In Tab. 1 sind die experimentell bestimmten und die theoretisch berechneten Werte für K, Rb und Cs aufgeführt.

Man bemerkt, daß bei Berücksichtigung der hier erreichten Meßgenauigkeit von 15% das rPodukt der Quotienten $(N/N_a) \cdot (\sqrt{m/m^*}) = A$ für K und Rb als gleich 1 angesehen werden kann, was soviel bedeutet, daß bei diesen beiden Metallen die Leitungselektronen als frei anzusehen sind, in Übereinstimmung mit anderen Meßergebnissen [3]. Auffallend ist jedoch die starke Abweichung bei Cs, was zum Schluß zwingt, daß bei diesem Metall die Leitungselektronen schon stark vom Verhalten eines freien Elektronengases abweichen.

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Anomalous Proton Conductance and the Mechanism of Dipole Rotation in Water and Ice

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In recent publications [1] EIGEN and DE MAEYER have examined the experimental data on anomalous proton mobility in relation to the various theories of proton conductance. Whilst we are in general agreement with the conclusions of these authors concerning the mechanism of proton conductance in aqueous solutions, several points have been raised [1] which require clarification, as below.

1. The rate-determining step and rotation of H_2O molecules

By estimating the relative rates of H_2O dipole rotation between successive proton transfer events and of proton tunneling, we have sought to deduce the rate-determining step in proton mobility in aqueous acid solutions [2]. In this calculation, the dipole reorientation rate used was estimated from that found for relaxation in ice ($c \cdot 10^6$ sec^{-1}). The choice of this figure has been questioned [1] and it has been suggested that a more appropriate rate might be that (viz. 10^{11} sec^{-1}) for relaxation in liquid water. However, in order to evaluate the rate-determining step in proton mobility, we require to know for a given proton flux, the probability that a given water molecule in a chain of hydrogen-bonded water molecules in water will be thermally reoriented into a configuration favourable for rapid proton transfer by tunneling, *between* the moment of passage of one proton along this chain and that of the next in the same direction. In ice, the heat of activation for dipole rotation is about [3] 13.3 kcal mole^{-1}, yet for water it is only about [4] 3.9 kcal mole^{-1} at 0 °C. This difference is unlikely to be due to any appreciable dissociation of hydrogen bonds in water compared with that in ice since the heat of fusion of ice is only about one tenth the heat of sublimation of ice and even at the boiling point, the proportion of hydrogen bonds broken can only be small. Owing to the much higher proton concentration in water than in ice [5] it is more reasonable to interpret the dielectric relaxation behaviour in pure ice as being governed by "libration" — "free rotation" transitions in the absence of proton fields, whilst in the case of water, as being determined mainly by rotations of water molecules induced by the fields of H_3O^+ ions which have arrived as neighbours to these water molecules by successive proton transfer events. Field-induced rotations would tend to be more numerous in water than in ice on account of the higher proton concentration in water and aqueous acid solutions than in ice. The heat of activation for relaxation in water and acid solutions can then be lower because the strong fields of the migrating protons assist the rotation of water dipoles by the mechanism discussed previously [2]. The relaxation rate of 10^{11} sec^{-1} in water is therefore rather to be associated with these rotations induced by the fields of hydroxonium ions than with thermally induced rotations probably at non-ionic defect sites [6] which appear to occur in ice. It is, however, the rate of the thermally induced rotations, *i. e.*, those which occur *between* proton transfer events which is required for the purpose of evaluation of the *rate-determining step* in proton mobility in aqueous acid solutions. Although we have used the relaxation frequency for rotation of dipoles in ice, this does not imply that we regard the overall relaxation rate in water as the same as that in ice; experimentally, these rates differ in fact by a factor of about 10^5.

The self-consistency of the proposed change of mechanism has been checked [4] by calculating the relative probabilities of relaxation by the field-induced mechanism, (I), and thermal reorientation mechanism, (II). Processes I and II can be shown [4] to have comparable rates at proton concentrations of the order of magnitude of 10^{-5} g ion l^{-1}, i. e., similar to that for which the change of mechanism for proton mobility is indicated [2, 7].

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2. *The Potential Energy Barrier*

The validity of the potential barrier used in our calculations [2] has also been questioned [1] on the grounds that for the proton jump distance taken (0.35 Å, corresponding to an O – O distance of 2.45 Å), the considerations of HUGGINS [8] would indicate, in fact, no potential barrier for proton transfer between adjacent oxygen atoms. This conclusions seems to be unjustified since it appears that HUGGINS' treatment applies only to proton transfer between two oxygen atoms in the hypothetical case of OH . . . O and not, as we have considered [2], to proton transfer *from* an H_3O^+ ion *to* an adjacent water molecule. The potential barrier for the latter process is different from that for the case examined by HUGGINS since the interaction energies and the force constants relevant to the two cases are different, the bond energy between H^+ and H_2O in H_3O^+ being 180 kcal mole^{-1} and that in OH being 100 kcal mole^{-1}. The relevance of the work of HUGGINS is also rendered doubtful for the following reasons: in KH_2PO_4 the O – O distance is 2.55 Å, *i. e.* below the critical distance of 2.65 Å for which the calculations of HUGGINS indicate no potential barrier for H transfer; however, the residual entropy of KH_2PO_4 indicates [9] that the H atom is asymmetric in the bond, as in ice, so that there must be two potential energy minima for H in the hydrogen bond and not one. The potential barrier used in our calculations is hence not invalidated by HUGGINS' calculations.

3. *The Probability of Proton Tunneling*

Following our initial calculations [2] using a classical energy distribution of states for the OH bond, we have examined the effect of making a quantum sumation [10] as discussed by EIGEN and DE MAEYER [1]. The proton tunneling probability is found to be even greater than that calculated semi-classically so that our conclusions [2] regarding the rate-determining step in proton mobility in aqueous acids are unchanged.

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Stigmatisch abbildende bildfehlerfreie Massenspektrometer

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Vor kurzem [1] veröffentlichten wir gut realisierbare Fälle von stigmatisch abbildenden Massenspektrographen mit Doppelfokussierung 2. Ordnung an einer Stelle der geraden Bildkurve, bei welchen Toroidkondensatoren und homogene Magnetfelder verwendet werden. Bei diesen Apparaten verlaufen Ionen gleicher Energie zwischen beiden Feldern radial parallel. Inzwischen haben wir auch Fälle solcher stigmatisch abbildender Apparate berechnet, die ein radiales Zwischenbild der Richtungsfokussierung zwischen den Feldern haben und hauptsächlich als Massenspektrometer Verwendung finden können. Von HINTENBERGER und KÖNIG [2] wurden entsprechende Apparate mit ebener Abbildung mittels Zylinderkondensatoren und homogenen Magnetfeldern in großer Zahl berechnet.

Zu den im Falle ebener Abbildung zu erfüllenden fünf Bedingungsgleichungen [2] kommen im Fall stigmatischer Abbildung nach zwei hinzu, nämlich die axiale Abbildungsgleichung [3] und die Bedingung für das Verschwinden des radialen Bildfehlers axialer Herkunft

$$S_{1a} L_{33} + S_{1b} T_{33} \mp \tfrac{1}{2} S_{2a} P^2 = 0 . \qquad (1)$$

Wegen der Bedeutung des Faktors P siehe Anm. [4]. Er lautet allgemein

$$P = Q_3 - \left(\frac{a_e}{a_m} P_3 + \frac{d}{a_m} Q_3 \right) \operatorname{tg} \varepsilon' . \qquad (2)$$

(Wegen Q_3 und P_3 siehe Anm. [5].) Gl. (1) ist unabhängig von den anderen Bedingungsgleichungen erfüllbar durch zylindrische Krümmung einer der Stirnflächen des Toroidkondensators (Krümmungsradius q' bzw. q'') [3, 6].

Als weitere Bedingung wurde noch gleiche Neigung der Richtungs- und Energiefokussierungskurven am

	Φ_e	z^2	R'_e	$\frac{l'_e}{a_e}$	$\frac{l''_e}{a_e}$	$\frac{q''}{a_e}$	$\frac{a_e}{a_m}$	$\frac{d}{a_m}$	$\frac{k'}{a_m}$	$\frac{k''}{a_m}$	$\frac{l''_m}{a_m}$	$\frac{r_{R,E}}{a_m}$
a	80,35°	1,255	1	0,75	1,06	5,70	1,20	4,45	1,235	−0,315	0,315	0,929
b	90°	1,514	8,455	2,155	0	5,80	1,491	1,664	1,478	−0,601	0,601	1,132

Tab. 1.

[1] H. LIEBL u. H. EWALD, Z. Naturforschg. **14 a**, 199 [1959].
[2] H. HINTENBERGER u. L. A. KÖNIG, Z. Naturforschg. **12 a**, 773 [1957].
[3] H. LIEBL u. H. EWALD, Z. Naturforschg. **12 a**, 541 [1957].
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