passed through a tube filled with sodium fluoride (to remove hydrogen fluoride) and condensed in a Pyrex trap surrounded by fresh liquid air. A portion of the condensate was allowed to escape and about one-half of the remainder was distilled into an evacuated Raman tube which previously had been well heated while evacuated to remove any moisture. The Raman tube held about 25 cc. of liquid and was closed by means of a brass and steel needle valve joined to the tube with a thin layer of sealing wax or by a copper–Pyrex seal. While being filled, and during the exposure to radiation, the Raman tube was surrounded by a Dewar flask (silvered except for one portion where light was admitted to the tube) filled with fresh liquid air. The liquid air was filtered to remove any ice crystals; the Dewar flask was closed off from the atmosphere by a cork which supported the Raman tube, and it was provided with means for adding liquid air during the exposure. As exciting radiation the 5461 Å. line of mercury was used. The light was concentrated on the Raman tube by a cylindrical aluminum reflector, and radiation below 3700 Å. was removed by a filter of sodium dichromate solution.[6] In addition a filter of neodymium nitrate solution was used to cut down the intensity of the "yellow" lines of mercury, since it was expected from the evidence at hand that the Raman line would fall in the region adjacent. The plates used were Eastman, type I-C.

Results and Discussion.—In the first attempt a Pyrex Raman tube was used, and after about fifteen minutes of illumination a white precipitate began to form in the fluorine. The tube was later found to be etched, and following this a quartz Raman tube was used. Two photographs were taken with the quartz tube, one of one hour and one of four hours' exposure. Longer exposures seemed impractical because of the gradual attack of the container by the fluorine, and because of the formation of ice crystals in the liquid air with resulting optical difficulties. No Raman lines could be found on either plate. The absence of a Raman line may be attributed to poor scattering ability of liquid fluorine, or to the possibility of the line falling near or on a mercury line and being thus obscured.

The Entropy of Fluorine

Recently, Brockway[7] has taken electron-diffraction photographs of gaseous fluorine, and a value of 1.46 Å. has been obtained for the internuclear distance of the fluorine molecule in its normal electronic state. If one assumes that Badger's rule[8] holds here, the value 836 cm.$^{-1}$ is obtained for the fundamental frequency of vibration. Making use of these two data, a calculation gives 48.6 cal./deg. for the standard entropy, S^0_{298}, of fluorine at 25° and one atmosphere.

The authors wish to express their thanks to the National Research Council for a grant which defrayed in part the cost of this investigation.

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[6] According to v. Wartenberg and Taylor, *Nach. Ges. Wiss. Göttingen, Math.-Phys. Klasse*, 119 (1930), fluorine gas at 1 atm. absorbs radiation below about 4500 Å. We found that if the dichromate filter was removed at the end of an exposure, a white precipitate appeared in the liquid fluorine in two to three minutes when the container was of Pyrex, and fifteen minutes when of quartz.

[7] Private communication from Dr. L. O. Brockway. The internuclear distance given is, for experimental reasons, regarded as provisional.

[8] Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935).

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Refractive Indices at Low Temperatures[1]

BY ARISTID V. GROSSE

As is well known the refractive indices are usually determined at room temperature. Although a large number of substances have been measured above room temperature, the number of determinations below 0° is extremely scarce. A literature search has revealed that reliable data were available only on the three elements—oxygen,[2] nitrogen[3] and hydrogen,[4] at their respective boiling points.[4a]

The following simple self-explanatory device, Fig. 1, using dry ice as a cooling agent, but not limited thereto, shows how the well-known Abbé refractometer can be used for low temperature measurements, the lowest used so far being −50°. Efficient cooling to any desired temperature is accomplished by boiling an appropriate liquid, such as isobutane for −10°, methyl ether for −25° and propane for −42°. Finer temperature adjustments may be made easily by changing the total pressure of the system (by means of C and D).

Once the apparatus is available the cooling

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[1] Presented before the Petroleum Section of the American Chemical Society, Rochester Meeting, September, 1937.

[2] Liveing and J. Dewar, *Phil. Mag.*, [5] **40**, 268 (1895).

[3] Liveing and J. Dewar, *ibid.*, [5] **36**, 330 (1893).

[4] W. Meissner, *Verhand. Deut. phys. Ges.*, **14**, 540 (1913).

[4a] These values have quite recently been checked by E. F. Burton, see Abstracts, 94th Meeting Am. Chem. Soc., Div. of Phys. Chem., 1937, p. 15.

requires approximately five to fifteen minutes. After the refractometer is filled with a sufficient quantity of the cooling liquid a thermo-siphon effect is produced and very efficient cooling with a very steady temperature[5] is obtained.

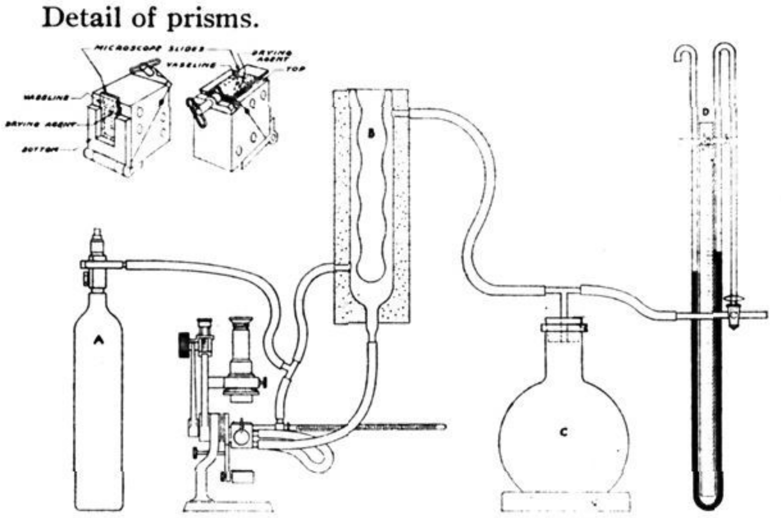

Fig. 1.

The prisms are covered with a section from a microscopic slide (see Fig. 1) to avoid frosting. They are placed in position with a little vaseline which gets sufficiently stiff at low temperatures. A few kernels of drying agent (calcium chloride, etc.) are inserted into the enclosed space and attached to its sides with vaseline. At very low temperatures (−30 to −50°) it is necessary to wet these slides with a little alcohol to keep them clear.

Under proper operating conditions the dividing line between the refractometer's black and white sight fields is practically as sharp and clear as at ordinary temperature. The same refractometer has been used over a dozen times for such measurements without any mishaps to the prism.

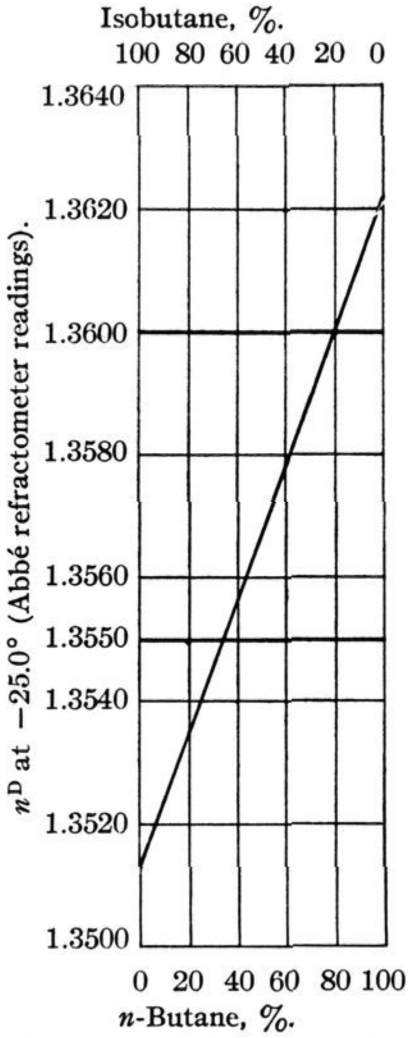

Fig. 2.—*n*- and isobutane mixtures.

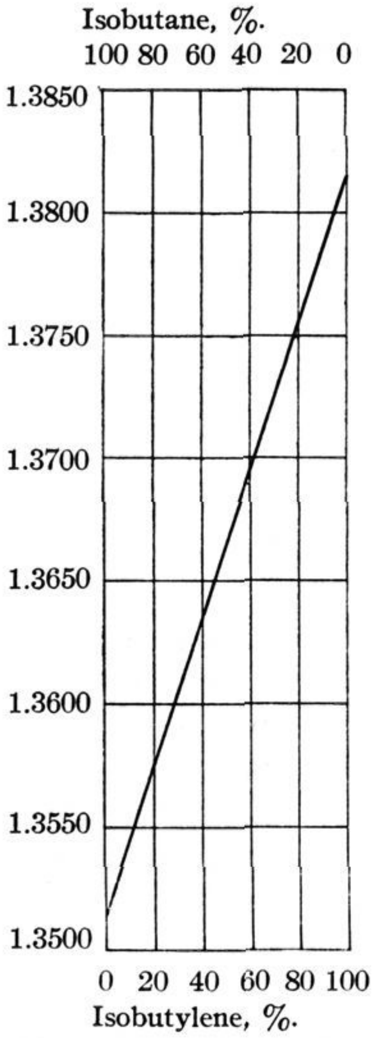

Fig. 3.—Isobutane and isobutylene mixtures.

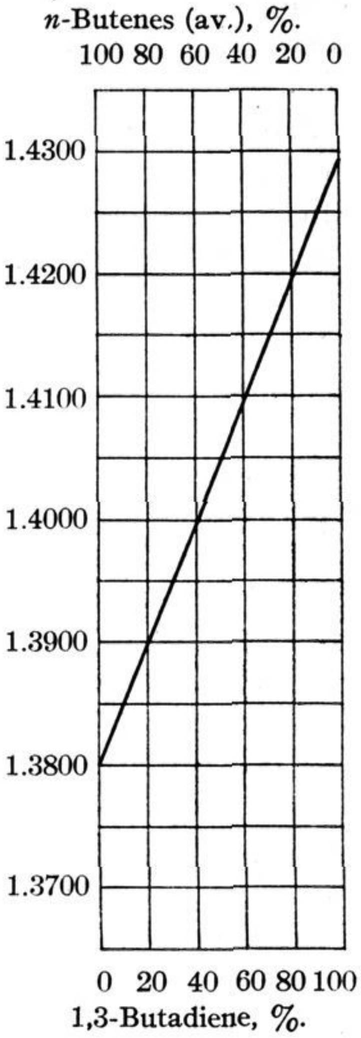

Fig. 4.—*n*-Butenes and 1,3-butadiene mixtures.

The results of some of the measurements are given in Table I.[6] The values given are actual scale readings of the Abbé refractometer and the correction due to change in the refractive index of the prism itself because of the low temperature may be discarded since it is within experimental error.[7]

Particularly interesting are the C_4 hydrocarbons. The refractive indices of the butanes are quite a range apart from the butenes and these again are separated by a wide gap from butadiene. Even the difference between *n*- and isobutane is so large that a refractive index measurement may be used for their quantitative estimation in a mixture of the two obtained, for instance, by isomerization (see Fig. 2). Similarly, in a mixture of isobutane and isobutylene or butenes and butadiene obtained, for example, by catalytic dehydrogenation, the constituents may be readily and rapidly evaluated by refractometric analysis (see Figs. 3 and 4).

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(5) For temperature measurements below −25° a calibrated thermocouple is inserted into the refractometer well instead of a thermometer.

(6) Additional and more detailed data will be published jointly with Carl B. Linn and R. Wackher.

(7) According to private communication from C. Zeiss, Inc., the dn/dt for the Abbé prism is only known in the range of 15–100° and -0.65×10^{-5} per degree; it should be smaller at low temperatures and the correction would amount at −25° to not more than 0.0002, *i. e.*, the experimental error of the determination.

TABLE I

	Compounds	B. p., °C., 760 mm.	n^D	Temp., °C.	d*n*/d*t*
C_1	CH_3Cl	−23.7	1.3830	−42.5	
	CH_3Br	+ 4.5	1.4631	−50.0	0.00066
			1.4432	−20.0	
C_2	$C_2H_5F^a$	−37.7	1.3057	−40.0	
	C_2H_5Cl	+13.1	1.4085	−50.0	.00057
			1.3913	−20.0	
	$(CH_3)_2O$	−24.9	1.3441	−42.5	
C_3	C_3H_6 (Cyclopropane)	−32.9	1.3799	−42.5	
	C_3H_8	−42.2	1.3395	−42.5	
	n-$C_3H_7F^b$	− 3.2	1.3496	−50.0	.00057
			1.3326	−20.0	
	i-$C_3H_7F^a$	−10.1	1.3406	−50.0	.00055
			1.3240	−20.0	
C_4	C_4H_6 (1,3 Butadiene)	− 2.6	1.4293	−25.0	
	C_4H_8 (Butene-1)	− 6.1	1.3803	−25.0	
	C_4H_8 (*i*-Butylene)	− 6.6	1.3814	−25.0	
	C_4H_{10} (*n*-Butane)	− 0.5	1.3621	−25.0	.00059
			1.3562	−15.0	
	C_4H_{10} (*i*-Butane)	−10.2	1.3514	−25.0	
C_7	C_7H_{16} (*n*-Heptane)	+98.4	1.4141	−25.0	.00060
			1.3870	+20.0	

[a] Prepared by Carl B. Linn and the author by direct addition of hydrogen fluoride to the corresponding olefin.

[b] Prepared by Carl B. Linn and the author by direct addition of hydrogen fluoride to cyclopropane.

Attention may be drawn to the fact that the refractive index of ethyl fluoride is, so far as we know, the lowest yet recorded for any liquid or solid compound.[8,9]

In the field of inorganic chemistry it would be very worth-while, particularly for analytical purposes, to obtain refractometric data on the volatile simple compounds of the metalloids, such as ammonia, hydrogen chloride, hydrogen bromide, hydrogen fluoride, hydrogen sulfide, sulfur dioxide, nitric oxide, nitrous oxide, chlorine and others.

It is hoped that the manufacturers of Abbé refractometers will be in a position to make a few minor mechanical changes and adjustments in the present model to make it more adaptable for low temperature measurements.

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(8) See "International Critical Tables," Vol. I, p. 276.

(9) Theoretically the *compound* with the lowest possible refractive index, n_D 1.16 at +19.0°, should be *hydrogen fluoride*, since its constituents, hydrogen and fluorine, have the lowest atomic refractions of all elements (AR_D = 1.100 and 0.997, respectively) and it has the lowest value for the expression Mol. ref./(Mol. vol. − mol. ref.), which should have a minimum for the lowest "*n*" according to the Lorenz–Lorentz formula. The *element* with the lowest index should be *fluorine*; the calculated value for n_D at −187.0° (= b. p. at 760 mm.) is approximately 1.09.

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Yellow and Colorless Modifications of Benzal- and N-3-Methylbenzal-hydantoin

BY DOROTHY A. HAHN AND MARGARET M. ENDICOTT

In view of the fact that benzalhydantoin recently has been obtained in the form of a white crystalline compound,[1] instead of a deep yellow compound as previously reported,[2] it may be of interest to state that both benzalhydantoin and N-3-methylbenzalhydantoin have been observed to exist in two crystalline modifications, one yellow and the other white. In both cases the difference between these two modifications appears to be limited to a difference in color, since the yellow and white varieties possess the same melting point (dec.) and exhibit the same chemical properties. Each of the two modifications of benzalhydantoin yields benzylhydantoin on reduction with hydrogen iodide and red phosphorus and each of the two modifications of N-3-methylbenzalhydantoin yields a corresponding single reduction product.

In both cases the yellow and white crystals may readily be transformed into each other. For example, if the yellow modification is dissolved in aqueous alkali and the solution neutralized immediately by the addition of a mineral acid, a *white* crystalline compound is precipitated. If, on the other hand, the latter is heated for some time in a boiling concentrated solution of glacial acetic acid, *yellow* crystals are deposited on cooling.

The fact that benzalhydantoin has been commonly described in the literature as a quite definitely yellow compound, would seem to be due to the accident that it was originally prepared by condensing hydantoin with benzaldehyde in an acid medium.[2] When the same condensation occurs in an alkaline medium, the product is white.[1] The synthesis of N-3-methylbenzalhydantoin, on the other hand, takes place in an alkaline solution[3] and the product is therefore commonly described as white. Under the conditions of the experiment as performed in this Laboratory, N-3-methylbenzalhydantoin separates in long, fine, soft, white needles, interlacing to form a mesh of fiber-like strands, which completely fill the space occupied by the solution. The product separates in much the same manner when recrystallized from boiling glacial acetic acid—provided that care is taken to see that the solution is not too concentrated. When, however, concentrated solutions of the reaction product in glacial acetic acid are boiled for more than a very short period of time, they deposit a heavy deep yellow precipitate which forms on the bot-

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(1) Boyd and Robson, *Biochem. J.*, **29**, 543, 545 (1935).

(2) Wheeler and Hoffman, *Am. Chem. J.*, **45**, 371 (1911).

(3) Litzinger, THIS JOURNAL, **56**, 673 (1934).