effects were clearly observed with all three mass-spectrometers. They were again much smaller or absent when a double filament source was used.

## III. Conclusions

If the RAYLEIGH distillation were the only discriminating effect, one could in principle deduce absolute isotopic abundances by taking the mean value of the RAYLEIGH curve. However, as RAYLEIGH curves with different average isotopic ratios are obtained when using different compounds or different filament materials, it cannot be decided which of the various methods yields the correct value. Furthermore, the ascertainment of an absolute value is questionable as long as the initial enrichment effect (cf. Fig. 4) is not understood.

	$\frac{^7\text{Li}}{^6\text{Li}}$	$\frac{^{41}\text{K}}{^{39}\text{K}}$	$\frac{^{87}\text{Rb}}{^{85}\text{Rb}}$		
Chemical compound	$\text{Li}_2\text{SO}_4$	$\text{K}_2\text{SO}_4$	$\text{Rb}_2\text{SO}_4$	$\text{RbNO}_3$	$\text{RbCl}$
$\frac{[m_2]}{[m_1]}$ on Ta	1.11	1.033	1.007	1.021	1.011
$\frac{[m_2]}{[m_1]}$ on W	$\pm 0.03$	$\pm 0.010$	$\pm 0.004$	$\pm 0.006$	$\pm 0.007$
$\sqrt{\frac{m_2}{m_1}}$	1.08	1.025	1.012		

Table 1. Difference in the measured isotopic abundances of lithium, potassium and rubidium due to filament material. The absolute isotopic ratios,  $[m_2]/[m_1]$ , were obtained by taking the mean value of the RAYLEIGH curves. The errors were calculated by quadratically adding the standard deviation,  $\sqrt{\Delta i^2/n-1}$ , of  $n$  different tantalum measurements to that of  $m$  tungsten measurements. Tantalum and tungsten measurements were alternately performed.

	on Ta	on W
$\frac{(^{87}\text{Rb}/^{85}\text{Rb}) \text{ from nitrate}}{(^{87}\text{Rb}/^{85}\text{Rb}) \text{ from sulphate}}$	$1.004 \pm 0.005$	$1.000 \pm 0.005$
$\frac{(^{87}\text{Rb}/^{85}\text{Rb}) \text{ from chloride}}{(^{87}\text{Rb}/^{85}\text{Rb}) \text{ from sulphate}}$	$1.019 \pm 0.007$	$1.015 \pm 0.005$
$\frac{(^{87}\text{Rb}/^{85}\text{Rb}) \text{ from chloride}}{(^{87}\text{Rb}/^{85}\text{Rb}) \text{ from nitrate}}$	$1.011 \pm 0.007$	$1.014 \pm 0.008$

Our results also show possible sources of error in relative measurements. In the first place, the initial enrichment effect may introduce an error because of its unreproducibility. Secondly, the observed variation due to different filament material and different chemical compounding shows the importance of having the samples investigated under identical condi-

tions. This, however, may sometimes be difficult to ascertain in the case of isotopic abundance measurements of natural samples.

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## The Separation of Light Gaseous Isotopes by Mass Diffusion Columns I

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A theoretical investigation of the factors affecting the efficiencies of mass diffusion columns, with particular emphasis on columns operated with partition membranes, for the separation of light gaseous isotopes, is extensively treated. Expressions are derived for the theoretical maximum separation factor and separative power and the optimum flow profile. The effects of partition membranes on column efficiencies are discussed and equations are derived to assess the performances of such columns. It appears that the membrane position in a column is rather critical and means to obviate unfavourable effects due to this, are suggested. Existing experimental results of GVERDTSITELI et al.<sup>1</sup> corroborate some of the main theoretical conclusions.

The elementary isotope separation effect, acting in the radial direction in a mass diffusion column (see Fig. 1), is induced by a continuous flow of vapour from a vapour supply tube to a condenser which is concentric with the vapour supply tube. The vapour stream creates a gradient of the partial pressure of the gas with which the column is filled. In the steady state a dynamic equilibrium is eventually achieved between the flow of gas moved towards the condenser by collisions with the vapour molecules and the back diffusion of the gas, due to the gas pressure gradient. Due to the differences in the diffusion rates of isotopes, lighter isotopes will generally diffuse more rapidly against the vapour and consequently become enriched to the center of the column.

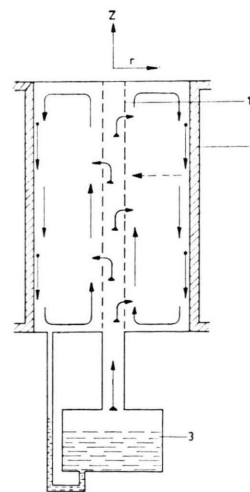


Fig. 1. Schematic diagram of a mass diffusion column. 1. porous vapour supply tube. 2. condenser. 3. boiler.  $\blacktriangleright$  vapour stream.  $\bullet \rightarrow$  condensate.  $\rightarrow$  counter-current stream.  $- - \rightarrow$  light isotope stream.

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