of the measurements.[9] Other examples are given by Brönsted.[10] For hydrogen-ion catalysis the salt effect is positive and for hydroxyl-ion catalysis negative. In all cases the effect is linear in dilute solution and consequently cannot depend on the activity of the reacting ion.

The author wishes to thank Professor J. N. Brönsted for many valuable suggestions.

Summary

1. A kinetic study has been made of a zero type reaction in which the reacting ion is trivalent.

2. The reaction serves as a critical test of the activity rate theory and the Brönsted formula. The results are in agreement with the Brönsted formula.

COPENHAGEN, DENMARK

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

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. VI THE ELECTRIC MOMENTS OF CERTAIN NITRO DERIVATIVES OF BENZENE AND TOLUENE

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Measurements of the dielectric constants of binary mixtures in which the first component, the solvent, is known to have no electric moment permit a calculation of the molar polarization, and therefore of the electric moment, of the second component. This calculation has been detailed in a number of places.[1,2,3] The purpose of this paper is to present dielectric constant and density data for solutions of a number of nitro derivatives of benzene and toluene in the non-polar solvent benzene, with the results of the calculations for the electric moments of the solute molecules.

The method used for the determination of the dielectric constants of the binary mixtures was given in the first paper of the series.[4] Their densities were determined by means of an Ostwald-Sprengel pycnometer. Both dielectric constant and density determinations were made at 25°; in every case the usual precautions for precision work were taken.

[9] Brönsted and Guggenheim, THIS JOURNAL, **49**, 2554 (1927).

[10] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

[1] Debye, "Handbuch der Radiologie" (Marx), **6**, 597 (1925).

[2] Lange, *Z. Physik*, **33**, 169 (1925).

[3] Williams and Krchma, THIS JOURNAL, **49**, 1676 (1927).

[4] Williams and Krchma, *ibid.*, **48**, 1888 (1926).

Purification of Materials

All substances used for the measurements reported were purified by the usual methods of crystallization or distillation or both. With the exception of the solvent, benzene, an outline of the method of purification for each particular substance used will not be given. These substances are tabulated with their melting points as determined by means of thermometers calibrated by the U. S. Bureau of Standards, and the method of purification used is indicated.

Benzene.—The benzene, obtained in a thiophene-free condition from the Eastman Kodak Company, was frozen out twice. After drying with phosphorus pentoxide it was fractionally distilled; boiling point (760 mm.) 80.10–80.20°.

Substituted Benzene Compounds

TABLE OF MELTING POINTS OF MATERIALS

Compound	Melting point, °C.	Compound	Melting point, °C.
Mononitrobenzene[a]	5.1– 5.4	*sym.*-Trinitrobenzene[b]	121.1–122.3
o-Dinitrobenzene[b]	116.0–116.5	*o*-Nitrotoluene[c]	−10.6–−10.9
m-Dinitrobenzene[b]	89.0– 89.5	*m*-Nitrotoluene[c]	15.5– 16.0
p-Dinitrobenzene[b]	171.5–172.0	*p*-Nitrotoluene[b]	52.2– 52.9

[a] Purified by fractional crystallization and distillation.

[b] Purified by recrystallization from benzene.

[c] Purified by distillation.

Results

The results of the experimental determinations are given in Table I. The columns of this table give, from left to right, the mole fraction of the benzene which was used as the solvent, M. F. C_6H_6; the density of the solution, d_4^{25}; the observed dielectric constant, ϵ; the molar polarization of the solution, $P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2}\frac{f_1M_1 + f_2M_2}{d} = f_1P_1 + f_2P_2$; and the molar polarization of the second component, $P_2 = \frac{P_{1,2} - f_1P_1}{f_2}$.

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA FOR MIXTURES

M. F. C_6H_6	d_4^{25}	ϵ	$P_{1,2}$	P_2
		Mononitrobenzene		
100.00	0.8731	2.283	26.74	348
96.88	.8850	2.98[a]	35.71	314
92.96	.9012	3.86	43.91	273
92.72	.9014	3.91	44.30	271
89.72	.9141	4.64	49.62	251
		o-Dinitrobenzene		
100.00	0.8731	2.283	26.74	800
99.63	.8761	2.48[a]	29.51	764
98.88	.8821	2.86	34.35	694
98.29	.8866	3.18	37.69	664
97.82	.8902	3.39	39.95	639

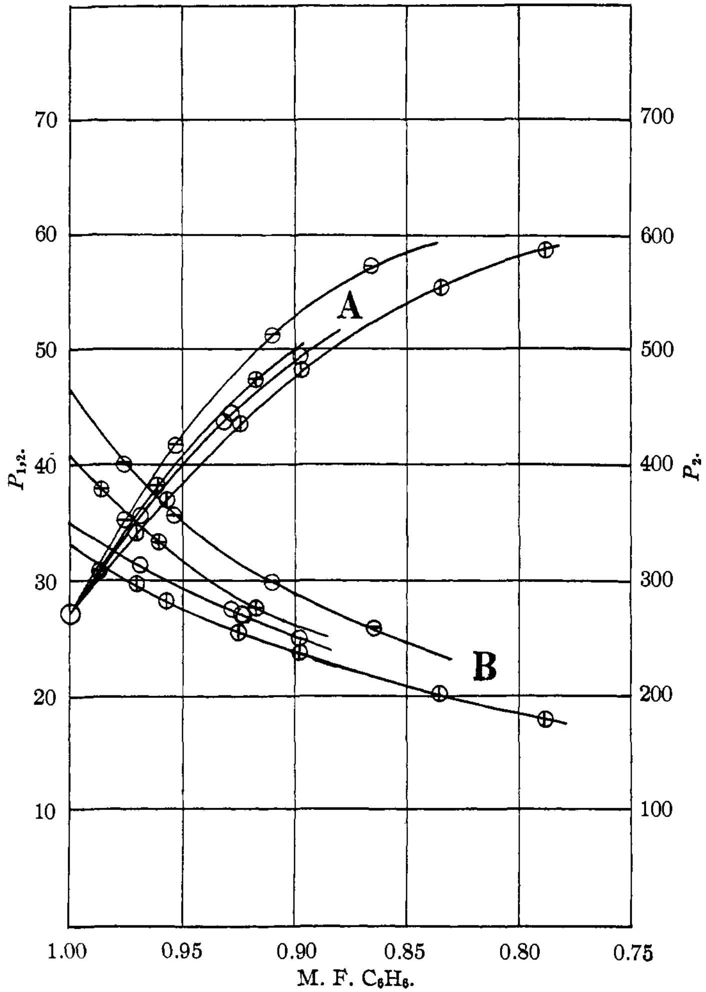
TABLE I (*Concluded*)

M. F. C_6H_6	d_4^{25}	ϵ	$P_{1,2}$	P_2
		m-Dinitrobenzene		
100.00	0.8731	2.283	26.74	338
98.46	.8852	2.60[a]	31.10	318
97.98	.8890	2.69	32.50	317
95.82	.9057	3.16	37.90	297
95.36	.9092	3.26	38.85	290
93.86	.9208	3.58	42.02	277
91.63	.9381	4.03	45.90	257
		p-Dinitrobenzene		
100.00	0.8731	2.283[b]	26.74	37.0
99.40	.8791	2.280	26.76	36.8
98.95	.8814	2.282	26.79	37.1
98.62	.8830	2.281	26.81	37.2
		sym.-Trinitrobenzene		
100.00	0.8731	2.283[b]	26.74	64.5
99.48	.8775	2.284	26.85	67.4
98.80	.8831	2.307	27.25	70.7
98.03	.8890	2.324	27.75	78.7
		o-Nitrotoluene		
100.00	0.8731	2.283	26.74	331
97.08	.8846	2.86[a]	34.45	297
95.80	.8892	3.08	37.21	284
92.46	.9022	3.77	43.70	254
89.50	.9135	4.36	48.70	237
83.50	.9284	5.34	55.70	203
78.80	.9492	6.20	58.80	179
		m-Nitrotoluene		
100.00	0.8731	2.283	26.74	407
98.74	.8782	2.62[a]	31.35	379
96.15	.8882	3.24	38.40	333
91.76	.9048	4.15	46.90	273
		p-Nitrotoluene		
100.00	0.8731	2.283	26.74	463
97.55	.8828	2.99[a]	35.80	400
95.38	.8911	3.58	41.87	355
90.93	.9082	4.77	51.15	298
86.52	.9248	5.88	57.60	257

[a] Correct to ±0.01.

[b] Correct to ±0.004.

In Fig. 1 are presented curves showing, first, the molar polarization of the solution plotted against the mole fraction of the solvent and, second, the molar polarization of the solute molecule plotted against the mole fraction of the solvent for mononitrobenzene and the nitrotoluenes. The latter curves are important in that they show exactly the manner in which the molar polarization of the second component, P_2, in infinitely dilute solution in the non-polar solvent is obtained. The molar polarization values of the second component for dilute solutions of finite concentration, obtained from the expression, $P_2 = (P_{1,2} - f_1P_1)/f_2$, are extrapolated to infinite dilution in the manner indicated. The curves for the other solute molecules are similar in all respects and have not been included.



⦶—*o*-Nitrotoluene, ⊕—*m*-nitrotoluene, ⊖—*p*-nitrotoluene, ○—mononitrobenzene; A—$P_{1,2}$ curves, B—P_2 curves.

Fig. 1.

Calculation of the Electric Moments of the Solute Molecules

The calculations of the electric moments of the various solute molecules were made in the manner described in a previous article,[3] and making like assumptions. The results of these calculations are given in Table II. The symbols used in the earlier article have been retained throughout.

TABLE II

ELECTRIC MOMENTS OF SOLUTE MOLECULES AT 25°

Molecule	P_2	P_2''	P_2'	$\mu \times 10^{18}$
Mononitrobenzene	348	33	315	3.90
o-Dinitrobenzene	800	35	765	6.05
m-Dinitrobenzene	338	35	303	3.81
p-Dinitrobenzene	37.0	35	2	0.32
sym.-Trinitrobenzene	64.5	40	24.5	1.08
o-Nitrotoluene	331	38	293	3.75
m-Nitrotoluene	407	38	369	4.20
p-Nitrotoluene	463	38	425	4.50

Discussion

The solute molecules were so chosen that the effect of the introduction of similar and dissimilar groups on the electric moment of the compound could be studied. Within the last two years data have accumulated so that the effect produced may be compared with the results of others. For example, Errera[5] has determined the electric moments of the various dichloro-, dibromo- and di-iodobenzenes, that is, benzene derivatives containing like atoms in various positions in the molecule. Smyth and Morgan[6] have also presented the results of experimental work and calculations for the dichlorobenzenes. Of the molecules studied in this article the dinitrobenzenes should show changes similar to those of the dichloro-, dibromo- or di-iodobenzenes. It is also possible to compare the results obtained for the nitrotoluenes, derivatives of benzene containing one positive and one negative group, with the calculations of Smyth and Morgan for the cresols.

For purposes of comparison Table III has been prepared. It is at once apparent that the changes produced in the electric moments of the molecules reported in this article parallel very closely the effects found by Smyth and Morgan,[6] not only in the case where similar atoms or groups of atoms are substituted in the benzene ring, but also in the case where dissimilar ones are substituted. And in the same manner that the moments of the various disubstituted compounds were calculated from vectorial considerations by these authors, it is possible to calculate the moments of the various dinitrobenzenes and nitrotoluenes, making use of the values $\mu = 3.90 \times 10^{-18}$ e.s.u. for nitrobenzene, and $\mu = 0.40 \times 10^{-18}$ e.s.u. for toluene.[7] The results of such calculations show an agreement with the experimentally determined values of the same order of magnitude

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[5] Errera, *Physik. Z.*, **27**, 764 (1926).

[6] Smyth and Morgan, THIS JOURNAL, **49**, 1030 (1927).

[7] Krchma and Williams, *ibid.*, **49**, 2408 (1927).

as that shown by Smyth and Morgan. In this connection an article by J. J. Thomson[8] is also of interest.

TABLE III

COMPARISON OF ELECTRIC MOMENT DATA

Smyth and Morgan[6]		Williams and Schwingel	
Substance	$\mu \times 10^{18}$	Substance	$\mu \times 10^{18}$
C_6H_5Cl	1.61	$C_6H_5NO_2$	3.90
o-$C_6H_4Cl_2$	2.30	o-$C_6H_4(NO_2)_2$	6.05
m-$C_6H_4Cl_2$	1.55	m-$C_6H_4(NO_2)_2$	3.81
p-$C_6H_4Cl_2$	0	p-$C_6H_4(NO_2)_2$	0.32
C_6H_5OH[a]	1.73	$C_6H_5NO_2$	3.90
o-$CH_3C_6H_4OH$[a]	1.54	o-$CH_3C_6H_4NO_2$	3.75
m-$CH_3C_6H_4OH$[a]	1.76	m-$CH_3C_6H_4NO_2$	4.20
p-$CH_3C_6H_4OH$[a]	1.81	p-$CH_3C_6H_4NO_2$	4.50

[a] Calculated by Smith and Morgan from data of Philip and Haynes, *J. Chem. Soc.*, **87**, 998 (1905).

The value of the moment found for symmetrical trinitrobenzene, $\mu = 1.08 \times 10^{-18}$ e.s.u., is, without doubt, too high. The same thing may be said of the value found for *p*-dinitrobenzene. From theoretical considerations zero values should have resulted. Owing to the limited solubility of these substances in benzene, the method of calculation becomes less accurate, so that the values obtained must be considered as being indistinguishable from zero.

Höjendahl, in a brief note to *Nature*,[9] has published the results of an experimental study in which the electric moments of a number of substituted benzene molecules are tabulated. In several cases a direct comparison between the results of Höjendahl and those of this article may be made. This comparison is given in Table IV.

TABLE IV

COMPARISON OF ELECTRIC MOMENT DATA

Molecule	$\mu \times 10^{18}$ (Williams and Schwingel)	$\mu \times 10^{18}$ (Höjendahl)
o-Dinitrobenzene	6.05	5.95
m-Dinitrobenzene	3.81	4.02
p-Dinitrobenzene	0.32	0.80
o-Nitrotoluene	3.75	3.62
p-Nitrotoluene	4.50	4.30

Since Höjendahl has taken the value $\mu = 3.75 \times 10^{-18}$ e.s.u. for the nitrobenzene molecule from the results of earlier work[1] and since the dielectric constant data were obtained with apparatus standardized using the data from which this value was calculated,[10] it would be expected that his results would be consistently lower than the ones reported in this

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[8] Thomson, *Phil. Mag.*, **46**, 513 (1923).

[9] Höjendahl, *Nature*, **117**, 892 (1926).

[10] Conversation with Dr. Höjendahl.

article, all of which are based on absolute measurements,[4] and which give a value, $\mu = 3.90 \times 10^{-18}$ e.s.u., for nitrobenzene in benzene solution. On this basis the results for *o*-dinitrobenzene and the nitrotoluenes must be virtually in agreement. In the case of the *p*-dinitrobenzene inaccuracies in the method of calculation which has to be employed will probably account for the high electric moment, $\mu = 0.80 \times 10^{-18}$ e.s.u., obtained by Höjendahl. Its value should approach zero.

The value obtained for *m*-dinitrobenzene, on the basis of the reasoning given above, is not in agreement with that reported in this article.

Höjendahl[10] has more recently repeated the measurements on the system benzene-*m*-dinitrobenzene, giving a value $\mu = 3.70 \times 10^{-18}$ for *m*-dinitrobenzene, one which is substantially in agreement with that presented in this article.

Summary

1. Dielectric constant and density data at 25° have been obtained for benzene solutions of nitrobenzene, *o*-, *m*- and *p*-dinitrobenzene, symmetrical trinitrobenzene and *o*-, *m*- and *p*-nitrotoluene.

2. The data have been applied to the calculations of the electric moments of the various solute molecules.

3. The results of these calculations have been critically discussed. In a number of cases they have been compared with the results of other investigators. They are in agreement with the physical basis provided by Errera, Smyth and Morgan, Thomson, and others, for the determination of the positive or negative character of the benzene substituents.

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A NEW METHOD FOR SEPARATING ARSENIC FROM ANTIMONY

BY LEROY W. MCCAY

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Introduction

The conversion of arsenic into arsenic acid according to Reich and Richter,[1] its precipitation as silver arsenate and the calculation of the arsenic from the weight of the salt, or the amount of silver in it, have been studied by Pearce and Low,[2] McCay[3] and, comparatively recently, by Eschweiler and Röhrs.[4]

[1] Post, "Chemisch-Technische Analyse," Vieweg and Son, Braunschweig, **1881**, p. 396; see also Dingler's *Polyt. Journ.*, **50**, 475 (1883).

[2] Pearce and Low, *Chem. News*, **48**, 85 (1883).

[3] McCay, *ibid.*, **48**, 7 (1883); *Am. Chem. J.*, **8**, 77 (1886).

[4] Eschweiler and Röhrs, *Z. angew. Chem.*, **36**, 464 (1923).