eter. These runs determine the proper ratio of compound to DEP, approximate the heat released for initial temperature settings on the rotating-bomb calorimeter, and test for ignitability and combustion of these solutions. Such trial runs could be conducted on the rotating-bomb calorimeter, but, if there is a detonation, the damage will be less severe in the stationary bomb.

Since the quantity of BFDNA was limited, small amounts were used to determine the heat of solution with DEP. One gram of BFDNA to 1 gram of DEP was mixed in the special calorimeter described under Apparatus. For the quantities used in the experiment, there was a cooling effect of approximately 0.65 calorie for the solution. This calorie change is included in the calculations shown in Table II.

All data reduction was performed on a digital computer (*3*). To correct for the heat of solution of CO_2 in the hydrofluoric acid solutions, the data of Cox and Head (*6*) were used. Heats of formation used were $CO_2(g) = -94{,}051$ cal/mol; $H_2O(l) = -68{,}317.5$ cal/mol (*14*).

The uncertainties assigned to gaseous carbon dioxide liquid water are 0.011 and 0.0144, respectively (*15*).

NOMENCLATURE

m = mass of (′) compound, (″) auxiliary material, (‴) polypropylene film, and (⁗) fuse in grams
n = number of moles of (′) compound, (″) auxiliary material, (‴) polypropylene film, and (⁗) fuse
n^i = initial number of moles of water in bomb
t_i = initial temp of calorimeter, °C
t_f = final temp of calorimeter, °C
t_h = ref temp to which combustion reaction is referred (25°C)
Δt_{corr} = rise in temperature of calorimeter because of thermal leakage of outer jacket
$\Delta t_c = t_f - t_i + \Delta t_{corr}$
ξ(calor) = energy equivalent of calorimeter, cal/deg
ξ(cont) = energy equivalent of contents, cal/deg [ξ^i (cont)$(t_i - 25)$ + ξ^f (cont)$(25 - t_f + \Delta t_{corr})$ where ξ^i (cont) and ξ^f (cont) are energy equivalents of contents before and after combustion, respectively]
ΔE_{ign} = energy released because of ignition, cal
$\Delta E_{corr\ ss}$ = energy reduction to standard states, cal (*10, 13*)
$\Delta E_{dec}(HNO_3)$ = energy released from formation of nitric acid, cal
ΔE(solution) = energy released because of mixing of BFDNA and DEP before loading bomb
ΔE_c° = standard energy of idealized combustion reaction, cal/mol
ΔH_c° = standard heat of combustion of compound at constant pressure, kcal
ΔH_f° = enthalpy of formation of BFDNA, kcal/mol

LITERATURE CITED

(1) Adolph, H. G., Kamlet, M. J., *J. Org. Chem.*, **34** (1), 50 (1969).
(2) Baroody, E. E., Carpenter, G. A., Robb, R. A., Zimmer, M. F., *J. Chem. Eng. Data*, **13** (2), 215 (1968).
(3) Baroody, E. E., Wynne, J., Zimmer, M. F., U. S. Naval Propellant Plant, Naval Weapons Rep. 8686, Tech. Rep. 154 (1964).
(4) Cameron, A. E., Wichers, E., *J. Amer. Chem. Soc.*, **84**, 4175 (1962).
(5) Cohen, E. R., DuMond, J. W. M., *Rev. Mod. Phys.*, **37**, 537 (1965).
(6) Cox, J. D., Head, A. J., *Trans. Faraday Soc.*, **58**, 1839–45 (1962).
(7) Good, W. D., Scott, D. W., Waddington, G., *J. Phys. Chem.*, **68**, 1080 (1959).
(8) "Handbook of Chemistry and Physics," 43rd ed., p 1165, Chemical Rubber Co., Cleveland, Ohio, 1961-62.
(9) Hubbard, W. N., Scott, D. W., Waddington, G. in "Experimental Thermochemistry," F. D. Rossini, Ed., Interscience, New York, N.Y., 1956, Chap. 5, pp 75-128.
(10) Rossini, F. D., *ibid.*, Vol I, 1962, pp 90, 107.
(11) Rossini, F. D., *ibid.*, p 81.
(12) Rossini, F. D., *ibid.*, p 93.
(13) Skinner, H. A., *ibid.*, Vol II, pp 25-8.
(14) Wagman, D. D., Kilpatrick, J. E., Taylor, W. J., Pitzer, S. P., Rossini, F. D., *J. Res.*, **34**, 143 (1945).
(15) Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schumm, R. H., NBS Technical Note 270-3, p 22 (1968).
(16) Zimmer, M. F., Baroody, E. E., Schwartz, M., McAllister, M. P., *J. Chem. Eng. Data*, **9**, 527 (1964).

RECEIVED for review August 20, 1970. Accepted June 3, 1971.

Refractive Index of Pure Water for Wavelength of 6328 Å at High Pressure and Moderate Temperature

EVERETT M. STANLEY
Naval Ship Research and Development Laboratory, Annapolis, Md. 21402

The refractive index is one of the optical properties that can be used to study the short-range molecular interaction in solid, liquid, and gaseous materials at high pressure. The refractive index of liquid water at elevated pressures has been investigated and reported by Rosen (*2*) and more recently by Waxler and Weir (*5*), and Waxler et al. (*6*) who have analyzed their results in terms of molecular effects. The results reported here are absolute refractive index measurements at pressure and for a wavelength of 6328 Å, using a different experimental technique. They supplement the results of Rosen (*2*), Waxler and Weir (*5*), and Waxler et al (*6*).

EXPERIMENTAL

Instrumentation. The refractive index is measured by an interferometer of the Fabry-Pérot type (*1*) that has been modified for use in a pressure vessel. Figure 1 is a simplified diagram of the interferometer which consists of two 5-mm diameter gold-surfaced half mirrors (*B*) held rigidly in a housing of titanium (*D, E*) with the gold surfaces facing inward and separated by a hollow cylindrical spacer of titanium (*C*), 2.9566 mm length (which is also the liquid sample length or thickness). The mirror surfaces are not exactly parallel so that the inter-

The absolute refractive index of pure water for a wavelength of 6328 Å was measured in a temperature range of 1° to 60°C for pressure from atmospheric to 1406 kg/cm² with a Fabry-Pérot interferometer placed in an optical pressure vessel. The experimental error is estimated as ±0.00006, and experimental results are compared with the literature and the disparities discussed.

ference fringes generated are not complete circles as in the classical setup of Fabry and Pérot.

The relationship between a sample of thickness, t, and refractive index, n, a light source of wavelength, λ, and the number of fringes generated, m, is given by the expression

$$m\lambda = 2\,tn \tag{1}$$

With the application of hydrostatic pressure, a change in n will occur along with a decrease in t, resulting in a change in m. Differentiating Equation 1 and rearranging give

$$dn = (\lambda/2\,t)dm - (ndt/t) \tag{2}$$

Thus, for a constant temperature, by counting the number of fringes, dm, that move past a reference point with a change in pressure, by calculating the change in sample thickness, dt, with pressure, by knowing the wavelength, λ, and refractive index, n, the change in refractive index, dn, can be calculated.

The associated instrumentation used in this experiment, Figure 2, consists of: a light source, which is a helium-neon laser with a previously determined wavelength of 6328 Å, an optical pressure vessel, a pressure generating and measuring system consisting of a hand screw pump and a Heise bourdon-tube pressure gage, a quartz crystal temperature-measuring system, and a temperature controlling and circulating water bath.

Procedure. The interferometer and pressure vessel were cleaned thoroughly and rinsed several times with the fluid under investigation before each experiment. The interferometer was filled under vacuum with pure water and placed in the pressure vessel also filled with pure water. After the interferometer had been loaded into the pressure vessel, the vessel was placed in the regulated temperature bath. The pressurizing system, which was filled with pure water from the pressure vessel to the accumulator and with oil from the accumulator to the pumps, was connected and optical alignment established.

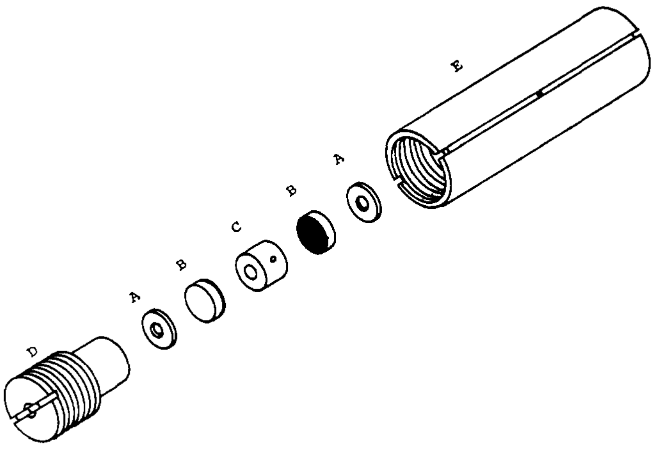

Figure 1. High-pressure Fabry–Pérot interferometer

- A. Gaskets
- B. Half mirrors
- C. Spacer
- D. Removable end plug
- E. Holder

Four equally spaced values of pressure were chosen between atmospheric and 1406 kg/cm² while temperature points were picked for 1° and 5°C and every 5°C thereafter to 30°C and every 10° to 60°C. The pressure was next raised to the desired level and the whole system was allowed to reach thermal and pressure equilibrium, which was generally achieved in a period of 15 to 30 min and verified visually by cessation of fringe movement on the screens.

After the conditions of pressure and temperature have been achieved and the optics adjusted to place a leading edge of a fringe on a screen reference mark, the pressure was reduced very slowly by backing off the hand screw pump and the fringes were counted as they moved past the reference mark. When atmospheric pressure was reached, at least 15 min were allowed for the experiment to achieve thermal equilibrium, and a final reading to the nearest 0.1 fringe is made and recorded. For each datum point at a specified temperature and pressure, at least two runs were made with different samples of water. If the readings did not agree to within 0.00005 unit of refractive index, then the measurement was repeated until agreement was achieved.

INDEX CALCULATIONS AND CORRECTIONS

The refractive index at a temperature, t; pressure, p; and wavelength, λ, will be designated by the notation $n_\lambda^{t,p}$. Now

$$n_{6328}^{t,p} = n_{6328}^{t,o} + dn \tag{3}$$

Thus for any measurements of $n_{6328}^{t,p}$, $n_{6328}^{t,o}$ and dn must be known.

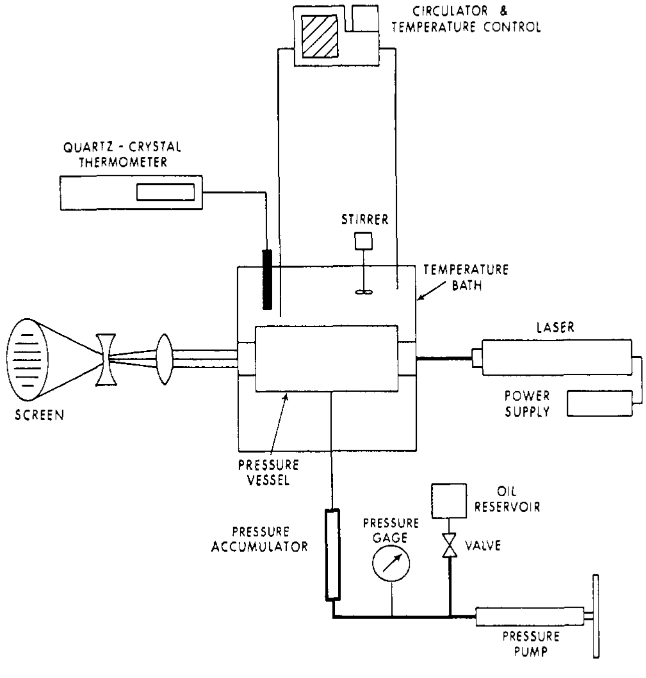

Figure 2. Experimental setup

Substituting Equation 2 into 3 gives

$$n_{6328}^{t,p} = n_{6328}^{t,o} + (\lambda/2\,t)dm - ndt/t \qquad (4)$$

The data of Tilton and Taylor (*4*) were used to calculate $n_{6328}^{t,o}$, and this was converted to absolute values (*3*) by multiplying n by 1.000292.

Since λ and t are known and dm is measured, the only variable needed to calculate $n_{6328}^{t,p}$ is dt, the change in thickness of the spacer or sample length due to pressure.

The change in thickness of the spacer in the interferometer was calculated by the equation

$$dt/t = \left(-\frac{1}{3}\right)\frac{p}{K} \qquad (5)$$

where p is the hydraulic pressure and K is the bulk modulus of the material. Because the windows of the pressure vessel did not form part of the interferometer system, any distortion generated by pressure was not of consequence in the measurements. Further, since the pressure was the same on both sides of the optical flats of the interferometer in the pressure vessel, any distortion created here was also negligible.

ACCURACY AND ERROR

The temperature of the bath around the pressure vessel was measured and controlled to ±0.01°C, and the pressures were measured and controlled to ±1.4 kg/cm².

Sensitivity of the measurements was to the nearest 0.1 fringe or 0.00001 in refractive index.

The pure water used in this experiment was distilled water which had been run through an ion exchange column and whose electrical conductivity measurements gave a reading of approximately 0.6×10^{-6} mhos per cm.

The average standard deviation for all the values of refractive index measurements of pure water is 0.00003. The initial refractive index calculations for pure water are accurate to ±0.000001 according to Tilton and Taylor (*4*), and the resultant experimental error is estimated to be ±0.0006.

RESULTS

The results are listed in Table I in units of absolute refractive index.

DISCUSSION

Comparison with Historic Data. An exact comparison of the data of Table I with the results given in the literature is not possible because the wavelengths and temperatures used do not coincide. However, a plot of Δp vs. Δn is shown in Figure 3 for the data of Rosen (*2*) at a wavelength of 5790 Å and 25°C, for the data of Waxler et al (*6*) at wave-

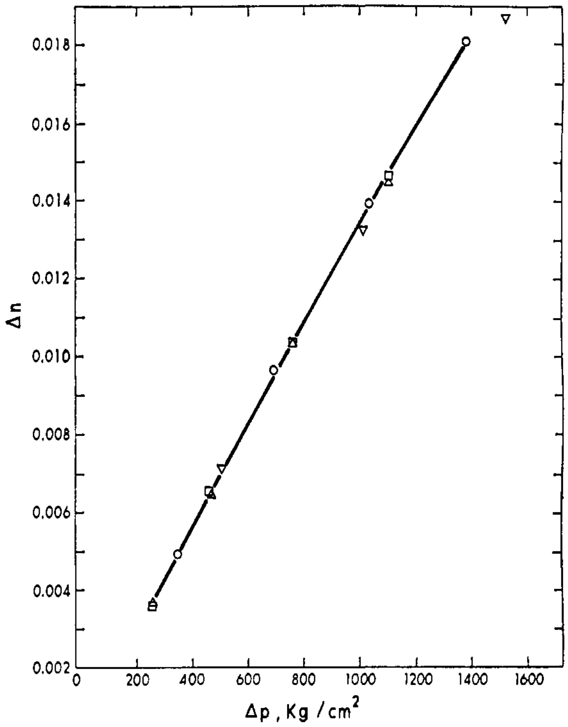

Figure 3. Comparison of Δn as a function of Δp for historic and experimental data of refractive index for pure water at 25° C and various wavelengths

○. 24.98°C, 6328A, Stanley
△. Waxler and Weir, 6438A, 24.80°C
□. Waxler and Weir, 5875A, 24.80°C
▽. Rosen, 5790A, 25°C

Table I. Absolute Values of Refractive Index of Pure Water for a Wavelength of 6328 Å, Temperatures from 1–60°C and Pressures from Atmosphere to 1406 kg/cm²

	Temperature, °C										
Pressures	1.03	5.03	10.02	15.01	20.01	24.98	29.98	39.96	49.95	54.96	59.95
Atmospheric	1.33309	1.33302	1.33283	1.33252	1.33212	1.33165	1.33109	1.32977	1.32821	1.32734	1.32643
352 Kg/cm²	1.33865	1.33843	1.33811	1.33762	1.33718	1.33664	1.33601	1.33462	1.33305	1.33219	1.33129
	1.33870	1.33845	1.33812	1.33762	1.33720	1.33663	1.33605	1.33465	1.33307		1.33129
								1.33462	1.33301		1.33123
								1.33465	1.33307		1.33127
703 Kg/cm²	1.34379	1.34336	1.34302	1.34243	1.34190	1.34123	1.34061	1.33916	1.33755	1.33668	1.33581
	1.34380	1.34331	1.34296	1.34237	1.34189	1.34124	1.34060	1.33918	1.33755		1.33581
								1.33913	1.33751		1.33575
									1.33754		1.33578
1055 Kg/cm²	1.34847	1.34810	1.34757	1.34693	1.34623	1.34550	1.34485	1.34342	1.34175	1.34088	1.34001
	1.34854	1.34813	1.34755	1.34698	1.34635	1.34560	1.34488	1.34341	1.34176		1.34001
		1.34810	1.34752	1.34692				1.34344	1.34170		1.33993
									1.34175		1.33993
1406 Kg/cm²	1.35284	1.35248	1.35180	1.35112	1.35037	1.34955	1.34886	1.34735	1.34569	1.34478	1.34390
	1.35290	1.35250	1.35184	1.35110	1.35035	1.34955	1.34889	1.34737	1.34569		1.34390
							1.34886	1.34741	1.34567		1.34387

lengths of 6438 Å and 5875 Å and 24.8°C, and for the data reported here for 6328 Å and 25°C. The data given here and those of Waxler et al. (*6*) are in agreement to the curve within experimental error (0.00006 and 0.0001, respectively). For low pressure, atmospheric to 700 kg/cm^2, the data of all authors are within agreement but at higher pressures the data of Rosen (*2*) vary significantly from the results reported here and those of Waxler et al. (*6*). No reasons for these differences can be given without a detailed examination of the experimental instrumentation and procedures used. However, not having to correct for the distortion of the optical windows in the pressure vessel and measurement with an interferometer, which is very sensitive, suggest that the experimental data reported here and the data of Waxler and Weir (*5*) and Waxler et al. (*6*) are the more accurate.

LITERATURE CITED

(1) Fabry, C., Pérot, A., *Ann. Chem. Phys.*, **7**, 115 (1899).
(2) Rosen, J. S., *J. Opt. Soc. Amer.*, **37**, 932 (1947).
(3) Tilton, L. W., *J. Res. Nat. Bur. Stand.*, **14**, 393 (1935).
(4) Tilton, L. W., Taylor, J. K., *ibid.*, **20**, 419 (1938).
(5) Waxler, R. M., Weir, C. E., *ibid.*, **69A**, 163 (1963).
(6) Waxler, R. M., Weir, C. E., Schamp, H. W., *ibid.*, **68A**, 489 (1964).

Received for review November 5, 1970. Accepted March 19, 1971. The opinions expressed in this paper are those of the author and do not necessarily represent those of the U. S. Navy or the Naval establishment at large. This work was supported by the NAVSHIPS (Naval Ships System Command) Ocean Science Program.

Determination of Activity Coefficients of Thiocyanic Acid and Salting-Out Effects in Mixture of Electrolytes from Extraction Data

KAREL S. DE HAAS
National Nuclear Research Centre, Pelindaba, Private Bag 256, Pretoria, South Africa

Activity coefficients of aqueous HSCN, determined in a previous publication, were used to determine activity coefficients of HSCN in the presence of foreign electrolytes. Determinations, made in systems containing an electrolyte with a common ion ($HClO_4$ and NaSCN) and in a system containing no common ion ($NaClO_4$), were derived from distribution data using a nonpolar organic solvent, xylene. Salting-out capacities of the three foreign electrolytes were compared by determining Harned's coefficients for each system.

Extractions of metal thiocyanate complexes from aqueous solutions into water-immiscible solvents have extensive uses in separation of metals with similar chemical properties, such as zirconium and hafnium (*3*, *8*). In most of these systems, the metal thiocyanates are extracted from highly salted solutions, but the extraction behavior of HSCN in such solutions has always been difficult to explain. HSCN does extract from an aqueous solution into a polar solvent, isobutyl methyl ketone (IBMK), and into a nonpolar solvent, xylene (*6*). The activity coefficients of aqueous HSCN have been determined by Bartlett et al. (*2*).

Using the above data, the author has determined the activity coefficients of HSCN in the presence of foreign electrolytes. These results could be useful in the elucidation of the role played by HSCN in the extraction of metal thiocyanates. Xylene was used for the extraction of HSCN since the dissociation of HSCN in a nonpolar solvent is negligible. Similar work has been conducted on HNO_3 in the presence of HCl (*9*), $HClO_4$ (*7*), and $CaCl_2$ (*1*) and on HCl in the presence of NaCl (*4*).

EXPERIMENTAL

Thiocyanic acid was prepared by mixing equivalent amounts of sodium thiocyanate and hydrochloric acid and was extracted into IBMK. Any HCl or NaSCN mechanically entrapped in the IBMK was completely removed by washing the IBMK three times with water. Upon back-extraction of the IBMK with water, aqueous HSCN was obtained. Any IBMK entrapped in the aqueous phase was removed by extraction with benzene which, in turn, was removed by bubbling nitrogen through the solution. The final concentration of aqueous HSCN was determined volumetrically.

During determination of activity coefficients by Bartlett et al. (*2*), the presence of H_2S could be detected above the solution when left overnight, indicating aqueous HSCN decomposition which was prevented by preparing fresh samples every 4 hr.

The activity coefficients of HSCN, in the presence of a second electrolyte, were determined from distribution data. The HSCN was distributed between an aqueous solution containing variable concentrations of the electrolyte and xylene. Extraction experiments were carried out by the batch extraction method in a thermostat bath kept at 25.0 ± 0.5°C. Equilibrium in the extraction of HSCN into xylene was reached within 2 min. Separation of the two phases was aided by centrifugation.

Equilibrium concentrations of HSCN in both phases were determined by direct titration with standard sodium hydroxide, using bromocresol green as indicator. In the titration of HSCN in xylene with aqueous NaOH, distribution of HSCN between xylene and water is an equilibrium reaction. Since NaOH neutralizes HSCN in the aqueous phase, the equilibrium reaction at the end point is shifted over completely to the aqueous phase. To ensure that the end point had been reached, the xylene–water mixture was shaken well for a further 3 min.