ingly the results obtained for cell resistance would not reveal the true electrolytic resistance, but rather the cell impedance. If the usual parallel R–C circuit is assumed for a conductance cell, the apparent resistance equivalent of the impedance will be lower than the resistive component and the high field conductance quotients calculated from the data will be too large. Furthermore, should the capacitive component of the cell impedance change with field, additional difficulties of interpretation would result. This may be the explanation for the high values of Wien effect for potassium chloride reported in ref. 2, and for the disparity between our data and those of ref. 2 for glycine. It would require quite involved instrumentation to provide the successive pulse method of Blüh and Terentiuk with a means for reactive balancing at a 100 pulses/second repetition rate unless the rate of rise of the field were made quite slow.

We found no evidence in the series of measurements reported herewith of unusual or notable dielectric behavior of the glycine solutions with increasing field. As with the determinations on acetic acid,[5] it was found necessary to employ hydrochloric acid as reference electrolyte in order to avoid apparent bridge unbalance due to polarization occurring in different degree in the measurement and in the reference cells.

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The High Field Conductance of Lanthanum Ferricyanide at 25°[1]

BY DANIEL BERG AND ANDREW PATTERSON, JR.

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The high field conductance of lanthanum ferricyanide is of interest because the compound is a 3–3 valence-type electrolyte. Conductance data at low fields are available for it,[2] and it thus is possible to test the Onsager–Wilson theory[3] as well as the correction thereto suggested by Bailey and Patterson.[4] Previous determinations on 2–2 valence-type electrolytes have been reported for magnesium sulfate,[5] zinc sulfate[6] and copper sulfate.[7] High field conductance measurements for lanthanum ferricyanide have not been previously reported. We have determined the high field conductance of aqueous solutions of lanthanum ferricyanide, approximately 10^{-4} molar, relative to potassium chloride at 25°.

Determinations were made on three solutions of lanthanum ferricyanide of slightly differing concentration. The procedure employed was identical with that of Gledhill and

(1) Contribution No. 1132 from the Department of Chemistry, Yale University.

(2) C. W. Davies and J. C. James, *Proc. Roy. Soc. (London)*, **A195**, 116 (1948).

(3) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1950.

(4) F. E. Bailey and A. Patterson, THIS JOURNAL, **74**, 4428 (1952).

(5) F. E. Bailey and A. Patterson, *ibid.*, **74**, 4428 (1952).

(6) J. A. Gledhill and A. Patterson, *J. Phys. Chem.*, **56**, 999 (1952).

(7) D. Berg and A. Patterson, THIS JOURNAL, **74**, 4704 (1952).

Patterson.[6] All measurements were made with four microsecond pulse duration. The lanthanum ferricyanide employed was a C.P. sample from the Delta Chemical Works, New York City; it was prepared from lanthanum nitrate and potassium ferricyanide and it is thus probable that there was some potassium nitrate present as contaminant. The sample was guaranteed to be better than 99% pure; we shall discuss the probable purity of the sample in terms of the conductance results obtained with it. The lanthanum ferricyanide was used in the form of a strong stock solution, approximately 0.013 molar; the solutions for conductance determinations were prepared by weight dilution with conductivity water in the conductance cells. The potassium chloride reference solutions were of such concentration as to give a suitable resistance in the comparison cell, and thus near 3×10^{-4} molar. The temperature was maintained at 25 ± 0.015° referred to a recently calibrated platinum resistance thermometer.

The results are presented in Fig. 1 as three curves, B, C and D, for solutions of concentrations 1.032 × 10^{-4} molar, 1.025 × 10^{-4} molar, and 1.023 × 10^{-4} molar, respectively, based upon the formula La-$(Fe(CN)_6)\cdot5H_2O$. Curve A is a portion of the data computed according to the procedure outlined in ref. 4; curve E is for the Onsager–Wilson theory.[3] It will be observed that at 200 kv./cm. the fractional high field conductance quotient has a value of some 20% compared with a value of 3.3% for magnesium sulfate and with a value of 0.41% for potassium chloride, all at equivalent concentrations. At the same field the Onsager–Wilson theory yields a value of 7.39%, and the calculation of Bailey and Patterson[4] a value of 36.3%; both values depart widely from the quantity experimentally observed, curve B. The experimental results bend over in the manner characteristic of strong electrolytes even though the fractional high field conductance quotient is quite large. Filled circles near curve B will be discussed below.

In previous work we have found that a small amount of electrolytic impurity in the presence of an electrolyte under study may profoundly alter the shape of the Wien effect curve and the magnitude of the Wien effect. Glycine was found[8] to be especially sensitive in this respect: only 10^{-5} mole of ammonium chloride in a 0.6 molar glycine solution was sufficient entirely to alter the nature of the results obtained. It is thus necessary to demonstrate the effects of possible impurities such as potassium nitrate on the high field conductance results.

If we assume that there was present in the lanthanum ferricyanide 1% of potassium nitrate, and if we further assume that the same results would obtain if the pure salts were placed in separate conductance cells rather than (as in the actual experiment) in the same conductance cell, and the two cells then operated in parallel, we may calculate as follows: For potassium nitrate the value of Λ^0 is 145 and the concentration is 10^{-6} molar; for the lanthanum ferricyanide Λ^0 is 168 and the concentration is 10^{-4} molar. The resistance of the potassium nitrate solution will thus be approximately 100 times that of the lanthanum ferricyanide. If the resistance of the lanthanum ferricyanide solution is 1010 ohms and that of the potassium nitrate 101,000 ohms, the parallel circuit will have a resistance of 1000 ohms. If the resistance of the lantha-

(8) D. Berg and A. Patterson, *ibid.*, submitted for publication.

num ferricyanide cell decreases to 840 ohms as a result of the application of a 200 kv./cm, field, the fractional high field conductance quotient will be 20.2%. Under the same field the potassium nitrate cell will decrease in resistance to 100,600 ohms to yield a quotient of 0.4%. The parallel resistance of the two cells with field applied will be·833 ohms, and the computed fractional high field conductance quotient is then 20.0%. The resulting conductance measurement on the combined solution is thus in error by 0.2 in the term $\Delta\lambda/\lambda_0$ (%) at 200 kv./cm. If there is less potassium nitrate present, the error will be smaller. An error of 0.2 in $\Delta\lambda/\lambda_0$ (%) is almost ten times the reproducibility of results for repeated determinations on the same solution at the same field, but it is obviously only 1% of the quantity being measured. In view of the large Wien effect obtained experimentally, the shape of the Wien effect curve (Fig. 1), and the calculation, above, we are inclined to believe that the effect of electrolytic impurities such as potassium nitrate is in this case quite small; such would definitely not be the situation in an absolute conductance measurement, in contrast with the present measurements, which are relative only. We have checked these ideas by the addition of small amounts of potassium nitrate to the solutions of lanthanum ferricyanide; indeed, with potassium nitrate of 1.29×10^{-4} molar concentration and lanthanum ferricyanide of 0.648×10^{-4} molar concentration together, the high field conductance curve of the mixture lies two units above curve E at 200 kv./cm. The results reported herewith, curves B, C and D, are thus thought to be accurate to well within the factor of 0.1%, absolute, which has previously been claimed.[9]

In similar determinations with magnesium, zinc and copper sulfates the agreement between the experimental results and the corrected theory was considerably better than obtained in the present case. With a 3–3 electrolyte the influence of the value of $K(0)$ chosen is particularly important. Referring to equation (8) of ref. 4, we observe that the value of α at zero field is necessarily smaller for the weaker 3–3 electrolyte, and the change of α with increasing field proportionately greater than for 2–2 electrolytes. Stated in another fashion, the weak electrolyte high field effect is much more

TABLE I

CORRECTED ONSAGER–WILSON THEORY FOR THE HIGH FIELD CONDUCTANCE OF LANTHANUM FERRICYANIDE RELATIVE TO POTASSIUM CHLORIDE AT 25° USING SELECTED VALUE OF $K(0) = 3.702 \times 10^{-4}$

LaFe(CN)$_6$, 1.025×10^{-4} molar　　　KCl, 3.0×10^{-4} molar
　　　$\Lambda^0 = 168.9$　　　　　　　　　　　$\Lambda^0 = 149.85$

Field, kv./cm.	$F(b)$	α	$\alpha\{\Lambda^0 - \frac{S\Lambda_x}{(\alpha c)^{1/2}}\}$	$\frac{\Delta\lambda}{\lambda_0}$ corr., %	$\frac{\Delta\lambda}{\lambda_0}$ rel., %
0	1	0.8790	135.23	0.00	0.00
20	1.9559	.88435	139.64	3.26	3.16
40	3.4545	.9301	148.88	10.10	9.90
80	8.9549	.9708	157.16	16.21	15.91
100	13.6226	.9805	159.18	17.71	17.37
180	57.7882	.9953	162.56	20.21	19.81
200	79.5997	.9965	162.92	20.47	20.05

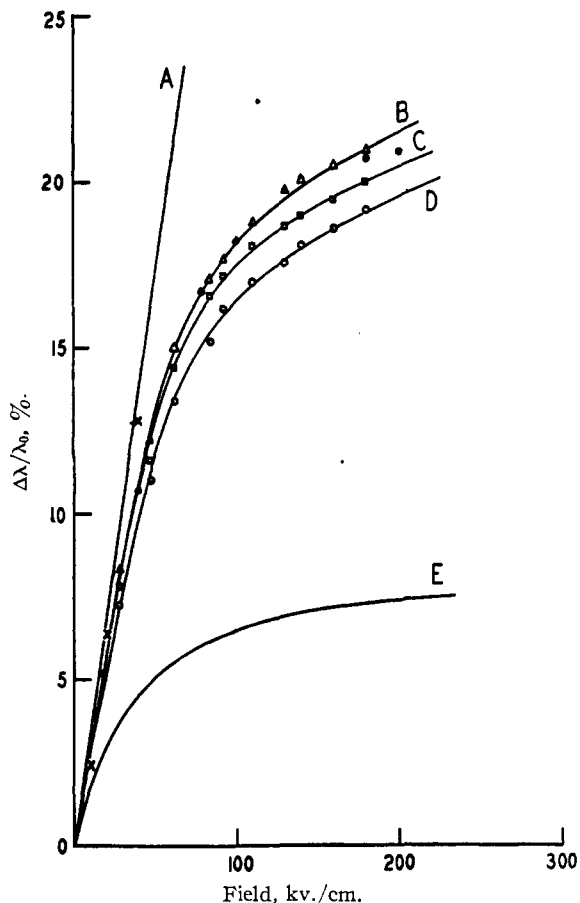(9) F. E. Bailey and A. Patterson, This Journal, **74**, 4426 (1952).

Fig. 1.—The high field conductance of aqueous solutions of lanthanum ferricyanide: A, (x) corrected Onsager–Wilson theory as in ref. 4; B, (△) 1.032×10^{-4} molar solution; C, (□) 1.025×10^{-4} molar solution; D, (O) 1.023×10^{-4} molar solution; E, Onsager–Wilson theory as in ref. 3; filled circles between curves B and C, corrected Onsager–Wilson theory using selected value of $K(0) = 3.50 \times 10^{-4}$.

important than the strong electrolyte high field effect for a 3–3 electrolyte. Since the value of the high field conductance quotient is a sensitive function of $K(0)$, we have utilized the experimental results of the present paper to compute a value of $K(0)$ which is concordant with the experimental results. Because the quantities α and $K(0)$ are interrelated, this computation required a certain amount of successive approximation. The values of $K(0)$, α, field and $\Delta\lambda/\lambda_0$ chosen or computed are given in Table I in the same form as Table I of ref. 4. Consistent values of $\alpha = 0.8790$ and $K(0) = 3.702 \times 10^{-4}$ were obtained; the expressions

$$\log \frac{\alpha^2 c}{3(1 - \alpha)} + \log \frac{y^2 \pm}{y_u} = \log K(0) \qquad (1)$$

where

$$\log \frac{y^2 \pm}{y_u} = -9 \left\{ \frac{\Gamma^{1/2}}{1 + \Gamma^{1/2}} - 0.20\,\Gamma \right\} \qquad (2)$$

with the terms as defined by Harned and Owen,[3] were used to relate α and $K(0)$. The value of $K(0)$ obtained by Davies and James was 1.82×10^{-4}. The filled circles lying between curves B and C of Fig. 1 are plotted from data computed in the same

way as Table I, but for $K(0) = 3.50 \times 10^{-4}$ and $c = 1.025 \times 10^{-4}$ molar. The data for the last column of Table I lie very close to curve C. Thus a difference of this order in $K(0)$ gives rise to a difference in $\Delta\lambda/\lambda_0$ (%) of one unit. This procedure therefore constitutes a sensitive method for estimation of $K(0)$.

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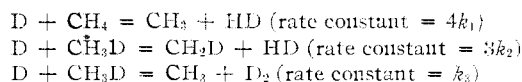YALE UNIVERSITY
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Exchange Reactions of Methane and Monodeuteromethane with Atomic Deuterium

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The reaction of atomic deuterium, produced by the discharge-tube method, with methane has been investigated a number of times.[1] The reaction takes place at an appreciable rate only at elevated temperatures, as it appears to have both a relatively high activation energy and a relatively low steric factor.[2] As yet, no unequivocal choice of mechanism for the exchange has been possible. The suggestions are (a) hydrogen abstraction, $D + CH_4 = CH_3 + HD$, followed by exchange of the methyl radical prior to stabilization as a deuteromethane, and (b) an inversion process, $D + CH_4 = CH_3 + H$. Since CH_3 radicals are known to exchange rapidly with D atoms,[3] in excess of the latter mechanism (a) would lead to CD_4 as the major exchange product. With mechanism (b) operative, the major product would be CH_3D. In the present work, the distribution of product deuteromethanes from the $D + CH_4$ reaction has been determined by means of mass spectrometry. CD_4 was found to constitute about 80% of the exchange product, most of the remaining deuteromethane being CHD_3. Strong evidence is thus provided that mechanism (a) alone accounts for this exchange.

In an extension of this work, the analogous $D + CH_3D$ reaction was investigated with a view to determining the nature of possible isotope effects. In terms of mechanism (a), the rate-determining reactions to be considered are

$$D + CH_4 = CH_3 + HD \text{ (rate constant } = 4k_1)$$
$$D + CH_3D = CH_2D + HD \text{ (rate constant } = 3k_2)$$
$$D + CH_3D = CH_3 + D_2 \text{ (rate constant } = k_3)$$

k_2 and k_3 should differ in magnitude due to zero-point energy differences. Taking the values of the C–H and C–D stretching frequencies in CH_3D to be 3000 and 2200 cm.$^{-1}$,[4] one can readily estimate the rate constant ratio $k_3/k_2 = 0.40$ at $350°$.[5] Whence, if k_1 and k_2 are assumed identical, the relative rates

(1) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1946, pp. 253–259.

(2) T. G. Majury and E. W. R. Steacie, *Disc. Far. Soc.*, "The Reactivity of Free Radicals," Toronto, Sept. 1952, Paper No. 4.

(3) N. Trenner, K. Morikawa and H. S. Taylor, *J. Chem. Phys.*, **5**, 203 (1937).

(4) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 309.

(5) H. Eyring and F. W. Cagle, Jr., *J. Phys. Chem.*, **56**, 889 (1952).

of exchange of CH_3D and CH_4 should be $(3k_2 + k_3)/4k_1 = 0.85$. In the present study, known mixtures of CH_3D and CH_4 were exchanged with atomic deuterium, and it was found that the CH_3D/CH_4 ratio did not change within the experimental error during 50% reaction. Since it is inconceivable that k_2 and k_3 be identical, it appears that k_2 must in fact be greater than k_1. Support for this hypothesis comes from the data on electron-impact bond-breakage probabilities for C–H in CH_4, C–H in CH_3D and C–D in CH_3D. A ratio of $1.00:1.21:0.46$ is obtained if one averages the results of the several studies reported.[6] If the D-atom exchange rate constants bear the same type of relationship to one another, nearly identical rates of exchange for CH_4 and CH_3D are to be expected, since in this event $(3k_2 + k_3)/4k_1 = 1.02$.

Experimental

The exchanges were effected in a conventional Wood tube type of apparatus,[7] utilizing a water-jacketed discharge-tube and a 2.5 liter spherical reactor flask. The reactor was enclosed by an electrically-heated transite oven, and its temperature controlled manually, temperature readings being taken on three strategically placed thermocouples on the walls of the bulb. Atom concentrations, which ranged between 10 and 20% in the various experiments, were estimated by means of a Wrede–Harteck gage. The glass surface of the reactor was "poisoned" toward hydrogen atom recombination by a coating of pyrophosphoric acid, which proved quite effective even at the elevated temperatures of the experiments. The methane reactant was introduced into the center of the reaction vessel at a rate of about 1 cc. per minute at N.T.P. At the low pressure within the reactor (0.5 mm.) rapid diffusional mixing with the excess of partially dissociated deuterium took place (rate of deuterium flow was 65 cc. per minute at N.T.P.). On leaving the reactor, the methane products and a small amount of deuterium were retained in a silica gel trap maintained at liquid air temperature. At the completion of the run, usually of 10 to 15 minutes duration, the methanes were separated from the adsorbed deuterium by repeated distillation between two alternately chilled silica gel traps. The methanes were then completely desorbed by warming to $-80°$ and samples taken for mass spectrometric assay.

Pure methane was prepared by the hydrolysis of methylmagnesium iodide in an atmosphere of hydrogen. The Grignard was prepared as a paste in dioxane, and aqueous dioxane added as hydrolyzing reagent. The gas was purified by passage through traps at Dry Ice and liquid air temperatures, and finally condensed into a pumped-down liquid-oxygen-cooled trap at $-215°$. Monodeuteromethane of high purity was similarly prepared, using rigorously dehydrated solvent and 99.97% heavy water. The methane/deuteromethane mixtures were made up manometrically. Deuterium was produced by the electrolysis of 99.97% heavy water containing a little NaOD. Small samples of CH_2D_2 and CHD_3 were prepared for mass spectrometer calibration purposes by the action of aluminum/mercury couple on CH_2I_2 and $CHBr_3$, respectively, in the presence of 99.97% heavy water.

The mass spectrometric analyses were performed on a Consolidated Engineering Corporation mass spectrometer. Calibration spectra of CH_4, CH_3D, CH_2D_2 and CHD_3 were obtained from samples of these gases as prepared above, while that of CD_4 was calculated from the spectrum of CH_4, to which it is closely enough analogous for our purpose.[6b,c] The parent peak sensitivities of the various methanes were assumed identical in making the composition computations. The percentages quoted for CH_4, CH_3D, CHD_3 and CD_4 are probably accurate to within one unit, but there is more uncertainty concerning the CH_2D_2 due to the large overlap of

(6) (a) M. W. Evans, N. Bauer and J. Y. Beach, *J. Chem. Phys.*, **14**, 701 (1946); (b) V. H. Dibeler and F. L. Mohler, *J. Research Natl. Bur. Standards* **45**, 441 (1950); (c) D. O. Schissler, S. O. Thompson and J. Turkevich, *Disc. Far. Soc.*, **10**, 46 (1951).

(7) Reference (1), p. 33–36.