"equilibrium" loads at which the hair fiber neither contracts nor extends.

5. The influence of temperature on the elasticity of hair has been investigated. The elasticity of hair increases with increasing temperature in the Hooke's law region. The results obtained on other portions of the stress–strain curve are somewhat ambiguous except on the contraction limb of the 20% stress–strain loop. In this region the elasticity decreases with increasing temperature and accordingly indicates a rubber-like behavior.

6. It is concluded that Astbury's newer structure for $\alpha$-keratin is much too condensed and the suggestion is made that the principal feature of $\alpha$-keratin is the close packing of successive alternate amino acid residues along the peptide chain.

7. It is suggested that the stretching of hair from about 3 to 20% extension involves a process which resembles a thixotropic gel–sol transformation. This transformation is mainly responsible for the irreversible nature of the extension–contraction process.

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[CONTRIBUTION FROM THE SCHOOL OF MEDICINE, ST. LOUIS UNIVERSITY]

# A Study of Some Reactions between Dry Inorganic Salts. VI. The Reciprocal System $CsCl + KBr \rightleftarrows CsBr + KCl$ below the Fusion Temperature[1]

BY J. WM. VOGT WITH LYMAN J. WOOD

It has been previously reported[1a] that when an equimolar mixture of cesium chloride and potassium bromide is heated at from 50 to 100° below the fusion temperature it is partly converted into cesium bromide and potassium chloride. If the heating is continued for a sufficient length of time an equilibrium is established which is represented by the equation

$$CsCl + KBr \rightleftarrows CsBr + KCl$$

The same equilibrium mixture is obtained if an equimolar mixture of cesium bromide and potassium chloride is heated at the same temperature. When the equilibrium mixture is quickly cooled to room temperature, it is found to consist of two binary solid solutions, one of which is made up of cesium chloride and cesium bromide and the other of which is made up of potassium chloride and potassium bromide. Preliminary results obtained for this reaction indicated that equilibrium mixtures result at various temperatures and for different starting compositions. In the work that is now being reported the range of the starting compositions has been widened, the temperature has been more carefully controlled and new techniques have been introduced that have resulted in more satisfactory analytical data.

**Materials, Apparatus and Methods.**—The potassium chloride and potassium bromide were Analytical Reagent quality and the cesium chloride and cesium bromide were C. P. stock supplies from the Maywood Chemical Company. The chemicals were fused and, after cooling, were ground and kept in a desiccator until needed. In general, larger amounts of the CsCl–CsBr mixtures were used than in previous work, thus minimizing the effect of the unavoidable error in weighing. Also, for the most part, the whole of any given mixture was used for any given heat treatment whereas in previous work mixtures were sometimes subdivided before heating, which would produce errors in composition in case the mixing was not thorough. A miniature mixing mill was devised for mixing samples that were to be subdivided.

The compositions of the equilibrium mixtures were determined by the method of X-ray crystal analysis, using the same X-ray diffraction equipment as previously described. Several changes in manipulation, however, were made. A bearing and pulley wheel were mounted on the cassette in such a way that the small sample tube could be rotated. This was considered to be quite important since spotted interference lines had often been obtained when photographing reaction mixtures that had not been melted.

In the earlier work with this reaction the interference pattern of the sample was photographed on one edge of the film and that of the standard was photographed on the other. Some of the starting mixture, which was not subjected to the heat treatment, was generally used as the standard. In this way differences in density between the sample and the standard were avoided but there was introduced the possibility of a greater or smaller amount of interaction between the components of the standard. It was believed at the time that the amount of such reaction was entirely negligible but it has since been found that such was not always the case. Any small amount of cesium bromide resulting from the interaction of a CsCl–KBr standard mixture could form a solid solution with the residual cesium chloride and the use of any of the interference lines of this solid solution, on the assumption that they were due to pure cesium chloride, would lead to erroneous measurements. Because of the uncertainty

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[1] Read at the Detroit Meeting of the American Chemical Society, April, 1943.

[1a] H. L. Link and Lyman J. Wood, THIS JOURNAL, **60**, 2320 (1938); **62**, 766 (1940).

in the absolute values of these standard lines the cube edge measurements previously reported by Link and Wood were carefully repeated and small differences were found. These small differences in absolute values in no way affect the conclusions formerly drawn which are completely confirmed by the measurements reported below.

In the present work powdered aluminum was used as a standard of reference and was found to offer several important advantages. The aluminum powder, prepared by filing a sheet of pure aluminum, was mixed directly with the unknown sample and both interference patterns were photographed together on the same edge of the film. The aluminum powder served as a diluent as well as a standard, making the cesium salts more easily photographed, and eliminated uncertainties resulting from a comparison of sample and standard lines on opposite edges of the film. The only difficulty encountered arose from the fact that occasionally an aluminum line and a sample line occurred so near each other that neither line could be measured safely. However, this difficulty was not serious since the nature of the sample patterns had previously been determined and it was necessary to measure only a very few lines. Many careful measurements showed that better results could be obtained if the camera radius was determined for each individual film and this procedure was followed consistently in obtaining all results reported below.

The accuracy obtained in measuring the lines was improved appreciably by the use of a traveling microscope. A light line was drawn on the film by means of a razor edge parallel to the edge of the pattern and about midway between the ends of the interference lines and one or two cross scratches were made on the line. The film was first placed in a holder equipped with a hair line and after setting the hair line over a standard line the distance between the hair line and one of the cross scratches was carefully measured by means of the traveling microscope. This same procedure was then carried out for an interference line of the mixture being analyzed after which the *d* value corresponding to this unknown line could be calculated. The setting of the hair line over the interference line was the same as in the former procedure and represented no advantage but any uncertainty as to the measurements between a given hair line setting and a cross scratch was eliminated since these measurements could be duplicated with high accuracy (0.001 cm. or less). The accuracy of the method is discussed further under the section on experimental results (see Table I).

The same electric muffle furnace was used for heating the samples as before but several important improvements were made. Careful calibration of the furnace showed a considerable temperature gradient from front to back but very little from side to side. A crucible rack was constructed so that rows of three crucibles could be heated at almost exactly the same temperature. The crucibles were suspended with their bottoms approximately 0.25 inch from the floor of the furnace. At first the furnace temperature was controlled manually by means of a variac transformer, the temperature being checked every hour during the day and night by means of a Leeds and Northrup type K potentiometer. It was found possible to maintain the temperature to within approximately ±2.0°. During the latter runs the furnace temperature was controlled more carefully by a photoelectric cell and thyratron tube, an arrangement found to be entirely satisfactory.

## Experimental Results

**Cube Edge Values of Aluminum, Cesium Chloride and Cesium Bromide.**—Since it was proposed to use the $Al_{311}$ and the $Al_{222}$ interference lines as reference lines, their *d* values were carefully determined by mixing pure aluminum powder with sodium chloride and proceeding as described above. The cube edge values obtained for aluminum in this manner are recorded in Table I. In a similar manner cube edge values for cesium chloride and cesium bromide (Table I) were also obtained, the 220 and 310 interference lines being measured in each case. These interference lines were used as calibration and reference points in analyzing the equilibrium mixtures. While the analytical results based on these lines will be valid, cube edge values for aluminum, cesium chloride and cesium bromide calculated from them cannot be expected to show perfect agreement with more probable values calculated from a larger number of lines. Nevertheless, they do show good agreement with the apparently best values from the literature which are 4.0413 Å. for aluminum,[2] 4.113 Å. for cesium chloride[3] and 4.286 Å. for cesium bromide.[4]

Table I

Cube Edge Values in Å. for Aluminum, Cesium Chloride, Cesium Bromide

| | Al | CsCl | CsBr |
|---|---|---|---|
| | 4.0405 | 4.1142 | 4.2840 |
| | 4.0408 | 4.1146 | 4.2854 |
| | 4.0400 | 4.1156 | 4.2862 |
| Average | 4.0404 | 4.1148 | 4.2852 |

In the previous work[2] it has been reported that the cube edge values of the CsCl–CsBr solid solutions were in good agreement with the requirements of Vegard's Additivity Law.[5] When carefully investigated by means of the new technique, the results reported in Table II were found to deviate slightly from the additivity law. The cube edge values of Table II were plotted against composition and the resulting calibration curve

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(2) E. R. Jette and Frank Foote, *J. Chem. Phys.*, **3**, 605–16 (1935).

(3) E. Broch, I. Oftedal and A. Pabst, *Z. physik. Chem.*, **3**, 209–14 (1929).

(4) W. P. Davey, *Phys. Rev.*, [2] **21**, 145 (1923).

(5) Vegard, *Z. Physik*, **5**, 16 (1921).

(Fig. 1) was used for obtaining the composition of any given solid solution from its cube edge.

TABLE II

CsCl–CsBr SOLID SOLUTIONS OF KNOWN COMPOSITIONS

| Mole % of CsBr | Heat treatment | Cube edge $CsX_{220}:Al_{311}$ | Cube edge $CsX_{310}:Al_{311}$ |
|---|---|---|---|
| 25 | Melted | 4.1555 | 4.1573 |
| 50 | Melted | 4.2049 | 4.2045 |
| 50 | Heated 392 hours at 400° | 4.2061 | 4.2080 |
| 62.5 | Melted | 4.2261 | 4.2253 |
| 75 | Melted | 4.2446 | 4.2429 |
| | | 4.2422 | 4.2470 |
| 87.9 | Melted | 4.2674 | 4.2670 |
| 92.5 | Melted | 4.2708 | 4.2756 |

**The Reaction** CsCl + KBr ⇄ CsBr + KCl **at 477 and at 400°.**—Various mixtures comprising the reciprocal system CsCl + KBr ⇄ CsBr + KCl, made by intimately mixing 250 mesh powders, were heated at 477 and at 400° until equilibrium was reached. It was found that a three-day heating period was sufficient at 477° although most of the mixtures were given a preliminary heating before the final three days. During the final heating period the temperature variation was not greater than ±5.0°. The heating period at 400° was fourteen days. It has been shown previously[2] that these equilibrium mixtures are made up only of the binary solid solutions KCl–KBr and CsCl–CsBr and that it is therefore necessary to analyze only one of these solid solutions. The CsCl–CsBr solid solution was analyzed in each case by the method of X-ray analysis by the new technique described above. The number of moles of cesium bromide in each equilibrium was obtained in this way and tabulated in Table III. It is to be noted that in case 2 and case 3 more cesium bromide was found than for case 1 while in case 4 and case 5 the amount of cesium bromide that reacted with the potassium chloride was more than in case 1. All of these results are in qualitative agreement with the law of mass action.

TABLE III

REACTION NO. 11 AND THE LAW OF MASS ACTION

| Case no. | Molar ratio CsCl | KBr | CsBr | KCl | Moles of CsBr in equilibrium mixture 477°C. | 400°C. |
|---|---|---|---|---|---|---|
| 1 | 100 | 100 | | | 88.8 | 90.0 |
| 2 | 100 | 200 | | | 98.1 | 99.1 |
| 3 | 200 | 100 | | | 97.9 | 99.6 |
| 1 | | | 100 | 100 | 88.8 | 90.0 |
| 4 | | | 200 | 100 | 184.5 | 187.0 |
| 5 | | | 100 | 200 | 83.5 | 85.2 |

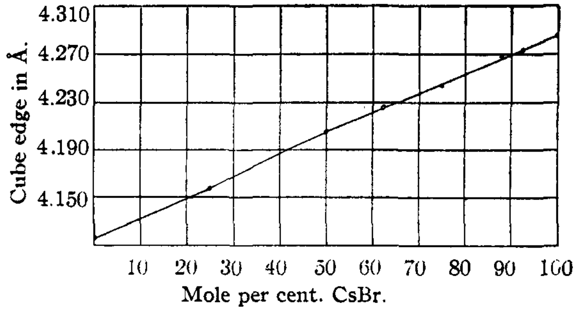

Fig. 1.—Showing variation of cube edge with composition in CsCl–CsBr solid solution.

The results shown in Table III for 477° are mean values of the results listed in Table IV. Each equilibrium mixture was approached from opposite directions as indicated by the letters under the case numbers. Under the first letter is described the composition before heating of the mixture containing both cesium chloride and potassium bromide (reactive pair) and under the second letter is described the composition before heating of the mixture containing both cesium bromide and potassium chloride (balanced pair). That equilibrium has been reached is indicated by the very excellent agreement between the cube edge values for the CsCl–CsBr solid solutions formed in each pair of equilibrium mixtures. In no case is the deviation greater than ±0.001 Å. from the mean.

For each individual equilibrium mixture an equilbrium constant was calculated by means of the relationship

$$\frac{[CsBr] \times [KCl]}{[CsCl] \times [KBr]} = K$$

in which the quantities in the brackets are moles of CsBr, KCl, CsCl and KBr, respectively. An average value of 62.9 for *K*, obtained by using the

TABLE IV

EQUILIBRIUM AT 477°

| Case no. | Composition before heating CsCl | KBr | CsBr | KCl | Moles of CsBr and KCl in the balanced pair CsBr | KCl | Cube edge If the mass law holds | Observed |
|---|---|---|---|---|---|---|---|---|
| 1 A | 100 | 100 | | | 89.2 | 89.2 | | 4.268 |
| B | | | 100 | 100 | 88.4 | 88.4 | | 4.267 |
| 2 C | 100 | 200 | | | 98.6 | 98.6 | 4.283 | 4.283 |
| G | | 100 | 100 | 100 | 97.6 | 97.6 | | 4.281 |
| 3 D | 200 | 100 | | | 97.4 | 97.4 | 4.204 | 4.204 |
| H | 100 | | 100 | 100 | 98.4 | 98.4 | | 4.204 |
| 4 F | | | 200 | 100 | 184.0 | 84.0 | 4.273 | 4.272 |
| J | 100 | 100 | 100 | | 185.0 | 85.0 | | 4.273 |
| 5 E | | | 100 | 200 | 82.7 | 182.7 | 4.260 | 4.258 |
| I | 100 | 100 | | 100 | 84.2 | 184.2 | | 4.260 |

average composition for equilibrium mixtures 1-A and 1-B (Table IV) has been used in calculating cube edge values for the CsCl–CsBr solid solution for each case that should be obtained if there is quantitative agreement with the law of mass action. These are compared with the observed values in the last 2 columns of Table IV. In no case is the deviation of the observed value from the calculated greater than 0.002 Å., which is within the range of unavoidable experimental error. The equilibrium constant for case 1 was used in the calculations rather than the average value of 58 for all of the cases since many more observations were made for case 1 and hence this value for $K$ was considered to be more reliable. It perhaps should be pointed out that the absolute differences between the values of $K$ for a difference of 1 mole of cesium bromide in the equilibrium mixture varies greatly with the composition of the equilibrium mixture. In case 4 (Table IV) a difference of 1 mole of cesium bromide in the equilibrium mixture corresponds to a difference of 10 in the value of the equilibrium constant while in case 3 a difference of 1 mole of cesium bromide corresponds to a difference of 24 in the value of $K$. In case 2-G if the moles of cesium bromide were increased by 1 $K$ would increase from 38 to 68, an increase of 29 while in case 2-C if the moles of cesium bromide were increased by 1 the value of $K$ would change from 68 to 248, an increase of 180. It is not possible to say how much of the variation in the equilibrium constants is actual and how much is due to unavoidable experimental error involved in measuring the cube edges of the CsCl–CsBr solid solutions. The answer to this question will have to await a more precise method of analysis. It is doubtful whether more accurate measurements of cube edges would be of any value since the crystal planes of the solid solutions may not be perfectly formed.

A comparison of the corresponding values in the last two columns of Table III reveals that the number of moles of cesium bromide in the equilibrium mixture in each case is slightly higher at 400 than at 477° indicating that the reaction is exothermic when it proceeds in the direction of the balanced pair. If the equilibrium constant at 477° be taken equal to 63 and at 400° equal to 77 (an average value including results not shown in Table III) and $\Delta H$ be calculated, a value of $-2.6$ kilocalories is obtained whereas $\Delta H$ equals $-1.26$ kilocalories when it is calculated from the heats of formation. It is likely that no great significance should be attached to the fairly good agreement existing between these values. The heats of formation used in the calculation are for room temperature and they are not known between 400 and 500°. While it is possible that the heats of formation of potassium chloride and potassium bromide may not be very different at the higher temperatures, cesium chloride is known to undergo a transition[6] at 445° from a body-centered lattice to a face-centered lattice and 1.8 kilocalories of heat are absorbed per mole. If this transition occurs when cesium chloride is in solid solution with cesium bromide the equilibrium constants at 400 and at 477° could not be used for calculating $\Delta H$ as described above. If, on the other hand, the transition of cesium chloride does not occur when in solid solution with cesium bromide, its heat of formation might well be very different from that at room temperature. Furthermore, small changes in the cube edge of the CsCl–CsBr solid solution, falling within the limit of unavoidable experimental error, may produce quite large differences in the equilibrium constant and small changes in the equilibrium may bring about a relatively large change in $\Delta H$.

A study of this reaction is being continued in several directions. The range of the composition of starting mixtures is being widened and equilibrium at other temperatures is being investigated, especially at or near 445°, the transition temperature of cesium chloride. The data listed in Tables III and IV emphasize the need of a more precise method for analyzing the equilibrium mixtures and to this end attempts have been made to make use of the index of refraction of light but these efforts have thus far met with little success. The results of these studies are being described in a forthcoming paper.

## Summary

1. When an equimolar mixture of cesium chloride and potassium bromide (reactive pair) was heated for three days at 477° an equilibrium was produced as represented by the equation

$$CsCl + KBr \rightleftharpoons CsBr + KCl$$

An equilibrium mixture having this same composition was obtained when an equimolar mixture of cesium bromide and potassium chloride (balanced pair) was heated for three days at the same temperature.

2. When either cesium chloride or potassium bromide was added to the equimolar mixture of the reactive pair before heating, the equilibrium shifted to the right in quantitative agreement with the law of mass action.

3. When either cesium bromide or potassium chloride was added to the equimolar mixture of the balanced pair before heating, the equilibrium shifted to the left in quantitative agreement with the law of mass action.

4. The results obtained for this same reaction at 400° were likewise in accord with the law of mass action although the quantitative agreement was not quite so good as at the higher temperature.

St. Louis, Missouri Received September 28, 1943

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[6] G. Wagner and L. Lippert, *Z. physik. Chem.*, **B36**, 263 (1936).