nesium boride. Stock[1] observed, however, that magnesium boride forms only traces of boron hydrides when treated with liquid water, or with water vapor at 450°, and only hydrogen with water vapor at 900°. Magnesium boride is prepared by heating magnesium with boron trioxide, and generally has been considered to be Mg_3B_2. Recent work by Russell, Hirst, Kanda and King[2] and by Jones and Marsh,[3] has indicated the existence of several magnesium borides, but not an Mg_3B_2.

In our first work, magnesium boride was prepared from boron trioxide and magnesium according to the directions of Brandauer,[4] then ground in an iron ball mill with steel balls. The powdered boride was placed in a length of "Pyrex" tubing 1 cm. in diameter, where it was contained between glass wool plugs. The portion of the tubing containing the sample was enclosed in an electrical heating unit. Commercial cylinder hydrogen was passed through the tube and burned at a small jet at the exit. As the magnesium boride was heated, the flame remained colorless until the temperature reached about 400°, when the flame became a brilliant green. A cool glass plate held above the flame first received a deposit of liquid droplets (water) which evaporated as the plate warmed, leaving a solid, white deposit (boric oxide or boric acid). With the flame extinguished, a piece of moist red litmus paper held above the jet turned blue, and a piece of filter paper wet with 1% silver nitrate solution became a silvery black. A hanging drop of dilute potassium permanganate solution was decolorized. These reactions and the color of the flame indicated the presence of boron hydrides.

Volatile boron compounds also were obtained, although in lesser amounts, when the hydrogen was replaced by ethane, ethylene or methyl chloride. In no case was the exit gas spontaneously inflammable.

Magnesium boride prepared similarly, but ground in a porcelain ball mill with agate balls, gave only traces of boron hydrides when tested by the sensitive method of Etherington and McCarty.[5]

Table I summarizes our results with other metal borides. In each case, stoichiometric proportions of anhydrous reagents were pulverized and thoroughly mixed before firing in hydrogen to form the boride.

TABLE I

Boride mix.	Temperature of, °C. Formation	Reaction	Tests for boron hydrides Green flame	1% $AgNO_3$	Dil. $KMnO_4$
B + Ni	1500–1800	350–400	pos.	pos.	pos.
Ca + B_2O_3	400	400	pos.	pos.	
Al + B_2O_3	500	500	neg.	v.weak	v.weak
Zn + B_2O_3	250	250	pos.	pos.	pos.

In several of the above experiments, including the tests with magnesium boride, the hydrogen was alternately dried and saturated with water vapor without any significant effect on the production of boron hydrides.

Boron.—Negative results were obtained when a boron, prepared by the reaction of borax and aluminum, was fired to over 460° in hydrogen; mixing the boron with copper had no effect. However, a recent experiment with a sample of commercial boron gave strongly positive results at 840°, using hydrogen that had been passed through a "Deoxo" unit, then dried in a liquid nitrogen cooled trap packed with glass wool. The sample of boron was contained within the furnace tube in a quartz boat. The exit gas was passed through an uncooled trap and thence to a jet, where it burned with a green flame. When the exit trap was cooled with liquid nitrogen, the flame became colorless. After one hour, the contents of the trap were examined with a mass spectrometer; a spectrum characteristic of diborane was obtained.[6] The sample of commercial boron was analyzed by sodium peroxide fusion as described by Winslow and Liebhafsky[7] and found to contain 96.9% boron. A limited spectrographic analysis showed Fe, present; Ti, sl. trace; Mg, present; Ta, sl. trace; Ni, trace; Si, trace; Cu, present.

We wish to thank Dr. P. D. Zemany of this Laboratory for examining the reaction product with the mass spectrometer.

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(1) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 42.

(2) V. Russell, R. Hirst, F. A. Kanda and A. S. King, *Acta Cryst.*, **6**, 870 (1953).

(3) M. E. Jones and R. E. Marsh, THIS JOURNAL, **76**, 1434 (1954).

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(7) E. H. Winslow and H. A. Liebhafsky, *ibid.*, **64**, 2725 (1942).

RESEARCH LABORATORY
GENERAL ELECTRIC CO.
SCHENCTADY, N. Y.

Osmotic and Activity Coefficients of *p*-Toluenesulfonic Acid and *p*-Ethylbenzenesulfonic Acid and their Relationship to Ion-exchange Equilibria

BY O. D. BONNER, G. D. EASTERLING, D. L. WEST AND V. F. HOLLAND

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The determination of activity coefficients of cation-exchange resins, except for the most weakly cross-linked resins, is impossible because of the inability of the resins to swell sufficiently, when immersed in water, to form very dilute solutions. The monomeric structure representing these resins is very similar, however, to certain sulfonic acids which are not subject to this restriction. *p*-Toluenesulfonic acid (equiv. wt. 172.19), 2,5-dimethylbenzenesulfonic acid (equiv. wt. 186.22) and *p*-ethylbenzenesulfonic acid (equiv. wt. 186.22) are examples of acids which may be compared with this monomeric structure (equiv. wt. in the dry hydrogen form, 195–200).

Activity and osmotic coefficients of the lithium, sodium and potassium salts of *p*-toluenesulfonic acid have been previously determined.[1] The relative values of the activity coefficients for these salts and also for the acid should be of special significance in the interpretation of ion-exchange equilibria because of the rather unusual position of hydrogen ion in the ion-exchange selectivity scale. If the same standard state (*e.g.*, the hypo-

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(1) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

thetical one molal solution) is chosen for the ions in the resin and aqueous phase; and if the aqueous solution is very dilute, the selectivity coefficient or equilibrium quotient may be shown to be equal to the ratio of the activity coefficients of the two ions in the resin phase.[2] At any given concentration, the activity coefficients of most acids and their salts are usually in the sequence H > Li > Na > K, nitrates being a notable exception. For a more nearly correct correlation with ion-exchange equilibria these coefficients should be compared at constant water activity. The order of the sequence, however, would remain unchanged. If this sequence were also true for the resinates, the order of selectivity should be K > Na > H > Li. This would lead one to believe that the activity coefficients of the resinates, and possibly of the sulfonates, should be in the sequence Li > H > Na > K.

Experimental and Discussion

Activity and osmotic coefficients of *p*-toluenesulfonic acid and *p*-ethylbenzenesulfonic acid were determined by isopiestic comparison of these solutions with solutions of lithium chloride which were used as standards. Values of the osmotic and activity coefficients of lithium chloride are tabulated by Robinson and Stokes.[1] Osmotic coefficients were calculated by the equation

$$\gamma\phi = V_{ref}\frac{m_{ref}}{m}\phi_{ref} \tag{1}$$

Activity coefficients were calculated by an equation given by Robinson and Sinclair[3]

$$\ln \gamma = \ln \gamma_{ref} + \ln \frac{m_{ref}}{m} + \int_0^{m_{ref}} \left(\frac{m_{ref}}{m} - 1\right) d \ln \gamma_{ref}\, m_{ref} \tag{2}$$

Because of the hygroscopic nature of both sulfonic acids it was impossible to weigh them accurately. Solutions for isopiestic comparison were therefore prepared by dilution of a concentrated solution measured from a weighing buret. The concentrated solution was standardized by titration with standard alkali. The accuracy of concentrations determined in this fashion is, of course, limited to approximately 0.1%.

Tabulations of osmotic and activity coefficients as a function of concentration are given in Table I. The difference in the values of these coefficients of *p*-toluenesulfonic acid and *p*-ethylbenzenesulfonic acid at any concentration is appreciable even though they differ only by a CH_2 group. As the equivalent weight of the ion-exchange resin is nearer that of the *p*-ethylbenzenesulfonic acid than that of *p*-toluenesulfonic acid, it might be expected that the resin would more closely resemble the former substance in its osmotic properties.

TABLE I

TABLE OF OSMOTIC AND ACTIVITY COEFFICIENTS

	p-Toluenesulfonic acid		*p*-Ethylbenzenesulfonic acid	
m	ϕ	γ	ϕ	γ
0.1	0.922	0.759	0.914	0.758
.2	.899	.703	.890	.685
.3	.887	.660	.870	.635
.4	.877	.630	.851	.603
.5	.869	.608	.831	.570
.6	.861	.589	.812	.542
.7	.854	.573	.793	.516
.8	.849	.559	.774	.492
.9	.843	.546	.755	.469
1.0	.838	.535	.738	.449
1.2	.830	.515	.708	.415
1.4	.824	.498	.687	.387
1.6	.817	.483	.673	.366
1.8	.812	.469	.664	.348
2.0	.809	.459	.659	.335
2.5	.806	.439	.662	.311
3.0	.816	.427	.680	.299
3.5	.837	.425	.705	.292
4.0	.867	.430	.734	.289
4.5	.899	.437	.774	.292
5.0	.936	.448	.809	.296

TABLE II

OSMOTIC PROPERTIES OF 4% DVB ION-EXCHANGE RESIN AND TOLUENESULFONATES

			p-toluenesulfonates, $m\phi = 1.85$		
	m	Relative selectivity	m	γ	γ_{Li}/γ_x
Li	2.39	1.00	2.07	0.566	1.00
H	2.32	1.30	2.30	.445	1.27
Na	2.69	1.49	2.40	.433	1.31
K	2.93	2.03	2.89	.322	1.76

Plots of the activity coefficients of *p*-toluenesulfonic acid and its lithium, sodium and potassium salts as a function of $m\phi$ (water activity) are shown in Fig. 1. Because of solubility limitations, observed and calculated properties may be compared only for resins of less than 4% DVB content. Selectivity coefficients representing the relative affinity of a 4% DVB resin for these ions have been reported.[2] Toluenesulfonate solutions of $m\phi = 1.85$ have very nearly the same concentrations as 4% DVB resins. Comparisons of concentrations and selectivities are shown in Table II. Since ion exchange resins are 1-0 electrolytes γ_{Li}/γ_x instead of $(\gamma_{Li}/\gamma_x)^2$ is used as the basis of comparison. It is to be realized, of course, that mixtures of toluenesulfonates would have activity coefficient ratios slightly different from those calculated for solutions of the pure substances due to interionic effects, and it is to be expected that perhaps the ethylbenzene sulfonates could be more favorably compared with ion-exchange resins due to their greater similarities in structure. This comparison also fails to consider the effect of osmotic pressure on the activity coefficients of the resinates. Even so, the maximum deviation between the calculated activity coefficient ratios for the *p*-toluenesulfonates and the resin selectivities is of the order of 14% for 4% DVB resins and hydrogen ion fits into the sequence in the correct position.

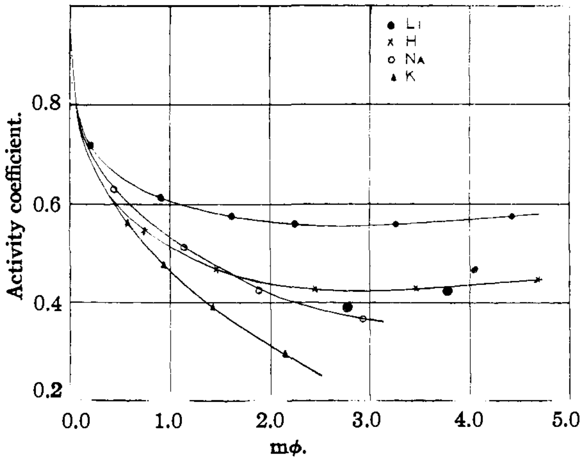

Fig. 1.—Activity coefficients of *p*-toluenesulfonates.

Acknowledgment.—The authors are indebted to Dr. R. H. Wiley for supplying the sample of *p*-ethylbenzenesulfonic acid used in this research and to the

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[2] O. D. Bonner, *J. Phys. Chem.*, **58**, 318 (1954).

[3] R. A. Robinson and D. A. Sinclair, THIS JOURNAL, **56**, 1830 (1934).

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTH CAROLINA
COLUMBIA, S. C.

The Heat of Formation of Tetrafluoromethane[1]

BY RALPH S. JESSUP, ROBERT E. MCCOSKEY AND RAYMOND A. NELSON

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The purpose of this note is to report a preliminary value for the heat of the reaction

$$CH_4(g) + 4F_2(g) \longrightarrow CF_4(g) + 4HF(g) \quad (1)$$

and a value for the heat of formation of CF_4 derived therefrom.

The measurements were made by "burning" weighed samples of methane with fluorine in a flame at constant pressure. The reaction took place in a copper reaction vessel immersed in the water of an electrically-calibrated calorimeter of the type described by Dickinson,[2] which was used to measure the heat of the reaction.

The construction of the burner is shown schematically in Fig. 1. Helium gas entering through the annular space surrounding the methane inlet tube was intended to keep the methane–fluorine flame from resting on the end of this tube. In preliminary experiments it was found that without the flow of helium the reaction was incomplete, as shown by the deposition of carbon around the methane port. With the arrangement shown in Fig. 1 the deposition of carbon was negligible.

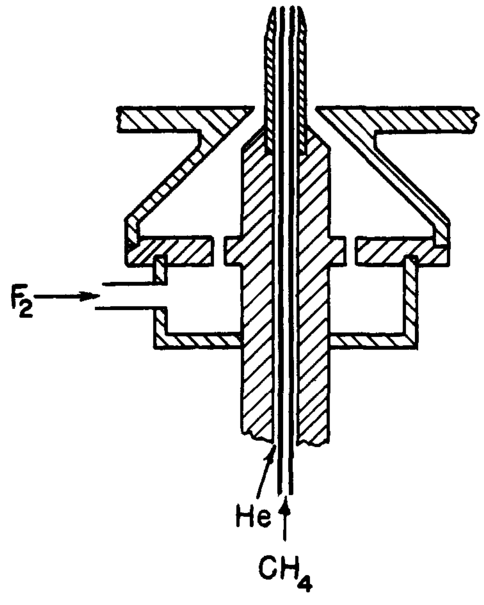

Fig. 1.—Schematic diagram of burner.

After leaving the reaction vessel the product gases passed through a helical monel tube, which served as a heat exchanger, before leaving the calorimeter. Hydrogen fluoride was removed from the fluorine before it entered the calorimeter by passing it over sodium fluoride maintained at Dry Ice temperature. Hydrogen fluoride formed in the reaction in the calorimeter was collected by means of a similar arrangement. The tetrafluoromethane formed was collected by condensation in a trap immersed in liquid nitrogen. The product gases were diluted with helium before entering the trap in order to reduce the partial pressure of the fluorine below its saturation pressure at the temperature of liquid nitrogen. Attempts to determine the amount of the reaction from the masses of HF and CF_4 formed were unsuccessful because of absorption of fluorine, or some of the impurities therein, by the sodium fluoride, and because of failure of the cold trap to retain all of the CF_4 passed into it. In the measurements reported the amount of reaction was determined by weighing the methane consumed.

The methane used was a purified sample which was analyzed by a mass spectrometer and found to contain the following amounts of impurities, expressed in mole per cent.: C_2H_6, 0.15; C_3H_8, 0.05; C_4H_{10}, 0.02; CO_2, 0.04; and N_2, 0.04. Impurities in the commercial fluorine used were determined by passing a measured amount of fluorine mixed with an equal volume of helium through a trap immersed in liquid nitrogen, weighing the condensate and analyzing it by means of a mass spectrometer. Similar analyses were made of the exhaust gases from the reaction vessel in each calorimetric experiment. Impurities found in the fluorine include CF_4, C_2F_6, C_3F_8, CO_2, water and air, together with small amounts of unidentified constituents. The total amount of impurities in the various tanks of fluorine ranged from near zero to about 4 mole per cent. The same impurities were found in the exhaust gases in any given experiment as in the fluorine used in that experiment, but usually in slightly different amounts. No fluorocarbons other than CF_4 were found in the exhaust gases unless they were also present in the fluorine used.

In calculating the results of the calorimetric experiments corrections were applied for the impurities in the methane, for reactions involving impurities in the fluorine, and for polymerization of hydrogen fluoride formed in the reaction. The correction for reactions involving impurities in the fluorine were calculated on the basis of the differences between the amounts of such impurities introduced with the fluorine, and the amounts collected in the products of the reaction. This correction is subject to considerable uncertainty because of possible errors of analysis, including errors resulting from the fact that some impurities were not identified, and because of uncertainty in estimated values for the heats of reaction of the impurities. Fortunately, the values found for the correction are relatively small, ranging from -0.5 to $+1.0$ kcal. per mole of CH_4 reacted. The correction for polymerization of hydrogen fluoride was calculated on the basis of P–V–T data by Long, Hildebrand and Morrell,[3] and was found to be about $+2.0$ kcal./mole of CH_4 under the conditions of the experiments (32° and a partial pressure of HF of about 170 mm. of mercury). The heat of formation of CF_4 was calculated from the measured heats of fluorination of methane (reaction 1), using the values $\Delta H_f = -17.94$ kcal./mole for the heat of formation of methane[4] at 32°, and $\Delta H_f = -64.2$ kcal./mole for the heat of formation of hydrogen fluoride.[5]

The results obtained, referred to a temperature of 32°, are tabulated.

Experiments 1 and 2 which gave the respective values -219.4 and -215.8 kcal. per mole for ΔH_f were rejected because of a leak in the methane line which was discovered after experiment 2.

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(1) This paper is based on research sponsored by the Ordnance Corps, U. S. Department of the Army.

(2) H. C. Dickinson, *Bull. Bur. Standard*, **11**, 189 (1914); Sci. Paper 230.

(3) R. W. Long, J. H. Hildebrand and W. E. Morrell, THIS JOURNAL, **65**, 182 (1943); see also R. L. Jarry and W. Davis, Jr., *J. Phys. Chem.*, **57**, 600 (1953).

(4) NBS Circular 461, Table 1w, 334 (1947).

(5) NBS Circular 500, Table 9-1, 19 (1952).