475 and 450 obtained by us. This fact indicates the approximate nature of the extrapolation, but lends support to the validity of the measurements since good agreement for the partial molal heat content relative to 0.05 M is obtained and since the maximum value of $\bar{L}_2$ is at the same concentration.

The Relative Partial Molal Specific Heat

Mean values of $\bar{C}_p - \bar{C}_{p_0}$ may be obtained directly by differentiation of equation (8), and are equal to the values of α given in Table III. For general purposes, however, it is better to employ the equation

$$\bar{C}_p - \bar{C}_{p0.05} = -NFT2b \qquad (9)$$

and the values of b' given in Table I and then add 17.2 cal., the value found for $\bar{C}_{p0.05} - \bar{C}_{p_0}$ from the temperature slope of $\bar{L}_2$. Since it is a simple matter to compute this quantity by equation (9), we have not compiled a table but have plotted in Fig. 2 the results at 25° against $m^{1/2}$. The curve L. S. represents the limiting slope of the Debye and Hückel theory, and the curve denoted R., that computed by Randall and Rossini.[13] The agreement with the calorimetric data is by no means as good as that obtained by Harned and Ehlers for hydrochloric acid solutions or by us for sodium hydroxide solutions. The discrepancy is of the order of that found by Harned and Nims in the case of sodium chloride solutions.

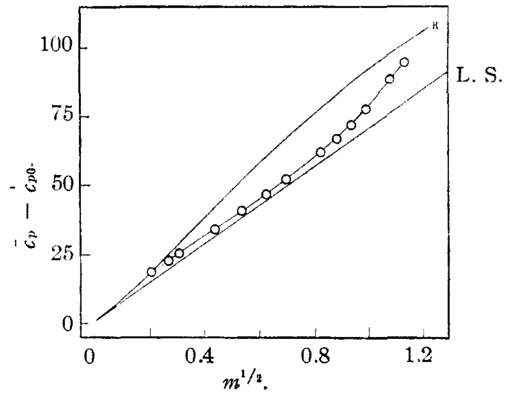

Fig. 2.—The relative partial molal specific heat of sodium sulfate in aqueous solution at 25°.

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[13] Randall and Rossini, This Journal, 51, 323 (1929).

Summary

1. Measurements of the cells

Pb(Hg) | $PbSO_4$ (s) | Na_2SO_4 (m) | Na_xHg |
Na_2SO_4 (0.05) | $PbSO_4$ (s) | Pb(Hg)

have been made from 0 to 40° at 5° temperature intervals.

2. From these calculations of the activity coefficient, the relative partial molal heat contents and specific heat of sodium sulfate in aqueous solution have been computed.

New Haven, Conn. Received December 21, 1933

NOTE

The Electric Moment of Dioxane

By C. H. Schwingel and E. W. Greene

During recent years 1,4-dioxane has been used to a limited extent as non-polar solvent for the determination of the electric moments of polar molecules. However, both Williams and Smyth have made measurements in non-polar liquids at a single temperature and have reported electric moments $\mu = 0.4 \times 10^{-18}$ and $\mu = 0.45 \times 10^{-18}$ e. s. u. for this compound.[1] According to Williams, "this value is so small that it is indistinguishable from zero by the method used."

In order to determine whether or not dioxane possesses a finite moment, it was thought worth while to study the effect of temperature on its polarization in the vapor state. This method for the determination of electric moments is more precise than the single temperature-solution method.

The table gives dielectric constant and polarization values obtained in our investigation of dioxane vapor. These data clearly indicate that 1,4-dioxane has zero electric moment. This is shown by the fact that the total molar polarization does not change with temperature.

Dielectric Constant and Polarization Data for 1,4-Dioxane Vapor

Temp., °K.	Press., mm.	$(\epsilon - 1)10^6$	P, cc.
337.0	104.4	377.4	25.1
337.1	108.1	381.4	24.6
339.0	126.7	439.6	24.3
341.2	97.3	334.6	24.2
384.7	178.3	558.0	24.8
385.0	180.5	563.7	24.8
385.2	184.2	555.2	24.0
442.0	203.5	538.5	24.1
487.0	233.2	566.6	24.5
		Av.	24.5 cc.

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[1] Williams, This Journal, 52, 1831–1838 (1930), and Smyth, *ibid.*, 53, 2115–2122 (1931).

With the solution method total polarizations of 26.0 cc. and 25.91 cc. were reported by Williams and by Smyth, respectively. These values appear to be too high, possibly due to the presence of moisture in the solution or to some solvent action. Using the value given by Smyth, $P_E = 21.6$ cc., and our value of 24.5 cc. for the total polarization, the atomic polarization for dioxane is 24.5 cc. − 21.6 cc. or 2.9 cc. This value for P_A is of an expected order of magnitude for a compound with a structure such as dioxane.

The apparatus used in this investigation has been described in the literature.[2]

The dioxane was dried for several days over metallic sodium and fractionally distilled. The fraction which boiled between 100.2 and 100.5° and which had a refractive index of 1.04208^{25}_{D} was employed.

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(2) Schwingel and Williams, *Phys. Rev.*, **35**, 855 (1930), Greene and Williams, *ibid.*, **42**, 119 (1932).

LABORATORY OF PHYSICAL CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Electrolysis of Ether Solutions of the Grignard Compound. Isolation, Identification and Quantitative Determination of Anodic Products

W. V. EVANS AND F. H. LEE

Little quantitative work has been done on the electrolytic products obtained at the anode during the electrolysis of the Grignard reagent. Jolibois[1] electrolyzed ethylmagnesium iodide expecting to isolate gaseous hydrocarbons but did not succeed. He assumed that methyl iodide instead of hydrocarbons was discharged.

Gaddum and French[2] aimed to reveal the mechanism of the reaction, but they used Grignard compounds which yield ether-soluble solid hydrocarbons. They were unable to tell where these hydrocarbons were formed, and their yield was poor. Rodebush and Peterson[3] thought the ethyl radical was liberated at the anode but they never isolated and identified it.

Along quite another line several workers have used different metals as anodes. Kondyrew and Manojew[4] found that a magnesium, zinc or aluminum anode will lose weight equivalent to the Faraday of electricity during electrolysis.

Recently French and Drane,[5] using aluminum, bismuth, gold, nickel, silver, tin, zinc, and cadmium as anodes, found that aluminum, zinc and cadmium were attacked while only aluminum exists in quantity in the solution. They comment that in cases where the anode was not attacked an equivalent amount of Grignard compound was decomposed. One well-known fact is that on electrolysis of the Grignard reagent using inert electrodes, magnesium is deposited on the cathode. One faraday of electricity liberates one equivalent of magnesium. This fact was demonstrated by Kondyrew,[6] who amalgamated his magnesium with mercury. We have checked this result, plating out the magnesium on platinum and determined the faraday equivalent. The present work was undertaken to determine the composition of the gaseous hydrocarbons evolved at an inert anode.

Experimental

The apparatus is shown in Fig. 1. The platinum electrodes 20 sq. cm. in area and 3 cm. apart were placed in the upper part of the cell, thus leaving a large space underneath for the accumulation of spongy magnesium.

A stirrer with a mercury seal was set between the electrodes. The gaseous products of electrolysis were led through a reflux condenser, washing bottle, delivery tube, salt water bath and finally to a eudiometer. No gas was evolved in the beginning of the electrolysis so the cell was allowed to run until the solution was saturated with the products of electrolysis and the temperature became constant. After the evolution of gas became constant, a copper coulometer was put in the circuit and a sample of gas collected. The volume of gas collected in the eudiometer (after correction) was taken as the total volume of hydrocarbons. The Grignard solutions were made by the usual method, heated in contact with excess magnesium, and analyzed by Gilman's acid titration method. A solution of 45% sulfuric acid was found suitable for removing ether from these hydrocarbons. The gases were collected over a saturated salt water solution. The gas was subsequently analyzed, mainly according to the method devised at the United States Bureau of Mines[7]

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(1) Jolibois, *Compt. rend.*, **155**, 353 (1912); **156**, 712 (1913).

(2) Gaddum and French, THIS JOURNAL, **49**, 1295 (1927).

(3) Rodebush and Peterson, *ibid.*, **51**, 638 (1929).

(4) Kondyrew and Manojew, *Ber.*, **58**, 469 (1925).

(5) French and Drane, THIS JOURNAL, **52**, 4924 (1930).

(6) Kondyrew, *J. Russ. Phys.-Chem. Soc.*, **60**, 545 (1928).

(7) Bulletin 197, U. S. Bureau of Mines.