

Erratum: Quantum Effects in Liquid Hydrogen

Jacob Bigeleisen

Citation: [The Journal of Chemical Physics](#) **40**, 2044 (1964); doi: 10.1063/1.1725450

View online: <http://dx.doi.org/10.1063/1.1725450>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/40/7?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Quantum effects of hydrogen atoms on the dynamical rearrangement of hydrogen-bond networks in liquid water](#)

J. Chem. Phys. **132**, 164507 (2010); 10.1063/1.3397809

[Quantum effects in the dissociative adsorption of hydrogen](#)

J. Chem. Phys. **110**, 8696 (1999); 10.1063/1.478859

[Isotopic Effects in Liquid Hydrogen](#)

J. Chem. Phys. **43**, 1836 (1965); 10.1063/1.1697024

[Comment on "Quantum Effects in Liquid Hydrogen"](#)

J. Chem. Phys. **40**, 2040 (1964); 10.1063/1.1725445

[Quantum Effects in Liquid Hydrogen](#)

J. Chem. Phys. **39**, 769 (1963); 10.1063/1.1734322

A promotional banner for AIP Applied Physics Reviews. The background is a blue gradient with a bright light source on the right and molecular models on the left. The text 'NEW Special Topic Sections' is prominently displayed in white. Below it, 'NOW ONLINE' is written in yellow, followed by 'Lithium Niobate Properties and Applications: Reviews of Emerging Trends' in white. The AIP Applied Physics Reviews logo is in the bottom right corner. On the left, there is a small inset image of a book cover for 'Applied Physics Reviews' showing a diagram of a device structure.

NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP Applied Physics
Reviews

Erratum: Cation Distributions in Nonstoichiometric Magnesium Ferrite

[J. Chem. Phys. **39**, 435-439 (1963)]

R. L. MOZZI AND A. E. PALADINO

*Solid State Physics Group, Raytheon Company
Waltham, Massachusetts 02154*

IN Sec. III, Data Evaluation, fourth paragraph, the last sentence should read, "The imaginary components were found to be negligible and the corrections, in electron units, applied to the scattering factors of Mg^{2+} , Fe^{3+} , and O^{2-} were 0.16, -3.9, and 0.04, respectively." The latter number was incorrectly typed as 0.4; the correct number was used in the original calculations.

Erratum: Magnetic Susceptibility of Partially Oxidized Copper Films at 25°C

[J. Chem. Phys. **39**, 409 (1963)]

A. W. CZANDERNA AND H. WIEDER*

*Union Carbide Corporation, Chemicals Division
South Charleston, West Virginia*

ON page 490, in the fourth line of the third paragraph, the value of χ_0 for $CuO_{0.67}$ should read $+3.9 \pm 0.3 \times 10^{-6}$ cgs·emu.

* Presently with Case Institute of Technology, Department of Physics.

Erratum: Quantum Effects in Liquid Hydrogen

[J. Chem. Phys. **39**, 769 (1963)]

JACOB BIGELEISEN

*Chemistry Department, Brookhaven National Laboratory,
Upton, Long Island, New York 11973*

THE following errata have kindly been called to my attention by Dr. M. Klein:

- (1) After Eq. (4.6) read $(T/\theta)^3$ instead of (T^3/θ) .
- (2) In Eq. (4.10) read

$$3 \ln\left(\frac{\theta'}{\theta}\right) + 3 \ln \frac{[1 - \exp(-\theta/T)]}{[1 - \exp(-\theta'/T)]}$$

instead of

$$\frac{3 \ln \theta'}{\theta + 3} \ln \frac{[1 - \exp(-\theta/T)]}{[1 - \exp(-\theta'/T)]}.$$

- (3) Table III read $(E_{0H_2} - E_{0XX})/(E_{0H_2} - E_{0D_2})$ instead of $(E_{0H_2} - E_{0XX})/(E_{0H_2} - E_{0H_2})$.

Erratum: Spectrum of Nd^{3+} in $LaCl_3$

[J. Chem. Phys. **39**, 2134 (1963)]

J. C. EISENSTEIN

National Bureau of Standards, Washington, D. C. 20234

IT has been kindly pointed out to the author by Dr. E. H. Carlson that there are several errors in Table II which involve levels of the ${}^2H_{11/2}$ term. The correct entries opposite ${}^2H_{11/2}$ in the fifth through tenth columns are as follows:

2μ	Position of level relative to center			$ s_1 $	
	Exptl.	Calc.	Diff.	Exptl.	Calc.
3	-30.49	-21.58	-8.91	9.11	7.02
1		-18.07			1.01
5	-13.66	-9.79	-3.87		2.70
3	10.55	6.86	3.69	0.65	0.44
1	23.20	14.10	9.10	11.35	12.00
5		28.45			0.49

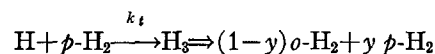
Erratum: Nuclear Spin Conservation in Ortho-Para Hydrogen Conversion

[J. Chem. Phys. **33**, 1830 (1960)]

DOYLE BRITTON AND Z. Z. HUGUS, JR.

*Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455*

EQUATION 7(b) should read



and the text immediately above this equation should be made consistent with this. The equations following 7(b) and the conclusions are correct as printed.

Notes

Dielectric Constant of Phosphoric Acid

RONALD A. MUNSON

General Electric Research Laboratory, Schenectady, New York 12301

(Received 16 October 1963)

THE measurement of the dielectric constant of a material possessing a high conductivity becomes increasingly difficult as the dielectric constant to conductivity ratio becomes small. The frequency selected

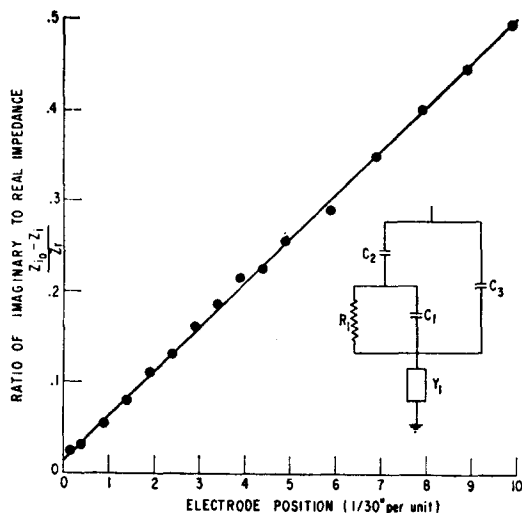


FIG. 1. Plot of the ratio of the imaginary to real impedance vs electrode position according to Eq. (3). Data obtained at 25°C and 19.32 Mc/sec.

for measuring the static dielectric constant should be high enough so that the displacement current is an appreciable fraction of the conductance current, and yet low enough to avoid the frequency range of dielectric dispersion. Owing to the high conductivity of phosphoric acid ($4.7 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$ at 25°C) the ratio of the displacement current to the conductance current is 1 to 100 at 20 Mc/sec. The method selected for measuring the dielectric constant of 100% phosphoric acid was a further development of a bridge method employed by Gillespie and Cole.¹ A condenser of variable electrode separation filled with phosphoric acid as dielectric was employed in one of the arms of a radiofrequency bridge (General Radio 916-A).² The variable geometry feature of the cell permitted correction for the electrode double-layer capacity and the reactances paralleling the condenser and to ground. The lead reactance was minimized by plugging the cell directly into the external bridge resistance. The lower section of the brass housing which contained a cylindrical Teflon cell was thermostated. The upper half of the housing screwed into the lower housing so that each revolution lowered the electrode $\frac{1}{30}$ th of an inch. The electrodes were of platinized thin platinum foil on stainless steel, and a Teflon FEP gasket sealed the lower electrode into the Teflon cell. One hundred percent phosphoric acid was prepared from analytical reagent 85% phosphoric acid by water removal under vacuum³ followed by a single recrystallization. The acid, which easily supercooled, was found to be $99.94 \pm 0.20\%$ phosphoric acid by acid-base titration.

The results indicate that at the relatively high frequencies employed the resistive part of the electrode impedance may be neglected.¹ Therefore we represent the double layer impedance by a capacitance C_2 in

series with the sample of admittance $1/R_1 + i\omega C_1$. The capacitance C_3 between the outer terminal of the bridge external resistance and the cell housing is in parallel with the above (Fig. 1). The short connection from cell housing to the ground terminal produces a series reactance (Y_1). The impedance measured by the bridge is given by

$$Z = Z_r + iZ_i = \frac{R_1}{(1 + \omega^2 C_1 C_3 R_1^2)^2 + \omega^2 C_3^2 R_1^2} + i \left[Y_1 - \frac{(1/\omega C_2) + \omega C_1 R_1^2 + \omega C_3 R_1^2}{(1 + \omega^2 C_1 C_3 R_1^2)^2 + \omega^2 C_3^2 R_1^2} \right], \quad (1)$$

where $5 \mu\text{F} \cong C_3 \ll C_2 \cong 50 \mu\text{F}$ and $\omega^2 C_1^2 R_1^2 \ll 1$. If A is the electrode area; ρ , the resistivity; and ϵ the permittivity of the sample, then R_1 is directly proportional to the electrode separation (x) with proportionality constant ρ/A and C_1 is inversely proportional to x with proportionality constant ϵA . The zero point of the electrode separation scale and ρ are obtained from a plot of Z_r vs x , which is a linear relationship for small x . Since Y_1 and C_2 are not dependent upon x we find at x equal zero,

$$Z_{i0} = Y_1 - 1/\omega C_2. \quad (2)$$

Thus

$$(Z_i - Z_{i0}) / -Z_r = \omega C_1 R_1 + \omega C_3 R_1 = \omega \epsilon \rho + \omega C_3 \rho x / A, \quad (3)$$

where the approximations employed in Eq. (1) have been used.

The reliability of the method was tested by measuring the dielectric constant of 100% sulfuric acid. At 10 Mc/sec a value of 106 ± 5 at $20 \pm 2^\circ \text{C}$ in agreement with previous measurements^{1,4} was obtained. Because of the higher conductivity and lower dielectric constant, the phosphoric acid results are less exact. Measurements made at 25.0°C at frequencies of 4.89 to 19.32 Mc/sec give an average value of 61 ± 12 .

These results when compared with those made in more dilute aqueous solutions of phosphoric acid confirm that the static dielectric constant of water-phosphoric acid mixtures exhibits a minimum as a function of composition as does that of sulfuric-acid-water mixtures.⁵ It has been suggested⁶ that hydrogen bonding among phosphoric acid molecules would at once account for the high phosphoric acid viscosity and allow high hydrogen ion mobility by means of Grotthuss chain conduction through the hydrogen-bonded structure. Hydrogen-bonded liquids generally possess high dielectric constants due to cooperative dipole orientation encouraged by hydrogen bonding. The dielectric constant confirms the associated character of phosphoric acid.

¹ R. J. Gillespie and R. H. Cole, *Trans. Faraday Soc.* **52**, 1325 (1956).

² D. B. Sinclair, *Proc. IRE* **28**, 497 (1940).

³ *Inorganic Synthesis*, edited by W. C. Fernelius *et al.* (McGraw-Hill Book Company, Inc., New York, 1939), Vol. I, p. 101.

⁴ J. C. D. Brand, J. C. James, and A. Rutherford, *J. Chem. Soc.* **1953**, 2447.

⁵ J. H. Cristensen, A. J. Smith, R. B. Reed, and K. L. Elmore (private communication, to be published).

⁶ N. N. Greenwood and A. Thompson, *J. Chem. Soc.* **1959**, 3485.

Preferential Hydrogen Loss in the Electron Impact Dissociation of Toluene-*d*₅

J. G. BURR AND R. A. MEYER

Radiation Chemistry Group of the North American Aviation Science Center, Canoga Park, California 91304

(Received 23 September 1963)

THE mass patterns of several different monodeuterio-toluenes and of toluene- α -*d*₃ show that H and D loss from the molecule ion is nearly statistical.^{1,2} Meyerson, and co-workers^{1,3} have interpreted this to mean that all of the H and D atoms in the parent ion become equivalent prior to loss of H or D, and the $C_7H_8^+$ parent is the precursor to a symmetrical $C_7H_7^+$ tropylium ion. This interpretation has been reinforced by evidence³ from the mass patterns of toluene-1-C-13,² several deuterated ethyl benzenes,¹ other alkyl benzenes,² cycloheptatriene,² and by thermochemical calculations.²

There is a slight preferential loss of D evident in the toluene-*d*₃ spectrum, and there are indications in the spectra of the monodeuteriotoluenes of a slight preference for loss of H or D from the methyl group of the toluene. Meyerson² has suggested that these facts indicate that a small fraction of the tropylium ion precursor (i.e., the $C_7H_8^+$ species) dissociates directly without prior randomization of the H and D atoms. We shall call this reaction the "direct dissociation" process.

The mass spectrum of ring-deuterated toluene, $C_6D_5CH_3$ (prepared in this laboratory by methylation of benzene-*d*₆) shows that there is a large preferential

loss of H from this molecule-ion. The spectrum is shown in Table I, along with spectra of toluene, toluene- α -*d*₃, and toluene-*d*₈ run at the same time. These monoisotopic spectra agree with the previously published spectra of toluene- α -*d*₃^{1,2} and toluene-*d*₈.²

We suggest that the greater preferential H loss in the toluene-*d*₅ spectrum reflects an enhancement of the direct dissociation process relative to the isotope scrambling process in $C_7H_8^+$. This distinction depends on separation of the isotope effect⁴ for the H and D loss from the structural specificity for H loss (from the methyl group of toluene-*d*₅) which is a consequence of the direct dissociation process.

The separation can indeed be made if the relative probabilities of H and D losses from the molecule-ions of the deuterated toluenes are reduced to pi and gamma factors⁵ and these factors are plotted as functions of the number of deuterium atoms in the molecule-ions. The pi and gamma plots for molecule-ions where all the C-H bonds are equivalent (ethylene and methane), which have been published,⁵ are smooth functions of the deuterium content of the molecule-ions. A nearly smooth curve has also been observed in the pi and gamma plots for H and D loss from seven deuterated biphenyl molecule-ions.⁶ The smoothness of such plots is a demonstration that the complex set of processes which determine the peak height ratios of parent ion to parent minus H (or D) approximate a monotonic function of the deuterium content of the molecule-ion. Points for pi or gamma factors which deviate from the smooth curves reveal enhancement of H or D loss from particular structural features. This structural specificity is shown to an extreme degree in pi and gamma plots for H and D loss from the molecule ions of deuterated ethanols^{7a} and methanols.^{7b}

Corresponding pi and gamma plots for the toluene spectra are shown in Fig. 1. Although insufficient data are available to make a complete gamma plot possible, it is still clear that the gamma factor for hydrogen loss

TABLE I. Partial mass spectra of deuterated toluenes in the parent-ion region (corrected for naturally occurring C-131).^a

Mass peak	$C_6H_5CH_3$	$C_6H_4DCH_3^1$	$C_6H_3CH_2D^1$	$C_6H_5CD_3^b$	$C_6D_5CH_3^c$	$C_6D_5CD_3^d$
Parent	100	100	100	100	100	100
Parent-1	164.4	132	129	97.2	77.4	...
Parent-2 (D loss)	(1.7 ^e)	14.3	17.2	46.6	67.3	130.5
P-1	20.54	18.85	18.43	19.44	25.80	...
πH	(1.00)	(1.02)	(1.00)	(0.946)	(1.26)	
P-2	...	14.3	17.2	15.53	13.46	16.31
πD		(0.77)	(0.93)	(0.756)	(0.655)	(0.794)

^a All spectra were run on a CEC 21-103C mass spectrometer using an ionizing voltage of 70 V.

^b The spectrum has been approximately corrected for 7.4% $C_7H_8D_2$ (determined from low voltage patterns).

^c The spectrum has been approximately corrected for 5.7% $C_7H_8D_4$ (determined from low voltage patterns).

^d The spectrum has been approximately corrected for 6.1% C_7HD_7 (determined from low voltage patterns).

^e Parent-2 in the toluene spectra is, of course, loss of 2H; this is obviously a minor process.