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Efficiency of the Electrolytic Separation of Potassium Isotopes

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The electrolytic separation coefficient, α , has been determined for the potassium isotope separation in the electrolysis of aqueous solutions of potassium chloride at a flowing mercury cathode. Suspension of purified potassium chloride crystals in a liquid mixture of bromoform, *n*-pentanol, and *n*-hexanol served as the analytical procedure in determining the isotopic composition of samples. Densities of the liquid suspension mixture as a function of temperature were independently determined. The electrolytic separation factor for the potassium isotopes was found to be 1.0054 ± 0.0005 for the temperature range of 15° – 50°C , and, within the limits of error, was independent of temperature, of the fraction electrolyzed, of the concentration of the electrolytic solution, of the current density, and of the amount of back reaction at the cathode. An empirical relation between the electrolytic separation factors of elements thus far investigated and their atomic weights is presented.

I. INTRODUCTION

THE electrolytic separation of isotopes other than those of hydrogen has received comparatively little attention. Washburn¹ showed that oxygen isotopes were noticeably separated by electrolysis and Johnston² determined the electrolytic separation factor, α , for O^{16} relative to O^{18} to be 1.008 ± 0.003 for the electrolysis of aqueous alkaline solutions between iron electrodes using a densimetric method of analysis.

Eucken and Bratzler³ were the first to investigate the electrolytic separation of lithium isotopes and were able to set 1.07 as an upper limit for α in the electrolysis of aqueous lithium

sulfate at a mercury cathode. Taylor and Urey⁴ electrolyzed aqueous lithium hydroxide at a mercury cathode and obtained an α of 1.020 on the basis of mass spectrometer analysis by Brewer. Holleck⁵ electrolyzed aqueous lithium chloride and obtained an α of 1.079 by a chemical atomic weight method of analysis. Taylor and Urey⁶ reported an α of 1.039 for the electrolysis of aqueous lithium chloride. Employing a densimetric method of determining relative atomic weights, Johnston and C. A. Hutchison⁷ obtained an α of 1.055 ± 0.005 for the electrolysis of aqueous and alcoholic solutions of lithium chloride at a mercury cathode. They were able to show, within their limits of observation, that the

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¹ E. W. Washburn, E. R. Smith, and F. A. Smith, *Bur. Stand. J. Research* **13**, 599 (1934).

² H. L. Johnston, *J. Am. Chem. Soc.* **57**, 484 (1935).

³ Eucken and Bratzler, *Zeits. f. physik. Chemie* **A174**, 269 (1935).

⁴ T. I. Taylor and H. C. Urey, *J. Chem. Phys.* **5**, 597 (1937).

⁵ Holleck, *Zeits. f. Elektrochemie* **44**, 111 (1938).

⁶ T. I. Taylor and H. C. Urey, *J. Chem. Phys.* **6**, 429 (1938).

⁷ H. L. Johnston and C. A. Hutchison, *J. Chem. Phys.* **8**, 869 (1940).

α -value was independent of the cell temperature, the fraction electrolyzed, the amount of back reaction at the cathode, and within a small range, independent of current density.

Johnston and the writer,⁸ employing a densimetric method of isotopic analysis, electrolyzed aqueous sodium chloride at a platinum anode and obtained an α of 1.0060 ± 0.0005 for the separation of chlorine isotopes. This work also showed no significant dependence of the α -value on the cell temperature, the fraction electrolyzed, the amount of back reaction at the anode, and the current density in the range of observation. The α -value on Acheson graphite, 1.0068 ± 0.0014 , which was computed from the data of Yacouban⁹ agrees with our own more precise value. The writer's recent redetermination¹⁰ of the α -value for chlorine, with similar apparatus but by a different procedure, resulted in the value, 1.0063. The linear average of α 's obtained from all the chlorine electrolyses gives $\alpha = 1.0061 \pm 0.0005$.

The purpose of the present paper is to report the results of an investigation on the electrolytic separation of potassium isotopes at a mercury cathode and to show the experimental relation between the α -values for the elements thus far investigated and their atomic masses.

II. EXPERIMENTAL DESCRIPTION

A. The Electrolysis

The apparatus used to carry out the electrolyses was similar to that of Eucken and Bratzler³ and to that of Johnston and C. A. Hutchison.⁷ The cell consisted of a four-liter round bottom Pyrex flask to the bottom of which was sealed an extension which supplied a means for a flowing mercury cathode. The cell contained a rubber stopper at its top through which passed a platinum lead to a platinum gauze anode, a thermometer for the measurement of the electrolyte temperature, and glass tubes for passage of gases from the cell which were formed during the electrolyses. These surfaces extending into the cell and the inner wall of the cell were coated with "biolloid" paraffin. The electrolyte employed was an aqueous solution of potassium

chloride. The chlorine evolved during the electrolyses was swept from the cell by a stream of nitrogen and absorbed in four traps, two of which contained sodium hydroxide and the remainder, acetone. The nitrogen stream also served to give constant stirring of the electrolyte and yielded what was thought to be a uniform mixture of the solution throughout an electrolysis. The mercury for the flowing cathode was supplied from a reservoir and the rate of flow through the cell was adjusted at values varying from 2.5 to 10 liters per hour for the various electrolyses. The temperature of the cell was regulated by an external water bath. By this means the temperature of the electrolyte could be controlled to within $\pm 3^\circ\text{C}$. The amalgam from the electrolyses was drained from the cell into an eight-liter Erlenmeyer flask which was heavily coated with paraffin and treated as described below.

B. Preparation of Reagents

Potassium chloride employed in the electrolyses was prepared by six successive precipitations from aqueous solutions by addition of pure hydrogen chloride.¹¹ The purification of potassium chloride, which was used in the preparation of standard crystals of normal isotopic composition for use as comparison crystals in the densimetric analyses, was effected by a method similar to that employed by Richards and Wells¹² in their determination of the atomic weight of sodium and chlorine. The beginning material in all cases was Baker's analyzed C.P. potassium chloride. Details of the purification procedure and evidence of its effectiveness have been published elsewhere.¹³

The amalgam formed during electrolysis was placed in eight-liter Erlenmeyer flasks which had been coated with paraffin. Pure hydrochloric acid¹⁴ was added in such quantity that its equivalent concentration was in slight excess of the concentration of the potassium ion to be liberated. Platinum foil was added to promote reaction of the amalgam. The resulting solution was boiled to dryness in a platinum container.

⁸ H. L. Johnston and D. A. Hutchison, *J. Chem. Phys.* **10**, 469 (1942).

⁹ K. V. Yacouban, *Helv. Chim. Acta.* **22**, 808 (1939).

¹⁰ D. A. Hutchison, *J. Chem. Phys.* **13**, 536 (1945).

¹¹ See reference 13 for details of purification.

¹² T. W. Richards and R. C. Wells, "A Revision of the Atomic Weights of Sodium and Chlorine," Carnegie Institute of Washington, Publication No. 28 (1905).

¹³ D. A. Hutchison, *Phys. Rev.* **66**, 144 (1944).

The residue was given two fractional crystallizations from water and then fused on platinum to eliminate traces of hydrochloric acid. The salt was then given eight more crystallizations from aqueous solutions. The material from each step of the crystallizations was centrifuged before the succeeding step. The resulting material was used in the preparation of crystals for suspension.^{14,15}

The mercury used for the flowing cathode was purified by washing with dilute nitric acid and water, drying with filter paper, and finally by two successive distillations in vacuum. The purification was repeated before using the mercury again.

Water used in all reagent preparations and purification procedures was obtained by double distillation from an aqueous alkaline permanganate solution in a fused quartz still. Various water samples tested had a specific conductivity of approximately 10^{-7} ohm⁻¹.

The suspension liquid used in the densimetric analyses was a mixture of organic liquids similar to that used by H. L. Johnston and C. A. Hutchison.⁷ The mixture had the following composition: bromoform, 40.00 ml; *n*-hexanol, 16.94 ml; *n*-pentanol, 16.00 ml. Baker's bromoform (boiling point range, 150°–151°C) U.S.P. IX, was washed with water, dried with calcium chloride, and distilled under vacuum. The middle third of the distillate was collected in a receiver containing a small amount of *n*-hexanol and *n*-pentanol (25 drops of each) which acted as a negative catalyst preventing decomposition. The composition was then adjusted to that of the above suspension liquid by adding drop by drop Eastman practical grade alcohols which had been double distilled. The density of this suspension mixture remained constant within the experimental limits of error ($\pm 5 \times 10^{-6}$ g/ml) of the density determination during the period of densimetric analyses.

C. The Isotopic Analyses and Fraction Electrolyzed

The isotopic analyses were made in an apparatus similar to that used by Johnston and the writer⁸ in their work on the electrolytic separa-

tion of chlorine isotopes and that used by Johnston and C. A. Hutchison⁷ in their work on the separation of lithium isotopes. Details of the isotopic analyses have previously been outlined for the work on lithium.⁷ In order to get reproducible suspension temperatures, it was found necessary to anneal the crystals at a temperature 50° below their melting point for a period of four hours with gradual cooling over a period of four hours and to store them over phosphorus pentoxide under vacuum. With these precautions suspension temperatures of individual crystals were reproducible to better than $\pm 0.002^\circ$ (equivalent to 3.3×10^{-6} g/ml in the density) except in step IV of electrolysis 12.

The density of the suspension liquid, as a function of temperature, was determined by careful hydrostatic weighings of a 9.4-ml Pyrex glass bob in air, in pure water, and in the suspension medium. The necessary corrections for the buoyancy of the bob in air and the thermal expansion of Pyrex glass were applied. The experimental data and details of the weighing procedure have been described elsewhere.¹³

Eighteen determinations of the density of the suspension medium over an approximate temperature range of 25.0° to 29.3°C yielded a good straight line with a slope of $-1.883 \pm 0.004 \times 10^{-3}$ g/ml/degree. Taking into account the thermal coefficient of expansion for potassium chloride,¹⁶ namely, α (cubical) = 113×10^{-6} , it is found that one degree in the ΔT of suspension corresponds to 1.659×10^{-3} g/ml in the isothermal density of the potassium chloride. This corresponds to 0.0623 unit in the atomic weight of potassium and to 3.11 percent in the distribution of the potassium isotopes. The determination of the suspension temperatures to within $\pm 0.002^\circ\text{C}$, which is some better than the limit of reproducibility (actual reproducibility is referred to here, not the probable error of suspension temperatures) thus corresponds to 6.2×10^{-3} percent in the isotopic abundance of the potassium.

The fraction of chemical equivalents of potassium ion electrolyzed was determined by analysis of the residual electrolyte. Samples of the residual electrolyte were boiled to dryness in a

¹⁴ See reference 13 for details of purification.

¹⁵ See footnote 2 of reference 13.

¹⁶ Klemm, Tilk, and Mullenheim, *Zeits. f. anorg. allgem. Chemie* **176**, 1 (1928).

TABLE I. Data for the separation of *K* isotopes in the single step electrolyses of aqueous KCl.

Run number	1	2	3	4	5	6	7	8
Average temperature (°C)	35	35	35	50	40	30	30	15
Current density (amp./cm ²)	0.139	0.099	0.060	0.099	0.099	0.099	0.099	0.099
Concentration of KCl at beginning (mols./liter soln.)	0.50	0.50	0.50	0.50	0.50	0.50	1.50	0.5
Equivalents of <i>K</i> in starting material	1.48817	1.41512	1.38902	1.50696	1.43252	1.42860	4.14090	1.49052
Equivalents of <i>K</i> liberated	0.10178	0.11714	0.12310	0.11486	0.08567	0.11292	0.30930	0.09487
Fraction of equivalents of <i>K</i> electrolyzed	0.071266	0.082777	0.088623	0.076219	0.059803	0.079042	0.074693	0.063648
Current efficiency ^b	0.78	0.75	0.82	0.77	0.55	0.76	0.69	0.64
Suspension temperatures of different crystal fragments relative to standard crystals taken as zero ^a	0.010 0.010 0.009 0.009 0.009 <i>I</i>	0.011 0.010 0.010 0.010 0.009 <i>I, I, I</i>	0.009 0.009 0.008 0.008 0.008 <i>I</i>	0.009 0.009 0.009 0.009 0.008 <i>I, I</i>	0.010 0.010 0.010 0.009 0.009 <i>I, I</i>	0.010 0.010 0.009 0.009 0.009 <i>I</i>	0.010 0.009 0.009 0.009 0.008	0.011 0.010 0.010 0.010 0.010 <i>I, I, I, I</i>
Average suspension ΔT	0.0094	0.0100	0.0084	0.0088	0.0096	0.0094	0.0090	0.0102
Change in the atomic weight of <i>K</i>	-0.000586	-0.000623	-0.000523	-0.000548	-0.000598	-0.000586	-0.000561	-0.000635
α	1.0054	1.0049	1.0049	1.0050	1.0055	1.0055	1.0051	1.0058

^a *I* indicates imperfect crystals not used to obtain the average ΔT .^b See p. 874 of reference 7.

platinum container. The resulting potassium chloride was then fused to remove traces of excess chloride ion. Solutions of this potassium chloride were titrated with standard silver nitrate solution. This furnished a satisfactory method of determining the number of residual equivalents of potassium ion, the whole procedure requiring about fifteen minutes. The number of equivalents electrolyzed was obtained by difference of the initial and residual number of equivalents of potassium ion.

III. EXPERIMENTAL RESULTS

Nineteen electrolyses were performed to determine the electrolytic separation factor, α .¹⁷ Experimental conditions were varied to determine their effect on the α -value. In Table I there are presented the data for eight single step electrolyses. In the first three the current density was varied with the cell temperature held constant at 35°C. In the fourth through the eighth electrolyses, the temperature was varied from 15° to 50°C with the current density held constant at 0.099 amp./cm.² The approximate concentration

of the electrolyte at the beginning of each electrolysis is recorded for the electrolyses of both Tables I and II. In order to increase the isotopic separation and thus increase the precision of the determination of α , four stepwise electrolyses were performed. The data for these electrolyses, nine through twelve, are given in Table II. The Roman numerals indicate the number of the step of a given electrolysis. The potassium chloride, obtained on reaction of the *K* amalgam from a given step, served as the starting material for the succeeding step. The ninth and tenth electrolyses were made in two steps, the eleventh in three steps, and the twelfth in four steps. The α 's obtained here for steps other than the first are cumulative¹⁸ α 's.

With each step of the electrolyses, five crystals of potassium chloride were prepared and suspended. If the ΔT of any of the five crystals deviated by a certain amount from the closely agreeing ΔT 's of remaining ones, then the non-agreeing ΔT was discarded on the basis that it was from an imperfect crystal. In this case new crystals were prepared and suspended until in all there were five crystals with ΔT 's with no large differences. Crystals were excluded as imperfect

¹⁷ α is defined by the relationship

$$d \ln K^{39} = \alpha d \ln K^{41} \quad (a)$$

where K^{39} and K^{41} represent the numbers of atoms of the isotopes with mass 39 and 41, respectively.

¹⁸ The cumulative α is that value taken as a constant through all steps of an electrolysis, needed to yield the experimental ΔT observed at the end of a given step.

TABLE II. Data for the separation of *K* isotopes in the stepwise electrolyses of aqueous KCl.

Run number	9I	9II	10I	10II	11I	11II	11III	12I	12II	12III	12IV
Average temperature (°C)	35	35	35	35	35	35	35	35	35	35	35
Current density (amp/cm ²)	0.090	0.099	0.099	0.099	0.099	0.099	0.099	0.099	0.099	0.099	0.099
Concentration of KCl at beginning (moles/liter soln.)	2.50	0.50	3.00	0.50	4.00	1.00	0.33	3.94	4.14	1.82	0.61
Equivalents of <i>K</i> in starting material	7.25062	0.42802	9.02098	0.51808	11.8393	2.55165	0.47121	17.7480	3.63492	0.88367	0.25813
Equivalents of <i>K</i> liberated	0.48040	0.09152	0.58162	0.41412	2.4185	0.53201	0.10026	4.3925	1.10236	0.29831	0.10442
Fraction of equivalents of <i>K</i> electrolyzed	0.066256	0.21382	0.064474	0.20060	0.16963	0.20850	0.21277	0.24749	0.30327	0.33758	0.40452
Current efficiency ^b	0.62	0.74	0.63	0.56	0.69	0.79	0.83	0.57	0.59	0.91	0.91
Suspension temperatures of different crystal fragments relative to standard crystals taken as zero ^a	0.010 0.009 0.009 0.009 0.009 <i>I, I</i>	0.018 0.018 0.018 0.018 0.017 <i>I</i>	0.009 0.009 0.009 0.008 0.008 <i>I</i>	0.019 0.018 0.018 0.018 0.018 <i>I, I, I</i>	0.010 0.009 0.009 0.009 0.008 <i>I, I</i>	0.018 0.018 0.018 0.018 0.017 <i>I</i>	0.027 0.026 0.026 0.025 0.025 <i>I, I</i>	0.009 0.009 0.009 0.008 0.008 <i>I, I</i>	0.019 0.017 0.017 0.017 0.016 <i>I, I, I, I</i>	0.025 0.025 0.024 0.024 0.022 <i>I</i>	0.035 0.033 0.032 0.031 0.029 <i>I, I</i>
Average suspension ΔT	0.0092	0.0178	0.0086	0.0182	0.0090	0.0178	0.0258	0.0086	0.0172	0.0240	0.0320
Change in the atomic weight of <i>K</i>	-0.000573	-0.001109	-0.005358	-0.001134	-0.000561	-0.001109	-0.001607	-0.000536	-0.001072	-0.001495	-0.001994
α	1.0052	1.0053	1.0049	1.0054	1.0055	1.0055	1.0053	1.0055	1.0056	1.0053	1.0054

^a *I* indicates imperfect crystals not used to obtain the average ΔT .^b See p. 874 of reference 7.

if their ΔT differed by more than 0.006°C from the average ΔT of the closely agreeing crystals. Tables I and II record the ΔT 's of all crystals suspended. Linear averages of the ΔT 's were taken for the computation of α since there were no large or systematic differences for the ΔT 's of any step.

α 's for each step were computed from the equation,

$$\alpha = \frac{\log \left[1 - F \left\{ 1 + \frac{dM_{\text{KCl}}\Delta T}{\rho_{\text{KCl}}(A_{41} - A_{\text{K}})} \right\} \right]}{\log \left[1 - F \left\{ 1 - \frac{dM_{\text{KCl}}\Delta T}{\rho_{\text{KCl}}(A_{\text{K}} - A_{39})} \right\} \right]} \quad (1)$$

in which F is the fraction of chemical equivalents of potassium ion electrolyzed in a given step of an electrolysis; M_{KCl} is the molecular weight of normal potassium chloride; A_{K} is the atomic weight of normal potassium; A_{39} and A_{41} are the mass values of K_{39} and K_{41} , respectively; ρ_{KCl} is the density of normal potassium chloride at the suspension temperature for standard normal crystals; d is the isothermal density change for a ΔT of one degree; and ΔT is the suspension temperature of crystals prepared from the potassium

amalgam minus the suspension temperature of standard normal crystals. This equation is an exact solution of equation (a) of reference 17 in terms of the experimentally measured quantities, F and ΔT . Values used for the constants in Eq. (1) are: $A_{39}^{19} = 38.975$; $A_{41}^{19} = 40.974$; $A_{\text{K}}^{20} = 39.096$; $M_{\text{KCl}}^{20} = 74.553$; $d = 1.659 \times 10^{-3}$ g/ml-deg.; and $\rho_{\text{KCl}}^{13} = 1.98651$ g/ml.

IV. DISCUSSION OF RESULTS

A. The Value of α and Its Dependence on Experimental Conditions

The least precisely determined quantity used in the computation of α is the ΔT of suspension. Therefore, it is worth while to consider the probable error of the ΔT 's in some detail. In previous work^{7,8} the experimental uncertainty of the ΔT 's was given an arbitrary assignment of $\pm 0.002^\circ\text{C}$. Suppose, for example, in electrolysis 1 we assign an uncertainty of $\pm 0.002^\circ\text{C}$ and a weight of unity to each of the five ΔT 's obtained. The value of the probable error, p_i , of the average ΔT obtained from internal consistency is

¹⁹ E. Pollard, Phys. Rev. **57**, 1186-7 (1940).²⁰ Eleventh report of the committee on atomic weights of the International Union of Chemistry, J. Am. Chem. Soc. **63**, 845 (1941).

$\pm 0.0009^\circ$. The probable error, p_e , obtained from external consistency is $\pm 0.0002^\circ$. The ratio, p_e/p_i , is 0.22. However, theory predicts that this ratio should not differ from unity by more than 22 percent. Thus, the arbitrary assignment of $\pm 0.002^\circ$ to the ΔT 's is too large. Let us consider the original measurement of a suspension temperature. It has been obtained in the present and previous works by the relation

$$T_S = (T_H + T_L)/2 \quad (2)$$

where T_S is the suspension temperature, and T_H and T_L are the high and low temperatures, respectively, that define a fall or rise of a crystal in the suspension medium.²¹ Relation (2) is about the best that can be assumed, especially when the difference, $(T_H - T_L)$, is of the same order of magnitude as the errors in T_H and T_L . If it is assumed that a temperature can be read with the aid of a magnifying glass from the Beckmann thermometer, which was employed, to within $\pm 0.001^\circ$, then by taking four measurements of both T_H and T_L , as was done in the present work, the probable error of either T_H or T_L is reduced to $\pm 0.0005^\circ$. From relation (3), there is produced a probable error of $\pm 0.00035^\circ$ in T_S . The relation used to compute the ΔT 's of suspension is,

$$\Delta T = T_A - T_N, \quad (3)$$

where T_A is the suspension temperature of crystals prepared from the amalgam and T_N is the suspension temperature for standard normal crystals. The error produced in each ΔT of Tables I and II by relation (3) is $\pm 0.0005^\circ$. The resulting probable error in the average ΔT for a single electrolysis is $\pm 0.00022^\circ$ by internal consistency and $\pm 0.00017^\circ$ by external consistency. The ratio, p_e/p_i , is then 0.77 in good agreement with that predicted by theory when no systematic errors are introduced with the temperature measurements and relation (2) is assumed correct. Certainly, because of the manner of measuring ΔT 's in this work, the assignment of $\pm 0.001^\circ$ as the error in the average ΔT 's should well include all errors.

The probable error of the α -value for each electrolysis was computed on the basis of the errors associated with each quantity in the right

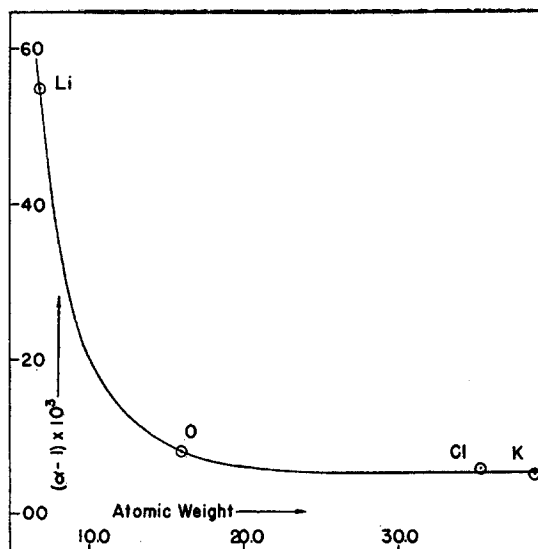


FIG. 1. Plot of $(\alpha - 1) \times 10^3$ against atomic weight.

member of Eq. (1). The probable errors in these α 's were used to assign weights to the nineteen α 's obtained. The resulting average α is 1.0054. The ratio, p_e/p_i , for the average α is 1.48 where theory predicts its deviation from unity should be only 10 percent. Hence, systematic errors were shown to be present in one or more stages of the work, and therefore, the above assignment of weights to the α 's was discarded. To obtain an average α , weights were arbitrarily assigned to each α numerically equal to the number of electrolytic steps employed in its determination, i.e., the single step α 's were given a weight of one, the double step α 's were given a weight of two, etc. The resulting average is 1.0054. The error limit was taken as the maximum deviation of individual α 's from this average which yielded ± 0.0005 .

The α -values for electrolyses 4-8 vary from 1.0058 to 1.0050 over the temperature interval of 15° - 50°C . If a deviation in the average ΔT of $\pm 0.001^\circ$ is assumed, the corresponding deviation in α is ± 0.0007 unit. It is doubtful if any significance can be attached to the above apparent variation of α with temperature since the variation is only slightly larger than that produced by an experimental uncertainty of $\pm 0.001^\circ$ in ΔT . Likewise, no significance can be attached to the slight variation of α with change in current density recorded for electrolyses 1-3. Within the

²¹ See reference 7 for the procedure of suspending crystals.

limits of observation, the α -value is not dependent on the amount of back reaction as shown by the current efficiencies, on the concentration of the electrolyte, or on the fraction of chemical equivalents of K ion electrolyzed. The value,

$$\alpha = 1.0054 \pm 0.0005,$$

can be stated as the electrolytic separation coefficient for the separation of potassium isotopes at a mercury cathode over the temperature interval of 15°–50°C.

B. The Relation Between α and the Atomic Weight

It is of interest to note the relationship which becomes apparent when the α -value for the separation of potassium isotopes obtained in the present work is compared with the α -values given in the introduction of this paper for the elements, lithium, oxygen, and chlorine. Assuming an α -value for hydrogen of 5.000, the α 's for these five elements have been plotted against their respective atomic weights. There results a good smooth curve. The actual value assumed for hydrogen, which Topley and Eyring²² found to vary from 2.8 to 7.6 depending on the nature of the electrode, will not change the shape of the curve appreciably for atomic weights greater than 5 or 6. Figure 1 presents that part of the curve with atomic weights above 6. Since these α 's have been determined at different electrodes (iron, mercury, and bright platinum) a cursory conclusion can be made that the mechanism of the separation is independent of the electrode material for elements with atomic weights greater than 5 or 6. The fact that the separation of oxygen and chlorine was effected at an anode and the separation of lithium and potassium was effected at a cathode would lead one to guess that the separation mechanism is similar at either anode or cathode, at least in its over-all effect.

The data presented in this work do not serve to distinguish among the various mechanisms²³ that

have been proposed to account for the electrolytic separation of isotopes. Efforts to explain the mechanism of separation have involved two kinds of factors: (1), kinetic factors determined by processes leading to different rates of electrolysis of the different isotopic species, and (2), an equilibrium factor due to isotopic exchange between the electrolyzed material and the residual electrolyte. Sufficient precise auxiliary data are not available to test directly the various proposed mechanisms. However, the dependence of the observed α -value on temperature may be employed to make a rough conclusion as to whether a kinetic or an equilibrium factor plays the major role in the separation. Neither the proposed kinetic mechanisms, which are based on different rate determining steps, nor the isotopic exchange mechanism possesses sensible temperature dependence and such small differences in the temperature coefficient of α as are predicted could not be detected by the relatively precise method of analysis employed in this work. On first consideration, it may appear that Bell's²⁴ kinetic mechanism, which is a quantum-mechanical application of Gurney's²⁵ theory of overvoltage, refutes the latter statement. Bell's mechanism is based on the supposition that the rate limiting step in the separation is the penetration of a solvent sheath surrounding a hydrated ion by an electron. On this basis, he predicts that the temperature dependence of the $\ln \alpha$ should be equal to $-\alpha/T$. This, however, appears to be incorrect. It is believed that the temperature coefficient of $\ln \alpha$ should be equal to $-\ln \alpha/T$. When this correction is made, it is seen that the Bell-Gurney mechanism, also, does not possess sensible temperature dependence.

If the observed α represents a partial approach to an exchange equilibrium in addition to a kinetic mechanism, and if the exchange α is assumed to differ markedly from a kinetic α , it would be expected that temperature would have a noticeable effect on the observed α , by bringing about a change in the extent to which equilibrium is approached. Since α is constant within the error limits of this determination over the temperature range of 15°–50°C, it is most probable

²² B. Topley and H. Eyring, *J. Chem. Phys.* **2**, 217 (1934).

²³ H. Eyring and A. Sherman, *J. Chem. Phys.* **1**, 345 (1933); Horiuti and Polanyi, *Nature* **132**, 931 (1933); R. P. Bell, *J. Chem. Phys.* **2**, 164 (1934); B. Topley and H. Eyring, *J. Chem. Phys.* **2**, 217 (1934); Fowler, *Proc. Roy. Soc. A* **144**, 452 (1934); Bowden and Kenyon, *Nature* **135**, 105 (1935); O. Halpern and Ph. Gross, *J. Chem. Phys.* **3**, 452 (1935); Butler, *Zeits. f. Elektrochemie* **44**, 55 (1938).

²⁴ R. P. Bell, *J. Chem. Phys.* **2**, 164 (1934).

²⁵ R. W. Gurney, *Proc. Roy. Soc. (London)* **A134**, 137 (1932).

that a kinetic mechanism effects the major part of the separation.

It is apparent that before any proper explanation of the mechanism of the electrolytic separation process can be forthcoming, there must be a much greater extension of the experimental material. The writer has work in progress at present on the electrolytic separation of nitrogen isotopes which is based on the discharge of the ammonium ion at a mercury cathode. The experimental curve of Fig. 1 predicts the α -value for

nitrogen to be near that of oxygen. It will be of interest to check this prediction. Because of the much more rapid method of mass spectrometer analysis employed in this nitrogen work instead of the long and tedious crystal suspension method employed in previous work, much greater variation in experimental conditions of the electrolyses are made available. It is hoped that the results of the nitrogen work will furnish experimental data that can serve as a more adequate basis for interpreting the mechanism of the separation.

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An X-Ray Diffraction Investigation of the Thermal Decomposition of Silver Oxalate*†

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A single crystal of silver oxalate was studied by x-ray diffraction during the process of thermal decomposition. The diffraction patterns indicated that some fragmentation of the single crystal occurred early in the reaction. Except for distortion, the monoclinic structure was maintained until all trace of silver oxalate disappeared. The gradual appearance of polycrystalline silver was apparent. The diffraction patterns showed that a portion of the silver assumed preferred orientations, the ratio of oriented to unoriented silver remaining constant throughout the reaction. Four different preferred orientations were found and were defined relative to the silver oxalate lattice.

SILVER oxalate, when heated, undergoes thermal decomposition, the products being metallic silver and carbon dioxide.^{1,2} The crystal structures of silver oxalate³ and metallic silver⁴ are known. It seemed quite probable, therefore, that information regarding the behavior of the silver oxalate structure during decomposition, the growth of silver, and its crystalline form and orientation with respect to the silver oxalate structure could be obtained by means of x-ray diffraction studies during the process of thermal decomposition. Such information is useful in connection with the development of photo-

thermographic processes⁵ and also in connection with the theory of photographic development.

A thick plate-like crystal of silver oxalate, prepared by slow evaporation of a concentrated ammoniacal solution,² was mounted on the goniometer head of a Weissenberg x-ray diffraction camera and so oriented as to rotate about its a axis. The crystal was then reduced to a cylindrical form having a diameter of approximately 0.4 mm, by rotating it against a small piece of sponge soaked in ammonium hydroxide. The goniometer head could be removed from the camera without disturbing the attached crystal.

The experimental procedure consisted in heating the crystal, still attached to the goniometer head, for a period of time in an oven at a controlled temperature ranging from 100° to 140°C for the various periods of heating. After each interval of heating, the crystal was returned to

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³ R. L. Griffith, *J. Chem. Phys.* 11, 499 (1943).

⁴ R. W. G. Wyckoff, *The Structure of Crystals* (Chemical Catalog Company, New York, 1931), second edition, p. 204.

⁵ U. S. Patent, 1,976,302, S. E. Sheppard and W. Vanselow (assigned to Eastman Kodak Company).