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PHYSICAL CHEMISTRY DIVISION

COMMISSION ON PHYSICOCHEMICAL MEASUREMENTS AND STANDARDS*

RECOMMENDED REFERENCE MATERIALS FOR REALIZATION OF PHYSICOCHEMICAL PROPERTIES

(Recommendations 1976)

EDITOR: K. N. MARSH

SECTION: PERMITTIVITY

COLLATORS: H. KIENITZ & K. N. MARSH

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INTRODUCTION

The symbol for relative permittivity (also called dielectric constant, capacivity, or specific inductive capacity) recommended by the IUPAC is ε_r (Ref. 1). A primary standard is not required since the relative permittivity is defined as the dimensionless ratio of the permittivity of the dielectric to the permittivity of a vacuum. It may be determined by obtaining the ratio of the capacitance of a capacitor completely filled with the dielectric (C) to the capacitance of the capacitor when evacuated (C_0). In practice, the permittivity of the dielectric is not normally compared with vacuum but with a reference gas or air. The relative permittivity of dry, carbon dioxide free, air at 293.15 K and 101.325 kPa is $1.0005364 \pm 3 \times 10^{-7}$ (Ref. 6). This value varies with the temperature and the percentage of carbon dioxide and moisture as given in section III 2. The capacitance is usually measured by a bridge or resonance method and suitable cells and bridge circuits have been described (Ref. 2). The measurement of relative permittivity can be made using either an absolute or a non-absolute technique. In the absolute method the effective capacity of the cell in vacuum C_0 is accurately determined from a measurement in vacuo. An alternative to a measurement in vucuo is to make a measurement using a reference gas at ambient temperature and pressure then make the small correction necessary to obtain the value of the capacitance in vacuo. Most three terminal and differential cell designs allow an absolute determination to be made. Some designs of two terminal cells, where the leads capacitance can be determined without recourse to the use of a reference liquid, can be used for absolute measurements (Refs. 3,4). The procedure is non-absolute when a liquid is used to obtain C_0. In general it is expected that a measurement made using an absolute technique enhances the probable accuracy and such measurements have been given more weight in the evaluation. Futher the more recent precision measurements, provided the purity of the sample has been adequately established, have been given a greater weighting in the evaluation. When designing a cell, notice should be taken of the problems associated with the use of metal films on glass to form the electrode (Refs. 3,5). The relative permittivity depends on frequency and the limiting value at zero frequency is termed the static relative permittivity. In this section the values of ε_r reported refer to the static relative permittivity.

Equipment for measuring relative permittivity can be either calibrated or checked with fluids of known relative permittivity, hence there is a need for selected reference materials. The criteria for selecting a reference material is that it should be chemically stable and easy to purify, its conductance should be small, and sufficient measurements of high precision should have been made in order to establish the reliability of the values (Refs. 7-9). Further, because of the high value of ε_r for water, the materials (except water) must be easy to dry.

The recommended values for the liquids are given at atmospheric pressure. The term 'atmospheric pressure' as used in this document indicates that the data refer to a sample at a nominal pressure of 10^5 Pa. The recommended values for the gases (except air) are given at 293.15 K and 101.325 kPa. Maryott and Buckley (Ref. 3) give an equation for calculating (ε_r-1) for a gas in the pressure range 93 to 107 kPa and the temperature range 283 to 303 K with an accuracy of 0.02 per cent.

$$(\varepsilon_r-1)(T,p) = (\varepsilon_r-1)(293.15\ \mathrm{K},\ 101.325\ \mathrm{kPa}) \left[\frac{p/\mathrm{kPa}}{101.325(1 + 0.003411(T/\mathrm{K} - 293.15))}\right]$$

The following provisos apply to the information on reference materials; (a) the recommended materials have not been checked independently by the IUPAC, (b) the quality of the material may change with time, (c) the quoted sources of supply may not be the exclusive sources because no attempt has been made to seek out all possible alternative sources, and (d) the IUPAC does not guarantee any material that has been recommended.

REFERENCES

1. *IUPAC Manual of Symbols and Terminology for Physicochemical Quantities and Units*, *Pure and Appl. Chem.* 51, 1 (1979).

2. W. E. Vaughan, C. P. Smyth, and J. G. Powles, *Techniques of Chemistry*, Vol. I, *Physical Methods of Chemistry*, Part IV, A. Weissberger and B. W. Rossiter (editors), p.351, Wiley-Interscience, New York (1972).

3. S. Sugden, *J. Chem. Soc.* 768 (1933).

4. R. H. Stokes, *J. Chem. Thermodynamics* 5, 379 (1973).

5. L. Hartshorn, J. V. C. Parry, and L. Essen, *Proc. Phys. Soc.* (*London*) B68, 422 (1955).

6. A. A. Maryott and F. Buckley, *Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State*. U.S. National Bureau of Standards Circular 537, U.S. Printing Office, Washington, D.C. (1953).

7. W. G. Amey and R. Hamburger, *Proc. Amer. Soc. Testing Mats.* 49, 1079 (1949).

8. R. F. Field, *Proc. Amer. Soc. Testing Mats.* 54, 456 (1954).

9. L. Essen and K. D. Froome, *Proc. Phys. Soc.* (*London*) B64, 862 (1951).

I REFERENCE MATERIALS FOR PERMITTIVITY IN THE LIQUID STATE

I/1

Physical Property: Relative permittivity, ε_r
Unit: Dimensionless
Recommended reference material: Cyclohexane, (C_6H_{12})
Range of variables: 283.15 to 348.15 K, atmospheric pressure
Physical state within the range: liquid
Class: Calibration and Test Material; Certified Reference Material
Contributors: H. Kienitz and K. N. Marsh.

***Intended usage*: Cyclohexane can be used for the calibration and for the testing of the performance of apparatus to be used for the measurement of the relative permittivity of liquids in the temperature range 283.15 to 348.15 K.**

Sources of supply and/or methods of purification: Cyclohexane is normally purified by fractional distillation of analytical grade material from sodium (Ref. 1) and the process of purification may be monitored by gas chromatography. Samples should be dried by either storing over sodium or passing through activated alumina immediately prior to use (Ref. 3). Samples of cyclohexane of purity approximately 99.95 mole per cent are available from suppliers (A), (B), (C), and (D).

Pertinent physicochemical data: Relative permittivity ε_r for cyclohexane

T_{68}/K	ε_r	T_{68}/K	ε_r
283.15	2.039 ± 0.0015	323.15	1.976 ± 0.001
293.15	2.024 ± 0.001	333.15	1.961 ± 0.001
298.15	2.016 ± 0.001	343.15	1.945 ± 0.001
303.15	2.008 ± 0.001	348.15	1.931 ± 0.001
313.15	1.992 ± 0.001		

The table has been compiled primarily from the absolute measurements of the relative permittivity by Stokes (Ref. 2) and Malmberg (Ref. 4). The results of these two investigations differ by 0.001 at 283 K decreasing in a regular manner to 0.0007 at 343 K. The careful measurements by Hartshorn, Parry, and Essen (Ref. 5) and by Mecke and Joeckle (Ref. 6) agree with the above recommendations at 293.15 K and 298.15 K if an uncertainty of 0.001 is ascribed to their results. This uncertainty is five times that estimated by the authors. The compilation by Maryott and Smith (Ref. 7) in 1951 recommended the values 2.023 ± 0.002 at 293.15 K and 2.015 ± 0.002 at 298.15 K which agree with the above recommendations within the stated uncertainties.

Hartshorn, Parry, and Essen (Ref. 5) in recommending cyclohexane as a reference material noted that the relative permittivity obtained by direct distillation of the sample was the same as that obtained after 3 months drying with calcium hydride. Unfortunately the four absolute measurements referenced above show a maximum spread in the value of ε_r of 0.0024 at 293.15 K so that the recommended uncertainty in the relative permittivity at that temperature cannot be reduced.

Supplier A provides cyclohexane suitable for the calibration of cells for the determination of relative permittivity. They state that the samples do not purport to be a standard of purity and are not free from traces of water. They note that test measurements on a representative sample at 303.15 K showed an increase of 0.0007 in the relative permittivity between samples dried over 'Drierite' and those saturated with water at 293 K. For samples given a limited exposure to air up to 65 per cent relative humidity it was estimated that the change in the relative permittivity of the supplied samples would be less than 0.0002. The measured relative permittivity on representative sample bottles were: 293.15 K, 2.02280 ± 0.00004; 298.15 K, 2.01517 ± 0.00004; 303.15 K, 2.00733 ± 0.00004 with an estimated accuracy of ±0.02 per cent or better. This reference material will be discontinued when current supplies are exhausted.

REFERENCES

1. J. A. Riddick and W. B. Bunger, *Techniques of Chemistry*, Vol II, *Organic Solvents*, Third Edition. A. Weissberger (editor), p.592. Wiley-Interscience, New York (1970).

2. R. H. Stokes, *J. Chem. Thermodynamics* 5, 379 (1973).

3. R. Mecke, R. Joeckle, and G. Klingenberg, *Ber. Bunsenges. physic. Chem.* 66, 239 (1962).

4. C. G. Malmberg (National Bureau of Standards) private communication.

5. L. Hartshorn, J. V. L. Parry, and L. Essen, *Proc. Phys. Soc. (London)* B68, 422 (1955).

6. R. Mecke and R. Joeckle, *Ber. Bensenges. phys. Chem.* 66, 255 (1962).

7. A. A. Maryott and E. R. Smith, *Table of Dielectric Constants of Pure Liquids*, National Bureau of Standards Circular 514, Washington D.C. (1951).

I/2

Physical Property: Relative permittivity, ε_r

Unit: Dimensionless

Recommended reference material: Tetrachloromethane, (CCl_4)

Range of variables: 273.15 K to 333.15 K, atmospheric pressure

Physical state within the range: liquid

Class: Calibration and Test Material

Contributors: H. Kienitz and K. N. Marsh

Intended usage: Tetrachloromethane can be used for the calibration and for the testing of the performance of apparatus to be used for the measurement of the relative permittivity of liquids in the temperature range 273.15 K to 333.15 K.

Sources of supply and/or methods of purification: Analytical grade tetrachloromethane that has been prepared by the direct chlorination of methane is normally purified by fractional distillation and the process of purification may be monitored by gas chromotography. Tetrachloromethane produced by the chlorination of carbon disulphide normally requires the removal of trace amounts of carbon disulphide. The usual procedure is to reflux the sample with one fifth the volume of five mass per cent aqueous sodium hydroxide solution, wash several times with water, dry with calcium chloride, then fractionally distil (Ref. 1). Before use the sample should be passed through type 4A 'Linde' molecular sieve (Ref. 5) or distilled from phosphorus pentoxide (Ref. 3). It should be noted that tetrachloromethane gives a reduced response while carbon disulphide gives little response when using flame ionization as the detector on a gas chromatograph. Carbon disulphide and water can be determined using a thermal conductivity detector and a 'Poropak type Q' column.

Pertinent physicochemical data: Relative permittivity ε_r for tetrachloromethane

T_{68}/K	ε_r	T_{68}/K	ε_r
273.15	2.278 ± 0.001	303.15	2.218 ± 0.001
283.15	2.258 ± 0.001	313.15	2.198 ± 0.001
293.15	2.238 ± 0.001	323.15	2.178 ± 0.001
298.15	2.228 ± 0.001	333.15	2.158 ± 0.001

The table has been compiled primarily from the absolute measurements of the relative permittivity by Mopsik (Ref. 2), by Stokes (Ref. 3), and by Mecke and Joeckle (Ref. 5). The spread in the values of ε_r from these three determinations is 0.0018 at 298.15 K. The measurements by Miller (Ref. 6), using benzene as the calibrating liquid [$\varepsilon_r = 2.2925 - 0.00198\ (T/K - 288.15)$] agree with the values of Stokes over the temperature range 238.15 to 313.15 K with a maximum difference of 0.0007. When the value for ε_r (benzene, 288.15 K) of 2.2940, interpolated from the above recommendations, is used, the maximum difference is 0.0013. The measured values of Mopsik, Stokes, and Hartmann, Newmann, and Schmidt (Ref. 4) at 323.15 K show a maximum difference of 0.0016. Hartmann *et al.* used the values measured by Mecke and Joeckle to calibrate their cell at 293.15 K. The values measured by Heston and Smyth (Ref. 7) and Le Fevre (Ref. 8) differ considerably from the recommended values at higher temperatures. The compilation by Maryott and Smith (Ref. 9) in 1951 recommended the values 2.238 ± 0.002 at 293.15 K and 2.228 ± 0.002 at 298.15 K which agree with the above recommendations within the stated uncertainties.

REFERENCES

1. J. A. Riddick and W. B. Bunger, *Techniques of Chemistry*, Vol. II, *Organic Solvents*, Third Edition, A. Weissberger (editor), p.773. Wiley-Interscience, New York (1970).

2. F. I. Mopsik, *J. Chem. Phys.* 50, 2559 (1969).

3. R. H. Stokes, *J. Chem. Thermodynamics* 5, 379 (1973).

4. H. Hartmann, A. Newmann, and A. P. Schmidt, *Ber. Bunsenges. physik. Chem.* 72, 877 (1968).

5. R. Mecke and R. Joeckle, *Ber. Bunsenges. physik. Chem.* 66, 255 (1962).

6. J. G. Miller, *J. Amer. Chem. Soc.* 64, 117 (1942).

7. W. M. Heston and C. P. Smyth, *J. Amer. Chem. Soc.* 72, 99 (1950).

8. R. J. W. Le Fevre, *Trans. Faraday Soc.* 34, 1127 (1933).

9. A. A. Maryott and E. R. Smith, *Table of Dielectric Constants of Pure Liquids*, National Bureau of Standards Circular 514, Washington D. C. (1951).

I/3

Physical Property: Relative permittivity, ε_r

Unit: Dimensionless

Recommended reference material: Benzene (C_6H_6)

Range of variables: 283.15 to 333.15 K, atmospheric pressure

Physical state within the range: liquid

Class: Calibration and Test Material

Contributors: H. Kienitz and K. N. Marsh

Intended usage: Benzene can be used for the calibration and for the testing of the performance of apparatus to be used for the measurement of the relative permittivity of liquids in the temperature range 283.15 to 333.15 K.

Source of supply and/or methods of purification: Analytical grade benzene is usually purified by shaking with aliquots of one tenth its volume of concentrated sulphuric acid until no colour appears in the acid layer. After a dilute sodium carbonate wash and repeated washes with water it is dried over calcium chloride then sodium and distilled in an efficient column from sodium or calcium hydride (Refs. 1 - 4). Hartshorn, Parry, and Essen (Ref. 2) noted the difficulty of removal of water from benzene and considered that it was not a reliable reference material. They recommended storing over calcium hydride for at least three weeks. Van der Maesen (Ref. 3) noted that after distillation from sodium it took six months of drying over sodium before a value constant to 10^{-4} in the relative permittivity was obtained. Mecke, Joeckle, and Klingenberg (Ref. 5) noted that it took 200 minutes of drying of a purified sample with phosphorus pentoxide before the relative permittivity became constant to 10^{-4}. The same value of the relative permittivity was obtained after drying for 10 minutes with type 4A 'Linde' molecular sieve which has been regenerated at 473 K. The recommended purification is by the standard procedure given above with a final drying over type 4A 'Linde' molecular sieve just prior to the measurement. The progress of the purification may be monitored by gas chromatography. Water may be determined using a thermal conductivity detector and a 'Poropak type Q' column. Samples of benzene of purity approximately 99.99 mole per cent are available from suppliers (B), (C), and (D).

Pertinent physicochemical data: Relative permittivity ε_r for benzene

T_{68}/K	ε_r	T_{68}/K	ε_r
283.15	2.304 ± 0.001	313.15	2.244 ± 0.001
293.15	2.2837 ± 0.0005	323.15	2.224 ± 0.001
298.15	2.2739 ± 0.0005	333.15	2.204 ± 0.001
303.15	2.264 ± 0.001		

This table has been compiled primarily from the absolute measurements of relative permittivity by Hartshorn, Parry, and Essen (Ref. 2), Van der Maesen (Ref. 3), Stokes (Ref. 4), and Mecke and Joeckle (Ref. 6). The spread in the values of ε_r for these four determinations is 0.0007 at 293.15 K. The absolute measurements of Heston and Smyth (Ref. 7) and the non-absolute measurements of Hartmann, Newmann, and Rinck (Ref. 8) agree to within 0.0012 of the recommmended values over the temperature range given. Hartmann *et al.* calibrated their cell using a value for ε_r(benzene, 293.15 K) of 2.2832 (Ref. 6). The compilation by Maryott and Smith (Ref. 9) in 1951 recommended the values 2.284 ± 0.002 at 293.15 K and 2.274 ± 0.002 at 298.15 K which agree with the above recommendations within the stated uncertainties.

REFERENCES

1. J. A. Riddick and W. B. Bunger, *Techniques of Chemistry*, Vol. II, *Organic Solvents*, Third Edition, A. Weissberger (editor), p.606. Wiley-Interscience, New York (1970).

2. L. Hartshorn, J. V. L. Parry, and L. Essen, *Proc. Phys. Soc. (London)* B68, 422 (1955).

3. F. Van der Maesen, *Physica* 15, 481 (1949).

4. R. H. Stokes, *J. Chem. Thermodynamics* 5, 379 (1973).

5. R. Mecke, R. Joeckle, and G. Klingenberg, *Ber. Bunsenges. physik. Chem.* 66, 239 (1962).

6. R. Mecke and R. Joeckle, *Ber. Bunsenges. physik. Chem.* 66, 255 (1962).

7. W. M. Heston and C. P. Smyth, *J. Amer. Chem. Soc.* 72, 99 (1950).

8. H. Hartmann, A. Newmann, and G. Rinck, *Zeit. Physik. Chem. (Frankfurt)* 44, 204 (1965).

9. A. A. Maryott and E. R. Smith, *Table of Dielectric Constants of Pure Liquids*, National Bureau of Standards Circular 514, Washington D.C. (1951).

I/4

Physical Property: Relative permittivity, ε_r

Unit: Dimensionless

Recommended reference material: Chorobenzene (C_6H_5Cl)

Range of variables: 293.15 to 323.15 K, atmospheric pressure

Physical state within the range: liquid

Class: Calibration and Test Material

Contributors: H. Kienitz and K. N. Marsh

Intended usage: Chlorobenzene can be used for the calibration and for the testing of the performance of apparatus to be used for the measurement of the relative permittivity of liquids in the temperature range 293.15 to 323.15 K.

Sources of supply and/or methods of purification: Analytical grade chlorobenzene is usually purified by repeated shaking with aliquots of one tenth its volume of concentrated sulphuric acid until no colour appears in the acid layer. After a potassium bicarbonate wash and repeated washes with water it is dried over calcium chloride and fractionally distilled (Ref. 1). McAlpine and Smyth (Ref. 2) recommend a second distillation after redrying over phosphorus pentoxide. Hartmann *et al.* (Ref. 3) dried chlorobenzene with phosphorus pentoxide, then distilled the sample in a 25 theoretical plate column and, just prior to use, dried it with type 4A 'Linde' molecular sieve. The process of purification may be followed by gas chromatography. Chlorobenzene should be used immediately after purification since Mecke and Rosswog (Ref. 4) noted that the relative permittivity increased by 0.0055 after 72 days, presumably due to photolysis.

Pertinent physicochemical data: Relative permittivity ε_r for chlorobenzene

T_{68}/K	ε_r	T_{68}/K	ε_r
293.15	5.70 ± 0.015	323.15	5.20 ± 0.02
298.15	5.62 ± 0.015		

This table has been compiled primarily from the absolute measurements of Mecke and Rosswog (Ref. 4), and the earlier references compiled by Maryott and Smith (Ref. 5). Hartmann *et al.* (Ref. 3), using the value of 5.6895 for ε_r(293.15 K) from reference 4, measured ε_r at 323.15 K. This value agrees within 0.017 with the measurement of Schornack and Eckert (Ref. 6) using a cell which was calibrated with a series of unspecified liquids. Mecke and Rosswog considered chlorobenzene to be unsuitable as a reference material because the relative permittivity does not remain constant when exposed to light.

The compilation by Maryott and Smith (Ref. 5) in 1951 recommended the values 5.708 ± 0.006 at 293.15 K and 5.621 ± 0.006 at 298.15 K. An analysis of the measurements referenced by Maryott and Smith and the measurement by Mecke and Rosswog indicate that the uncertainty quoted by Maryott and Smith was over-optimistic. Additional measurements on this compound seem desirable.

REFERENCES

1. J. A. Riddick and W. B. Bunger, *Techniques of Chemistry*, Vol. II, *Organic Solvents*, Third Edition, A. Weissberger (editor), p.767. Wiley-Interscience: New York (1970).

2. K. B. McAlpine and C. P Smyth, *J. Phys. Chem.* 3, 55 (1935).

3. H. Hartmann, A. Newmann, and G. Rinck, *Zeit. Physik. Chem. (Frankfurt)* 44, 204 (1965).

4. R. Mecke and K. Rosswog, *Ber. Bunsenges. physik. Chem.* 60, 47 (1956).

5. A. A. Maryott and E. R. Smith, *Table of Dielectric Constants of Pure Liquids*, National Bureau of Standards Circular 514, Washington D.C. (1951).

6. L. G. Schornack and C. A. Eckert, *J. Phys. Chem.* 74, 3014 (1970).

I/5

Physical Property: Relative permittivity, ε_r

Unit: Dimensionless

Recommended reference material: 1,2-Dichloroethane ($C_2H_4Cl_2$)

Range of Variables: 293.15 to 298.15 K, atmospheric pressure

Physical state within the range: liquid

Class: Calibration and Test Material; Certified Reference Material

Contributors: H. Kienitz and K. N. Marsh

Intended usage: 1,2-Dichloroethane can be used for the calibration and for the testing of the performance of apparatus to be used for the measurement of the relative permittivity of liquids in the temperature range 293.15 to 298.15 K.

Sources of supply and/or methods of purification: Analytical grade 1,2-dichloroethane is purified for relative permittivity measurements by washing with dilute potassium hydroxide, then water, drying over calcium chloride or phosphorus pentoxide followed by fractional distillation (Refs. 1,2). The process of purification may be monitored by gas chromatography. Hartshorn *et. al.* (Ref. 3) noted that a purified sample stored for several months showed the presence of a considerable concentration of ions. On removal of these ions (by the application of 300 V D.C. across the electrodes) they found that the relative permittivity decreased from 10.85 to 10.66 over a period of 24 hours. Samples of 1,2-dichloroethane are available from Supplier A.

Pertinent physicochemical data: Relative permittivity ε_r for 1,2-dichloroethane

T_{68}/K	ε_r	T_{68}/K	ε_r
293.15	10.65 ± 0.01	298.15	10.37 ± 0.01

This table has been compiled primarily from the absolute measurements by Hartshorn *et al.* (Ref. 3), Vernon *et al.* (Ref. 4), Sugden (Ref. 2), and Davies (Ref. 5). Determinations at temperatures other than those given above show no consistency. The compilation of Maryott and Smith (Ref. 6) in 1951 recommended the value 10.65 ± 0.01 at 293.15 K and 10.36 ± 0.01 at 298.15 K in agreement with the above recommendations. Their evaluation was primarily based on the results given in references 2, 4, and 5.

Supplier A provides **1,2-dichloroethane** for the calibration of cells for the determination of relative permittivity. They state that the sample does not purport to be a standard for purity and is not free from traces of water. The measured relative permittivity on representative bottled samples were: 293.15 K, 10.6493 ± 0.0008; 298.15 K, 10.3551 ± 0.0008; 303.15 K, 10.075 ± 0.0011. They state that the relationship

$$\varepsilon_r(t/°C) = 11.9480 - 7.03068 \times 10^{-2} t/°C + 2.7548 \times 10^{-4}(t/°C)^2 - 4.22 \times 10^{-7}(t/°C)^3$$

can be used to calculate the measured relative permittivity from 283.15 to 313.15 K without significant error and with an estimated accuracy of 0.05 per cent or better. This reference material will be discontinued when current supplies are exhausted.

REFERENCES

1. J. A. Riddick and W. B. Bunger, *Techniques of Chemistry*, Vol. II, *Organic Solvents*, Third Edition, A. Weissberger (editor), p.776. Wiley-Interscience, New York (1970).

2. S. Sugden, *J. Chem. Soc.* 768 (1933).

3. L. Hartshorn, J. V. C. Parry, and L. Essen, *Proc. Phys. Soc (London)* 68B, 422 (1955).

4. A. A. Vernon, J. Wyman, and R.A. Avery, *J. Amer. Chem. Soc.* 67, 1477 (1945).

5. R. M. Davies, *Phil. Mag.* 21, 1008 (1936).

6. A. A. Maryott and E. R. Smith, *Table of Dielectric Constants of Pure Liquids*, National Bureau of Standards Circular 514, Washington D.C. (1951).

I/6

Physical property: Relative permittivity, ε_r

Unit: Dimensionless

Recommended reference material: Methanol (CH_3OH)

Range of variables: 283.15 to 313.15 K, atmospheric pressure

Physical state within the range: liquid

Class: Calibration and Test Material

Contributors: H. Kienitz and K. N. Marsh.

Intended usage: Methanol can be used for the calibration and for the testing of the performance of apparatus to be used for the measurement of the relative permittivity of liquids in the temperature range 283.15 to 313.15 K.

Sources of supply and/or methods of purification: Analytical grade methanol is usually purified by distilling in an efficient column from magnesium activated with iodine (Ref. 1). Maryott purified methanol by distilling from magnesium ribbon (Ref. 2) while Srinivasan and Kay (Ref. 3) purified methanol by passage through a mixed bed ion exchange column from which all water had been leached, followed by fractional distillation under nitrogen. Methanol should be stored under an inert atmosphere prior to use. The process of purification can be followed by gas chromatography. The sample can be analysed for its water content by the use of a 'Poropak type Q' column and a thermal conductivity detector.

Pertinent physicochemical data: Relative permittivity ε_r for methanol

T_{68}/K	ε_r	T_{68}/K	ε_r
283.15	35.70 ± 0.03	298.15	32.66 ± 0.02
293.15	33.66 ± 0.03	313.15	29.86 ± 0.05

This table has been compiled primarily from the absolute measurements of Srinivasan and Kay (Ref. 3). The above recommended value at 298.15 K agrees, within the uncertainties given, with the non-absolute measurements by Albright and Gosting (Ref. 4), Hartmann *et al.* (Ref. 5) and Coleman (Ref. 6). At 313.15 K the measurement by Srinivasan and Kay (Ref. 3) agree to 0.03 with the measurements of Albright and Gosting (Ref. 4) but the non-absolute measurements of Hartmann *et al.* (Ref. 5) and Dannhauser and Bake (Ref. 7) are lower by 0.1. The compilation by Maryott and Smith (Ref. 8) in 1951 recommended the values 33.62 ± 0.07 and 32.63 ± 0.07 at 293.15 and 298.15 K respectively, which agree with the above recommendations within the stated uncertainties.

REFERENCES

1. J. A. Riddick and W. B. Bunger, *Techniques of Chemistry*, Vol. II, ***Organic Solvents***, Third Edition, A. Weissberger (editor), p.638, Wiley-Interscience, New York (1970).

2. A. A. Maryott, *J. Amer. Chem. Soc.* 63, 3079 (1941).

3. K. R. Srinivasan and R. L. Kay, *J. Solution Chem.* 4, 299 (1975).

4. P. S. Albright and L. J. Gosting, *J. Amer. Chem. Soc.* 68, 1061 (1946).

5. H. Hartmann, A. Newmann and A. P. Schmidt, *Ber. Bunsenges. physik. Chem.* 72, 877 (1968).

6. C. F. Coleman, *J. Phys. Chem.* 72, 365 (1968).

7. W. Dannhauser and L. W. Bake, *J. Chem. Phys.* 40, 3058 (1964).

8. A. A. Maryott and E. R. Smith, *Table of Dielectric Constants of Pure Liquids*, National Bureau of Standards Circular 514, Washington D.C. (1951).

I/7

Physical Property: Relative permittivity, ε_r

Unit: Dimensionless

Recommended reference material: Nitrobenzene ($C_6H_5NO_2$)

Range of variables: 293.15 to 298.15 K, atmospheric pressure

Physical state within the range: liquid

Class: Calibration and Test Material; Certified Reference Material

Contributors: H. Kienitz and K. N. Marsh

Intended usage: Nitrobenzene can be used for the calibration and for the testing of the performance of apparatus to be used for the measurement of the relative permittivity of liquids in the temperature range 293.15 to 298.15 K.

Sources of supply and/or methods of purification: Analytical grade nitrobenzene is usually purified by repeated fractional crystallization followed by distillation under reduced pressure (Ref. 1). Hartshorn *et al.* (Ref. 2) repeatedly distilled (at atmospheric pressure) an analytical grade sample, the final distillatin being from finely powdered alumina. No change was observed after allowing the liquid to stand over powdered calcium hydride for four weeks. Samples of nitrobenzene are available from supplier A.

Pertinent physicochemical data: Relative permittivity ε_r for nitrobenzene

T_{68}/K	ε_r	T_{68}/K	ε_r
293.15	35.72 ± 0.04	298.15	34.78 ± 0.04

This table has been compiled primary from the absolute measurements of Hartshorn *et al.* (Ref. 2) and Sugden (Ref. 3). There have been a few non-absolute measurements at other temperatures but they shown considerable disagreement. The compilation by Maryott and Smith (Ref. 4) in 1951 recommended the values 35.74 ± 0.07 at 293.15 K and 34.82 ± 0.07 at 298.15 K which agree with the above recommendations within the stated uncertainties. Futher measurements on this liquid would be desirable.

Supplier A provides nitrobenzene suitable for the calibration of cells used for the determination of relative permittivity. They state that the samples do not purport to be a standard of purity and are not free from traces of water. The relative permittivity on representative bottled samples were: 293.15 K, 35.7037 ± 0.001; 298.15 K, 34.7416 ± 0.001; 303.15 K, 33.8134 ± 0.003. They state that the relationship

$$\varepsilon_r(t/°C) = 39.9278 - 0.226899(t/°C) + 8.0801 \times 10^{-4}(t/°C)^2 - 1.267 \times 10^{-6}(t/°C)^3$$

can be used to calculate the measured relative permittivity from 283.15 to 313.15 K without significant error with an estimated accuracy of 0.04 per cent. The reference material will be discontinued when current supplies are exhausted.

REFERENCES

1. J. A. Riddick and W. B. Bunger, *Techniques of Chemistry*, Vol II, *Organic Solvents*, Third Edition, A. Weissberger (editor), p.795. Wiley-Interscience, New York (1970).

2. L. Hartshorn, J. V. C. Parry and L. Essen, *Proc. Phys. Soc. (London)* 68B, 422 (1955).

3. S. Sugden, *J. Chem. Soc.* 788 (1933).

4. A. A. Maryott and E. R. Smith, *Table of Dielectric Constants of Pure Liquids*, National Bureau of Standards Circular 514, Washington D.C. (1951).

I/8

Physical Property: Relative permittivity, ε_r

Unit: Dimensionless

Recommended reference material: Water (H_2O)

Range of variables: 273.15 to 373.15 K, atmospheric pressure

Physical state within the range: liquid

Class: Calibration and Test Material

Contributors: H. Kienitz and K. N. Marsh

Intended usage: Water can be used for the calibration and for the testing of the performance of apparatus to be used for the measurement of the relative permittivity of liquids in the temperature range 273.15 to 373.15 K.

Sources of supply and/or methods of purification: Either singly distilled or deionized water is suitable for relative permittivity measurements.

Pertinent physicochemical data: Relative permittivity ε_r for water

T_{68}/K	ε_r	T_{68}/K	ε_r
273.15	87.87 ± 0.07	323.15	69.90 ± 0.04
283.15	83.91 ± 0.07	333.15	66.79 ± 0.04
293.15	80.16 ± 0.05	343.15	63.82 ± 0.04
298.15	78.36 ± 0.05	353.15	61.03 ± 0.05
303.15	76.57 ± 0.05	363.15	58.32 ± 0.05
313.15	73.16 ± 0.04	373.15	55.72 ± 0.06

This table has been compiled primarily from the absolute measurements by Malmberg and Maryott (Ref. 1), Owen *et al.* (Ref. 2), Kay and coworkers (Refs. 3 - 6), and Dunn and Stokes (Ref. 7). The values given in references 2 to 6 agree to within 0.05 in the relative permittivity from 273.15 to 313.15 K. The results of Malmberg and Maryott and Dunn and Stokes are lower by about 0.15 from the values in references 2 to 6 at 273.15 K but decrease to agreement within 0.03 at 303.15 K. The results of Dunn and Stokes (Ref. 7) can be considered as absolute measurements since they used a conductance technique to determine the capacitance of the cell when evacuated. The non-absolute measurements of Lees (Ref. 8) agree to within 0.04 with those of Owen *et al.* in the range 273.15 to 323.15 K. Thus there are two sets of measurements which are inconsistent below 303 K hence the estimated uncertainty is greater at lower temperatures. The absolute measurements by Rusche and Good (Ref. 9) are higher by about 0.20 units from the recommended values. The compilation by Maryott and Smith (Ref. 10) in 1951 recommended the value 80.37 ± 0.08 and 78.54 ± 0.08 at 293.15 and 298.15 K respectively. These two estimates are consderably higher than the recent determinations referenced above. The recommended values above 343.15 K are based solely of the measurements of Malmberg and Maryott (Ref. 1) hence the greater estimated uncertainty.

REFERENCES

1. C.C. Malmberg and A. A. Maryott, *J. Res. Nat. Bur. Stand.* 56, 1 (1956).
2. B. B. Owen, R. C. Miller, C. E. Milner, and H. L. Cogan, *J. Phys. Chem.* 65, 2065 (1961).
3. K. R. Srinivasan and R. L. Kay, *J. Chem. Phys.* 60, 3645 (1974).
4. R. L. Kay, G. A. Vidulich, and K. S. Pribadi, *J. Phys. Chem.* 73, 445 (1969).
5. G. A. Vidulich, D. F. Evans, and R. L. Kay, *J. Phys. Chem.* 71, 656 (1967).
6. G. A. Vidulich and R. L. Kay, *J. Phys. Chem.* 66, 383 (1962).
7. L. A. Dunn and R. H. Stokes, *Trans. Faraday. Soc.* 65, 2906 (1969).
8. W. L. Lees, Ph.D. Thesis, Harvard University (1949).
9. E. W. Rusche and W. B. Good, *J. Chem. Phys.* 45, 4667 (1966).
10. A. A. Maryott and E. R. Smith, *Table of Dielectric Constants of Pure Liquids*, National Bureau of Standards Circular 514, Washington D.C. (1951).

II REFERENCE MATERIALS FOR PERMITTIVITY IN THE LIQUID AND REAL GAS STATE.

II/1

Physical Property: Relative permittivity, ε_r

Unit: Dimensionless

Recommended reference material: Hydrogen (H_2)

Range of variables: 14 to 20 K, saturated vapour line and at 293.15 K, 101.325 kPa

Physical state within the range: liquid and gas

Class: Calibration and Test Material

Contributors: H. Kienitz and K. N. Marsh

Intended usage: Liquid hydrogen can be used for the calibration and testing of the performance of apparatus to be used for the measurement of relative permittivity at low temperatures. Hydrogen gas at atmospheric pressure can be used for a similar purpose at 293.15 K.

Sources of supply and/or methods of purification: For measurements on the liquid a normal hydrogen sample should be prepared electrolytically. It should not have been liquified previously. For measurements at 293.15 K research grade hydrogen gas dried prior to use is satisfactory.

Pertinent physicochemical data: A. Liquid State - Relative Permittivity ε_r for hydrogen

T_{68}/K	ε_r	T_{68}/K	ε_r
14.035	1.2534	18.34	1.2399
14.745	1.2514	18.90	1.2351
15.38	1.2494	19.555	1.2351
16.295	1.2465	19.92	1.2338
17.29	1.2432	20.375	1.2320

This table has been prepared primarily from the absolute measurements by Kogan, Milenko, and Grigorova (Ref. 1). They claim an uncertainty in ε_r of $\pm 5 \times 10^{-5}$. The earlier measurements by Werner and Keeson (Ref. 2) are lower than the above results by an average of about 0.0007 but between 14 and 15 K the difference increases to 0.002. Werner and Keesom estimate their uncertainty as $\pm 5 \times 10^{-4}$. The measurement of Van Itterbeck and Spaepen (Ref. 3) at 20.35 K is lower than that of Kogan *et al.* by 0.006. The estimated uncertainty in the values given in the table are ±0.0008. The compilation of Maryott and Smith (Ref. 4) in 1951 recommended the value of 1.228 at 20.4 K which is lower than the above recommendation.

B. Gas State - There has been no precise measurements on the relative permittivity of hydrogen gas at 293.15 K since the compilation by Maryott and Buckley (Ref. 5) so their recommended value remains.

$$(\varepsilon_r - 1)10^6(H_2(g), 293.15\ K, 101.325\ kPa) = 253.8 \pm 0.3$$

REFERENCES

1. V. S. Kogan, Yu. Ya. Milenko, and T. K. Grigorova, *Physica* 53, 125 (1971).

2. W. Werner and W. H. Keesom, *Commun. Phys. Lab. Leiden* 16, No.178a (1926).

3. A. Van Itterbeck and J. Spaepen, *Physica* 9, 339 (1942).

4. A. A. Maryott and E. R. Smith, *Table of Dielectric Constants of Pure Liquids*, National Bureau of Standards Circular 514, Washington, D.C. (1951).

5. A. A. Maryott and F. Buckley, *Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State*, National Bureau of Standards Circular 537, Washington, D.C. (1953).

II/2

Physical Property: Relative permittivity, ε_r

Unit: Dimensionless

Recommended reference material: Oxygen (O_2)

Range of variable: 54.5 K to 84 K, saturated vapour curve and at 293.15 K, 101.325 kPa

Physical state within the range: liquid and gas

Class: Calibration and Test Material

Contributors: H. Kienitz and K. N. Marsh

Intended usage: Liquid oxygen can be used for the calibration and for the testing of the performance of apparatus to be used for the measurement of relative permittivity at low temperatures. Oxygen gas at atmospheric pressure can be used for a similar purpose at 293.15 K.

Source of supply and/or methods of purification: Laboratory grade oxygen purified by passing through a silica gel trap at 77 K before liquefaction is recommended (Ref. 1). For measurements at 293.15 K research grade oxygen dried prior to use is satisfactory (Ref. 1).

Pertinent physicochemical data: A. Liquid State - Relative permittivity ε_r for oxygen

T_{68}/K	ε_r	T_{68}/K	ε_r
54.478	1.5685	68.000	1.5384
55.000	1.5674	72.000	1.5294
56.000	1.5651	76.000	1.5203
62.000	1.5518	80.000	1.5111
64.000	1.5473	84.000	1.5018

This table has been prepared from the absolute measurements by Younglove (Ref. 1) who claims an uncertainty of 0.0005 in ε_r. The interpolated value at 81.95 K (1.5066 ± 0.0005) is in excellent agreement with the measurements of Lewis and Smyth (Ref. 2), (1.505 ± 0.001). The compilation by Maryott and Smith (Ref. 3) in 1951 recommended the value 1.507 at 80.0 K which differs from the value recommended in the table, 1.511. The difference occurs because of the difficulty in assessing the precision of the earlier measurements (Refs. 4,5).

B. Gas State - The only recent precise measurements on oxygen gas are those by Dunn (Ref. 6). He obtained

$$(\varepsilon_r - 1)10^6(O_2(g),\ 293.15\ K,\ 101.325\ kPa) = 494.3 \pm 0.2$$

which agrees within the uncertainty limits with the value of 494.7 ± 0.2 recommended by Maryott and Buckley (Ref. 7). In light of the result of Dunn (Ref. 6) the recommendation becomes

$$(\varepsilon_r - 1)10^6(O_2(g),\ 293.15\ K,\ 101.325\ kPa) = 494.6 \pm 0.2.$$

REFERENCES

1. B. A. Younglove, *J. Res. Nat. Bur. Stand.* 76A, 37 (1972).

2. G. L. Lewis and C. P. Smyth, *J. Amer. Chem. Soc.* 61, 3063 (1939).

3. A. A. Maryott and E. R. Smith, *Table of Dielectric Constants of Pure Liquids*, National Bureau of Standards Circular 514, Washington D.C. (1951).

4. E. Kanda, *Bull. Chem. Soc. Japan.* 12, 473 (1937).

5. W. Werner and W. H. Keesom, *Proc. Koninkl. Nederland. Akad. Wetenschap.* 29, 306 (1926).

6. A. F. Dunn, *Canad. J. Physics.* 42, 1489 (1964).

7. A. A. Maryott and F. Buckley, *Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State*, National Bureau of Standards Circular 537, Washington D.C. (1953).

III REFERENCE MATERIALS FOR PERMITTIVITY IN THE REAL GAS STATE

III/1

Physical Property: Relative permittivity, ε_r
Unit: Dimensionless
Recommended reference material: Nitrogen (N_2)
Range of variables: 293.15 K, 101.325 kPa
Physical state within the range: gas
Class: Calibration and test material
Contributors: H. Kienitz and K. N. Marsh

Intended usage: Nitrogen gas at atmospheric pressure can be used for the calibratation and the testing of the performance of apparatus to be used for the measurement of relative permittivity.

Sources of supply and/or methods of purification: Research grade nitrogen dried with P_2O_5 prior to use is satisfactory (Ref. 1).

Pertinent physicochemical data: Dunn (Ref. 1) made very precise measurements on the relative permittivity of nitrogen gas and obtained

$$(\varepsilon_r - 1)10^6(N_2(g),\ 293.15\ K,\ 101.325\ kPa) = 547.4 \pm 0.2$$

which agrees within the uncertainty limits with the value of 548.0 ± 0.5 recommended by Maryott and Buckley (Ref. 2). The new recommendation is

$$(\varepsilon_r - 1)10^6(N_2(g), 293.15\ K, 101.325\ kPa) = 547.7 \pm 0.3$$

REFERENCES

1. A. F. Dunn, *Canad. J. Physics.* 42, 1489 (1964).

2. A. A. Maryott and F. Buckley, *Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State*, National Bureau of Standards Circular 537, Washington, D.C.(1953).

III/2

Physical Property: Relative permittivity, ε_r

Unit: Dimensionless

Recommended reference material: Air (dry, carbon dioxide free)

Range of variables: 293.15 K, 101.325 kPa

Physical state within the range: gas

Class: Calibration and Test Material

Contributor: H. Kienitz and K. N. Marsh

Intended usage: Air (dry, carbon dioxide free) at atmospheric pressure can be used for the calibration and the testing of the performance of apparatus to be used for the measurement of relative permittivity.

Sources of supply and/or methods of purification: Air passed over sodium hydroxide to remove carbon dioxide then dried over phosphorus pentoxide is suitable (Ref. 1).

Pertinent physicochemical data: There have been no significant precise measurements since the compilation by Maryott and Buckley (Ref. 2). The recommended value for dry carbon dioxide free air remains at

$$(\varepsilon_r - 1)10^6(\text{Air}, 293.15\ K, 101.325\ kPa) = 536.4 \pm 0.3$$

Essen and Froome (Ref. 1) have given an equation for the dielectric constant of air which contains carbon dioxide and moisture

$$(\varepsilon_r - 1)10^6(T/K, p/Pa) = -0.4 + 1.5519p_1/T + 2.6612p_2/T + 1.2940p_3(1 + 5746/T)/T$$

where p_1, p_2, and p_3 are the partial pressures in pascals of air, carbon dioxide, and water vapour respectively and T is the temperature. This equation has been adjusted to agree with the recommended value of dry, carbon dioxide free, air given above.

REFERENCES

1. L. Essen and K. D. Froome, *Proc. Phys. Soc.* 64B, 862 (1951).

2. A. A. Maryott and F. Buckley, *Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State*, National Bureau of Standards Circular 537, Washington, D.C. (1953).

CONTRIBUTORS

Professor H. Kienitz (Deceased)
Am Kirschberg 12,
D-6719 Weisenheim/Berg,
(FEDERAL REPUBLIC OF GERMANY)

Associate Professor K. N. Marsh,
Department of Physical Chemistry,
University of New England,
Armidale N.S.W. 2351 (AUSTRALIA)

LIST OF SUPPLIERS

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C. Division of Chemical Standards,
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Teddington, Middlesex, TW 11 OLW
(U. K.)

D. A.P.I. Samples,
Carnegie-Mellon University,
Schenley Park,
Pittsburg, PA 15213 (U.S.A.)