Refractive Indices of Liquefied Gases

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OBSERVATIONS on refractive index of a liquid are usually limited to its boiling point. Above that temperature the sample would be lost before the prisms of a usual refractometer could be closed. Yet in view of increasing use of pure and mixed liquefied gases, refractive index is a property of interest above the boiling point.

Bleekrode (*1*, *15* p. 966), Dechant (*2*, *15* p. 966), and Nasini (*15* p. 966, *19*) reported refractive indices of certain condensed gases at high pressures, observed by special instruments, not applicable to routine test. Results are not concordant. Schmidt (*20*) has described a similar device.

A simple procedure for observing refractive index on most liquefied gases at temperatures even approaching the critical temperatures is presented here. This method employs an iso-optic or point at which two liquid phases have the same refractive index. This is indicated usually by a structural color of the emulsion from shaking the system (*9*).

The color sequence with rising temperature is light blue, indigo, purple, lilac, magenta, brick red, and yellow (with a few exceptions noted in Tables I and II). The temperature of change from indigo to purple is selected as the iso-optic. It is consistent with usual observations of index for the sodium *D* line because the observed color is complementary to that for which the indices are equal. This iso-optic can often be measured with a precision of about 0.2° C. Without color the observation of iso-optic temperature is much less accurate. However, those of the butanes were reported (*7*), before it was realized that color was available (*9*).

Water is used as a refractive index standard when possible, because of the well-known values of the index from −10° to 100° C. (*3*, *15* p. 956), its low miscibility with many liquefied gases, and its low temperature coefficient of refractive index (Figure 1). When the index of the sample is too high to match against water at practicable temperatures, as with chlorine, Freon 11, butadiene, carbonyl sulfide (and other liquefied gases at low temperatures), the reference liquid is a salt solution of suitable concentration. The still higher indices of methanethiol and methyl and vinyl bromides were matched with sugar solutions or ethylene glycol (Table I).

Certain fluorine compounds served to observe a few binary iso-optics with indices slightly below that of water (Table I). No solute is known which decreases the refractive index of water. To match it the low indices of propane, methyl ether, most of the Freons, and six other liquids were raised by slight dilution with a liquid of much higher index. Benzene and carbon disulfide were most satisfactory for this purpose. The optimum method of extrapolation of the observed index of the benzene mixture to that of the pure sample is linear on the basis of volumes of benzene per 100 volumes of total mixed volume, not per 100 volumes of total separate volumes. The mixed volume is preferably observed, not calculated from the density of the condensed gas, because in some of these systems there are substantial volume changes on mixing. Extrapolation on this basis is equivalent to assuming that deviations in refractive index are parallel with those in density. Mole fraction and weight percentage show substantial deviations from lineality in several of the known binary systems (*16*). Results for these iso-optics of diluted liquefied gases are presented in Table II.

EXPERIMENTAL

If the liquefied gas is not too soulble in water (which excludes ammonia, sulfur dioxide, and a few others), and if its index is at least 1.334 at 0° C., it is matched against water or an aqueous solution, usually brine, of suitable index.

A thick glass pressure tube, about 11 mm. in inside diameter and 16 mm. in outside diameter with a narrow neck, was charged with about 1.2 ml. of the reference liquid. This volume was kept small for aqueous liquids to minimize the risk of bursting the tube by freezing, although larger volumes can be frozen by cooling gradually with a swirling motion. No danger is involved unless there is also gas pressure. The tube was cooled in a dry ice–acetone bath, and a sample, 2 to 5 ml. from a lecture bottle, condensed into it through a capillary tube. The pressure tube was sealed by pulling off a small tip with a flame.

The temperature was adjusted with a water bath or with methanol and ice in a Dewar flask until on vigorous shaking and looking through the tube toward a window, the opalescent color changed from deep blue to purple, lavender, magenta, and yellow on warming, or back to blue on cooling, or the reverse. The operation is analogous to titration with an indicator. The refractive index of the reference liquid, and therefore of the sample, at this temperature, was read from a plot of its index (*15*, p. 956). For these binary iso-optics (Table I), the observed temperature is independent of the relative volumes of the layers. They are considered binary iso-optics, because the salt is assumed to be insoluble in the condensed gas. The refractive indices of salt solutions are interpolated as functions of temperature (*15* pp. 990, 997).

For substances of lower index, the higher index diluent was either measured or weighed accurately, following the usual charge of water. And the amount of liquefied gas was determined by weighing, as a check on the determination of total volume of the nonaqueous phase from a calibration of the tube. From the observed index of the nonaqueous layer and its composition by volume, that of the pure liquefied gas was calculated by linear extrapolation. Results of these diluted iso-optics are listed in Table II.

In the case of sulfur hexafluoride, it was almost necessary, because of its high freezing point, to have a solvent for it which was liquid at −78° C., so that the vapor could be bubbled through the solvent. Carbon disulfide, toluene, *n*-decane, and methylcyclohexane, tried for this purpose, were unsatisfactory, because they were not miscible with sulfur hexafluoride even at room temperature. *n*-Pentane and iso-octane served this purpose, although the capillary frequently plugged with crystals. The index of sulfur hexafluoride is so low that only moderate concentrations of it could be used in comparison with water. The precision is therefore low.

A visual autoclave (*10*) was used for carbon dioxide, ethane, ethylene, and nitrous oxide, which cannot be handled safely in sealed glass tubes. The autoclave was charged with a little water and a definite volume of diluent. Carbon tetrachloride was used as diluent for nitrous oxide to avoid any possible risk of explosion. The liquefied gas was added in increments from a steel lecture bottle by a

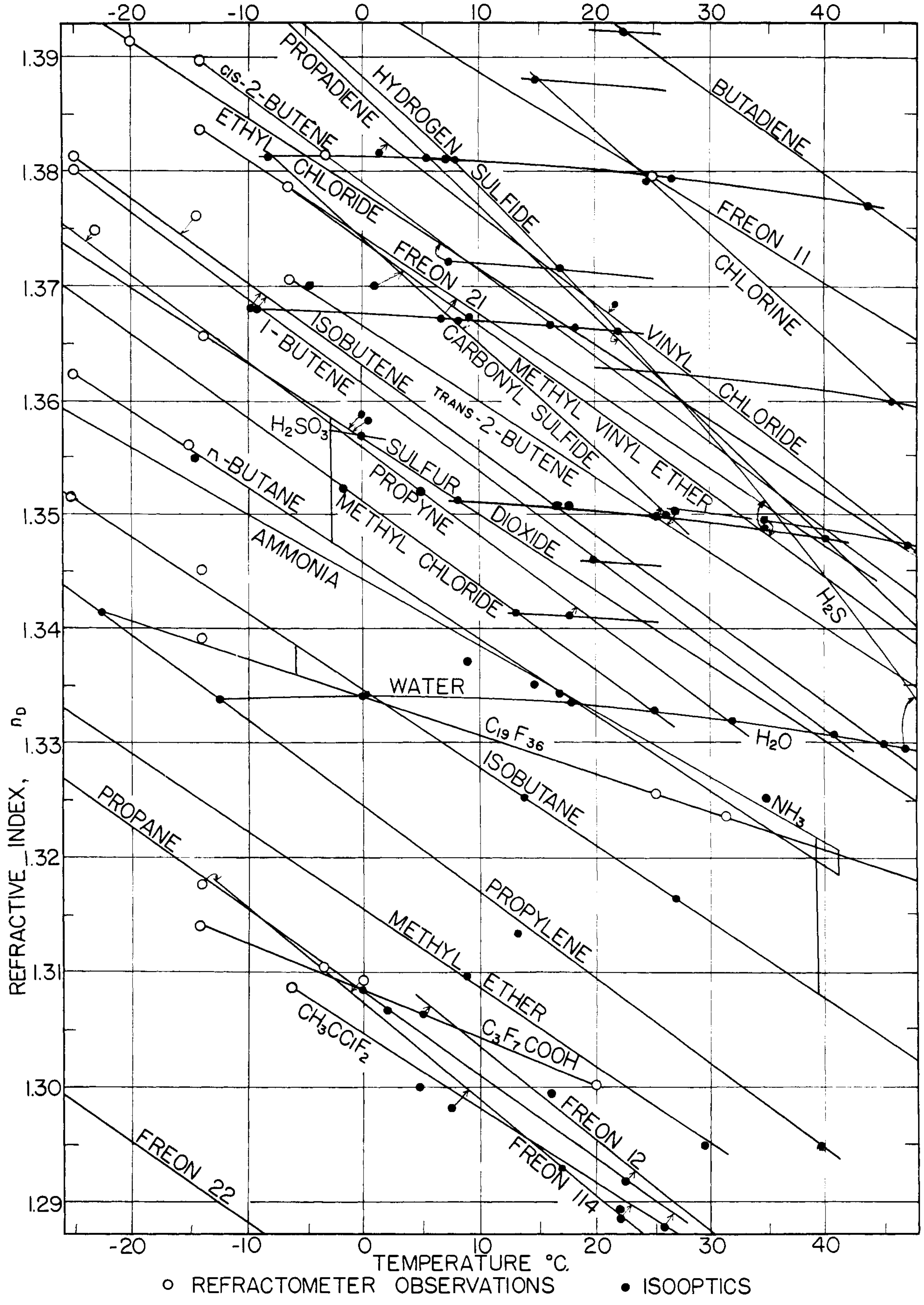

Figure 1. Refractive indices for liquefied gases at various temperatures

Table I. Binary Iso-Optics of Liquefied Gases

Liquefied Gas	Reference Liquid[a]	n_D^{25}	Iso-optic Temp., t	n_D^t
Ammonia	*n*-Butane	1.3290	18^b	1.3340
1,3-Butadiene	NaI	1.4106	−4	1.4116
	NaI	1.3919	23.2	1.3920
	NaCl	1.3794	44	1.3764
	NaCl	1.3660	62.8	1.360
n-Butane	NH_4OH (22% NH_3)	1.3455	-14.5^b	1.3550
	Ammonia	1.3297	18^b	1.3340
	Water	1.3325	19^c	1.3330
1-Butene	NH_4OH (22% NH_3)	1.3455	20	1.3465
	Water	1.3325	41	1.3305
cis-2-Butene	NaCl	1.3660	16	1.3669
	Water	1.3325	70	1.3251
trans-2-Butene	NaCl	1.3683	−4.5	1.3701
	NaCl	1.3504	27.4	1.3502
	Water	1.3325	55.7	1.3279
Carbonyl sulfide	NaCl	1.3794	−8.2	1.381
	NaCl	1.3660	9.2	1.3672
	NaCl	1.3497	25.7	1.3496
	NaCl	1.3497	26.7	1.3494
Chlorine	$CaCl_2$	1.3875	15.1	1.3880
	NaCl	1.3786	25	1.3786
	NaCl	1.3626	46	1.3595
Ethyl chloride	NaCl	1.3708	7^b	1.3721
	NaCl	1.3660	18^b	1.3667
	NaCl	1.3497	50^b	1.3461
Ethylene oxide	$C_{19}F_{36}$	1.3258	>104 (CST)	>1.296
Freon 11 (CCl_3F)	NaCl	1.3794	27^b	1.3790
	NaCl	1.3560	73^b	1.348
Freon 21 ($CHCl_2F$)	NaCl	1.3660	7.5^b	1.3665
	NaCl	1.3497	39.8^b	1.3475
	NaCl	1.3410	54.2^b	1.3366
	Water	1.3325	71^b	1.3250
	Ethyl sulfate	1.4002	−47	1.4224
Freon 114	Dry snow	...	-2^c	1.3090
Hydrogen sulfide	NaCl	1.3794	7.5	1.3808
	NaCl	1.3794	8.9	1.3806
	NaCl	1.3708	17	1.3714
	NaCl	1.3660	21.5	1.3662
	NaCl	1.3497	34.5	1.3485
	Water	1.3325	47.6	1.3291
	$C_{19}F_{36}$	1.3258	63.4	1.3111
Isobutane	NH_4OH (22% NH_3)	1.3455	$-36.5^{b,c}$	1.359
	Water	1.3325	0^b	1.3340
Isobutene	NaCl	1.3660	−9.7	1.368
	NaCl	1.3660	−9	1.3675
	NaCl	1.3497	16.9	1.3507
	NaCl	1.3497	18	1.3504
	Water	1.3325	44	1.3295
Methanethiol (methyl mercaptan)	Sugar	1.4393	2	1.4410
	Ethylene glycol	1.4291	13.5	1.4316
	Sugar	1.4205	36	1.4186
Methyl bromide	Sugar	1.4140	22.3	1.4143
	Sugar	1.3953	56.6	1.390
Methyl chloride	NaCl	1.3497	-1^b	1.3515
	NaCl	1.3410	12.8^c	1.342
	Water	1.3325	26^c	1.3324
	$C_{19}F_{36}$	1.3258	ca. 49 (CST)	(1.3161)
Methyl vinyl ether	NaCl	1.3683	1.1	1.3701
	NaCl	1.3504	34.8	1.3492
	Water	1.3325	66.3	1.3259
Perhaloheptane[d] (C_7ClF_{15})	Dry snow	...	-26^b	1.3101
Propadiene (allene)	NaCl	1.3796	6	1.3812
	NaCl	1.3660	22	1.3664
	NaCl	1.3497	40	1.3478
	Water	1.3325	59	1.3273
Propane	$C_{11}F_{20}$	1.3170	−42	1.339
	C_3F_7COOH	1.3000 (at 20°)	0	1.3082
Propylene	NH_4OH (22% NH_3)	1.3455	−45.3	1.360
	50% Methanol	1.3404	−38	1.3535
	$C_{19}F_{36}$	1.3258	−22.5	1.3415
	Water (subcooled)	1.3325	−12	1.3337
Propyne (methylacetylene)	NaCl	1.3497	5	1.3515
	NaCl	1.3410	17	1.3417
	Water	1.3325	32	1.3317
Sulfur dioxide	H_2SO_3[d]	...	0	1.356
	$C_{19}F_{36}$	1.3258	74	1.3073
Vinyl bromide	Ethylene glycol	1.4291	15.7	1.4312
	Sugar	1.4193	41	1.4171
Vinyl chloride	NaCl	1.3797	1.5	1.3815
	NaCl	1.3683	22.1	1.3689
	NaCl	1.3504	47.2	1.3471
	Water	1.3325	72.3	1.3247

[a] Salts, ammonium hydroxide, sulfurous acid, and sugar mean aqueous solutions, with the observed index shown. Others except snow, are pure liquids. $C_{11}F_{20}$ is perfluoromethyldecalin; $C_{19}F_{36}$ is perfluorononyldecalin. [b] Reverse order of colors. [c] Practically no color. [d] See text.

Table II. Iso-optics of Diluted Liquefied Gases with Water

Liquefied Gas	Vol. % of Diluent[a]	Iso-optic Temp., ° C.	Refractive Index at Iso-optic Temp.	
			Water	Liq. gas (extrap.)
Carbon dioxide	47.5	27[b, c]	1.3322	1.183
	33% CS_2	27[b, c]	1.3322	1.180
1,1-Difluoro-1-chlororethane	16.2	4.9	1.3329	1.2995
	21.0	22.0	1.3327	1.2885
	28.1	58.0	1.3275	1.2692
1,1-Difluoroethane	33.3	15.8	1.3333	1.2482
	41.2	54.4	1.3281	1.2222
Ethane	37	30[b, c]	1.3319	1.2365
	37.1	30[b, c]	1.3319	1.2362
	25.2% CS_2	32[b, c]	1.3316	1.2352
Ethylene	39.6	32.2[b, c]	1.3316	1.2257[d]
	25.2% CS_2	30[b, c]	1.3319	1.229[d]
Freon 12 (CCl_2F_2)	13.5	5	1.3339	1.3062
	17.2	16	1.3333	1.2992
	19.6	22.5	1.3327	1.2918
	25	48	1.3292	1.278
Freon 22 ($CHClF_2$)	27.9	16	1.3333	1.2683
	26.8	17	1.3332	1.2705
	30.4	28.7	1.3321	1.2607
Freon 114 ($(CClF_2)_2$)	10.5% CS_2	7.5	1.3338	1.298
	19.15	17	1.3332	1.2929
	20.6	22	1.3327	1.289
	24	30.5	1.3319	1.2805
	24.3	37	1.3311	1.2802
	25	41	1.3303	1.2778
Isobutane	4.5	14[b]	1.3334	1.3253
	8.84	27	1.3322	1.3161
	15.6	48.3	1.3291	1.3006
	16.15	55.5	1.3280	1.2992
Methyl ether	12.15	9.3	1.3336	1.3096
	18.6	29.5	1.3320	1.2948
Nitrous oxide	44.4% CCl_4	26.7[b, c]	1.3324	1.237
Propane	12.9	2	1.3340	1.3070
	13.3% CS_2	25.6	1.3324	1.2874
Propylene	10.75	13.5	1.3335	1.3133
	18.7	40	1.3305	1.2941
Sulfur hexafluoride	80.8% *n*-pentane	−10[b, e]	1.334	1.182
	26.3% *n*-pentane 42.9% MeC_6H_{11}	0	1.334	1.180
	77% iso-octane	36[b]	1.3310	1.161

[a] Benzene unless otherwise listed. [b] No opalescent color. [c] Observation in visual autoclave. [d] Above critical temperature. [e] Subcooled.

pressure connection, the amount being adjusted by further addenda or by partial release until the interface practically disappeared. No opalescent color was observed, because the agitation was far too slow to produce an emulsion. This decreased the precision. The levels of interface—made visible by traces of dust accumulated there—and meniscus were read accurately by a scale, giving from a calibration the volume of the nonaqueous layer. Extrapolations of these observations are presented in Table II.

Ammonia and sulfur dioxide required special treatment (Table III). Ammonia is miscible with water in all proportions, and so cannot be matched directly. It gives a good iso-optic at 18° C. with *n*-butane, whose index is now known as a function of temperature. A slight dilution of isobutane with a higher boiling and higher index hydrocarbon such as *n*-hexane, is necessary to give a color with ammonia even at −78° C. The same system gives varying opalescent colors over the entire range from −78° C. to room temperature.

Sulfur dioxide (Table III) has a limited solubility in water (25% by weight). A system of the liquid and water shows an iso-optic at 0° C., although the plots cross at 38° C. This is because the aqueous layer contains other molecular species such as sulfurous acid which affect the index. Reliable results were obtained by direct observation on a refractometer in a cold room at −14° C. (boiling point −10° C.), by a binary iso-optic of sulfur dioxide against perfluorononyldecalin, $C_{19}F_{36}$, at 74° C., and by matching of sulfur dioxide against mixtures of butanes and pentanes. Colors obtained with mixtures are almost independent of temperature from −78° to 0° C.

Table III. Iso-optics of Liquefied Gases with Mixed Hydrocarbons

Liquefied Gas	Reference Liquids	Temp., *t*	n^t_D
Ammonia	Isobutane–		
	12.5% *n*-Hexane	<−78	[a]
	15.4% *n*-Hexane	9	1.3365
	18.5% *n*-Hexane	14.5	1.3345
	26.2% *n*-Hexane	35	1.3248
Sulfur dioxide	*n*-Butane–		
	56% *n*-Pentane	<−78	[a]
	57% *n*-Pentane	0	1.3589
	71.6% Isopentane	1.5	1.3586

[a] These iso-optics show that the plots for these two inorganic liquids are only slightly less steep than those of the hydrocarbons.

Iso-optics of dry snow which had never been sintered were observed with perhaloheptane (approximately C_7ClF_{15} of n^{25}_D 1.2905) at −26° C. and with Freon 114 at −2° C. (below their boiling points) in open tubes by stirring with a thermometer. Corresponding experiments with propane, Freon 12, and 1,1-difluoro-1-chloroethane in sealed tubes failed to give a color, or disappearance of the crystals, perhaps because of a film of vapor on the surface of the snow crystals.

The results for ethylene, although mutually consistent,

Table IV. Low Temperature Refractometer Observations

Substance	Temp., ° C.	n_D	References
1,3-Butadiene	−25	1.4293	(*4*, *13*)
	−14	1.4228	(*12*)
	−6	1.422	(*4*)
n-Butane	−25	1.3621	(*4*, *13*)
	−15	1.3562	(*4*, *13*)
1-Butene	−25	1.3803	(*4*, *13*)
cis-2-Butene	−14	1.3895	(*12*)
trans-2-Butene	−6.3	1.3705	(*12*)
Cyclopropane	−80	1.4024	(*5*)
	−42.5	1.3799	(*5*, *13*)
	−32.75	1.3726	(*5*)
1,1-Difluoro-1-chloroethane	−6.3	1.3084	(*12*)
1,1-Difluoroethane	−72	1.3011	(*14*)
2,2-Difluoropropane	0	1.2904	(*14*)
Ethyl chloride	−50	1.4085	(*13*)
	−20	1.3913	(*13*)
	−3.5	1.3813	(*12*)
Ethylene	−100	1.3632	(*4*, *17*)
Ethylene oxide	−6.7	1.3669	(*12*)
	8.4	1.3599	(22)
Ethyl fluoride	−40	1.3057	(*13*)
Ethyl sulfate	−6.7	1.4101	(*12*)
Freon 11 (CCl_3F)	−14	1.4035	(*12*)
	−3.5	1.3971	(*12*)
	25	1.3794	(*12*)
Freon 21 ($CHCl_2F$)	−14	1.3837	(*12*)
Freon 114 ($(CClF_2)_2$)	−14	1.3174	(*12*)
	−3.5	1.3106	(*12*)
	0	1.3092	(*18*)
Heptafluorobutyric acid	−14	1.3140	(*12*)
(C_3F_7COOH)	20	1.3000	(*12*)
Isobutane	−45	1.3638	(*4*)
	−25	1.3514	(*4*, *13*)
	−14	1.3451	(*12*)
Isobutene	−25	1.3814	(*4*, *13*)
	−14	1.3762	(*12*)
Isopropyl fluoride	−50	1.3406	(*13*)
	−20	1.3240	(*13*)
50% Methanol (by volume)	−14	1.3490	(*12*)
Methanethiol (MeSH)	−6.7	1.4488	(*12*)
Methyl bromide	−50	1.4631	(*13*)
	−20	1.4432	(*13*)
Methyl chloride	−42.5	1.3830	(*13*)
Methyl ether	−42.5	1.3441	(*13*)
Methyl vinyl ether	−6.3	1.3784	(*12*)
Neopentane	0	1.3513	(*4*)
	6	1.3476	(*4*)
Nitrous oxide (N_2O)	−90	1.3305[a]	(*17*)
Perfluoromethyldecalin	−14	1.3310	(*12*)
($C_{11}F_{20}$)	62.2	1.3038	(*12*)
Perfluorononyldecalin	−14	1.3391	(*12*)
($C_{19}F_{36}$)	68	1.3092	(*12*)
Propadiene (allene)	−70	1.4444	(*4*)
	−40	1.4212	(*4*)
	−34.34	1.4169	(*4*)
Propane	−70	1.3587	(*4*)
	−50	1.3448	(*4*)
	−42.5	1.3395	(*4*, *13*)
Propylene	−80	1.3857	(*4*)
	−60	1.3713	(*4*)
	−47.8	1.3625	(*4*)
n-Propyl fluoride	−50	1.3496	(*13*)
	−20	1.3326	(*13*)
Propyne	−40	1.3863	(*4*)
(methylacetylene)	−23.3	1.3746	(*4*)
Snow (ice)	−3.5	1.3105	(*3*)
Sulfur dioxide	−14	1.3653	(*12*)

[a] This observation was assigned incorrectly to nitric oxide, NO. (*15*, p. 966, and also in International Critical Tables, Vol. I, p. 165.)

must be considered fictitious, because the temperature is above the critical temperature of ethylene, 9.5° C. Of course, the index of a gas above the critical temperature would vary with pressure or density. The observations on ethane, carbon dioxide, and nitrous oxide also may be somewhat high, because of the proximity of the critical temperature, and the presence of the diluent.

The indices of most of the higher boiling liquefied gases and also some of the reference liquids were observed directly on a refractometer in a cold room in which it had been stored overnight. These are listed in Table IV together with published values, and are plotted on the figure with open circles. Similarly, the indices of two fluorocarbon reference liquids were observed with a refractometer in a hot room. These refractometer observations were consistent with the iso-optics.

All of the results were plotted on a large scale as refractive index against temperature. Because this would be much too congested if reduced in size to a single page, Figure 1 shows only the central portion of this graph, with a scale more than twice as great. The figure includes a majority of the observations. Those plots which reach the side lines are partly dependent on observations beyond them, as given in the tables. Arrows are attached to a few of the points to show to which substance they belong.

DISCUSSION

Refractive indices of all substances except water, aqueous solutions, and hydrogen sulfide are plotted as straight lines. It is probable that all of the plots should be slightly convex, as are the corresponding plots of density. But the curvature may be too slight to detect with the available precision of measurement except near the critical temperature. The six iso-optics of hydrogen sulfide (critical temperature 100.4° C.) with aqueous liquids in Table I agree with the equation, $n_D = 1.3878 - 0.00078t - 0.00001t^2$ with a maximum deviation of 0.0005. However, there may be a small systematic error resulting from the increased solubility of hydrogen sulfide in the aqueous layer with lower salt concentrations and higher temperatures. [The solubility of liquid hydrogen sulfide in pure water at 25° C. is 8.9% by weight (*12*). All observations below 30° C. are subcooled with respect to crystalline hydrate.] This idea was supported by the iso-optic with perfluorononyldecalin. A plot of the following equation with lower curvature (shown in the figure) is consistent with all iso-optic except those at 34.5° and 47.6° C.

$$n_D = 1.3882 - 0.0009t - 0.000005t^2$$

However, this equation would not hold at temperatures above 64° C., because the curvature undoubtedly increases on approaching the critical temperature. A type of equation which allows for this increase in curvature is $n_D = A - Bt - C/(E - t)$, analogous to that for density (*6*, *8*); but data are still inadequate for determination of its constants for any substance. Smith (*21*) estimated that all substances should have an index of 1.126 at their critical temperatures. This is incongruous with Grosse's estimate (*13*) for the index of fluorine, 1.09 at its boiling point, −187° C.

Observations on substances with still lower critical temperatures than hydrogen sulfide (Table II) failed to show the postulated curvature, because the presence of the requisite diluent removed these substances from near-critical phenomena. What is needed for this purpose is a binary iso-optic, requiring a reference liquid immiscible with the samples, and with a comparable low index of 1.15 to 1.25.

Curiously, iso-optics with perfluorononyldecalin usually occur close to the respective critical solution temperatures.

Table V. Refractive Indices of Liquefied Gases[a]

Liquefied Gas	B.P., ° C.	n_D^{20}	n_D^{25}	Tables
Ammonia	-33.0	1.3327	1.3298	I, III
1,3-Butadiene	4.41	1.3940	1.3900	I, IV
n-Butane	-0.50	1.3326	1.3290	I, IV
1-Butene	-6.26	1.3460	1.3422	I, IV
cis-2-Butene	3.72	1.3632	1.3595	I, IV
trans-2-Butene	0.88	1.3533	1.3499	I, IV
Carbon dioxide	-78.5	1.190[c]	1.185[c]	II
Carbonyl sulfide	-50.2	1.3553	1.3506	I
Chlorine	-33.7	1.3834	1.3788	I
1,1-Difluoro-1-chloroethane	-9.2	1.2912	1.2882	II, IV
1,1-Difluoroethane	-24.7	1.2444[c]	1.2413[c]	II, IV
Ethane	-88.63	1.246[c]	1.241[c]	II
Ethyl chloride	12.3	1.3647	1.3614	I, IV
Ethylene	-103.7	(1.239)[b,c]	(1.234)[b,c]	II, IV
Ethylene oxide	10.5	1.351[c]	1.348[c]	I, IV
Freon 11 (CCl_3F)	23.77	1.3824	1.3794	I, IV
Freon 12 (CCl_2F_2)	-30.0	1.2950	1.2909	II
Freon 21 ($CHCl_2F$)	8.92	1.3602	1.3569	I, IV
Freon 22 ($CHClF_2$)	-40.6	1.267	1.264	II
Freon 114 ($(CClF_2)_2$)	3.55	1.2905	1.2865	I, II, IV
Hydrogen sulfide	-61.8	1.3682	1.3626	I
Isobutane	-11.73	1.3209	1.3175	I, II, IV
Isobutene	-6.90	1.3478	1.3440	I, IV
Methanethiol (MeSH)	5.96	1.4286[c]	1.4257[c]	I, IV
Methyl bromide	3.56	1.4164[c]	1.4130[c]	I, IV
Methyl chloride	-23.7	1.3365	1.3328	I, IV
Methyl ether	-24.9	1.3018	1.2984	II, IV
Methyl vinyl ether	8	1.3588	1.3552	I, IV
Nitrous oxide	-89.5	1.242[c]	1.238[c]	II
Propadiene (allene)	-34.34	1.3670	1.3620	I, IV
Propane	-42.07	1.2936	1.2900	I, II, IV
Propylene	-47.7	1.3095	1.3056	I, II, IV
Propyne (methylacetylene)	-23.1	1.3403	1.3365	I, IV
Sulfur dioxide	-10.0	1.3429	1.3396	I, III, IV
Sulfur hexafluoride (m.p. -56° C.)	-63.8	1.170[c]	1.167[c]	II
Vinyl bromide	15.8	1.4288[c]	1.4260[c]	I
Vinyl chloride	-13.9	1.3682	1.3642	I

[a] Selected from Figure 1, or interpolated from observations given in tables listed.
[b] Above critical temperature.
[c] Not plotted in Figure 1.

Substance	Critical Solution Temp., °C.	Iso-optic
Propylene	-12	-22.5
Isobutane	-6	0, estd.
Methyl chloride	49	49
Hydrogen sulfide	76	63.4
Sulfur dioxide	75	74
Ethylene oxide	104	110, estd.

For isobutane and ethylene oxide, since there is a blue opalescence just below the critical solution temperature, the iso-optic must be only slightly above it.

The liquid with the lowest index so far found is sulfur hexafluoride, with 78% fluorine, n_D^{25} 1.167. Very likely hexafluoroethane, with 82.6% fluorine, would have a still lower index, possibly lower than Grosse's estimate for hydrogen fluoride (*13*). Refractive index observations are summarized in Table V.

EXTENSION TO OTHER SUBSTANCES

The method presented is not well adapted to hydrogen halides, because of their high solubility in almost all transparent liquids (*11*). Alkylamines and probably phosgene would be excluded for the same reason, although these substances could be observed on a refractometer with only slight refrigeration.

On the other hand the method is readily adapted to observation of indices of corrosive substances which should not be used on a refractometer, such as fuming acids. Paraffin hydrocarbons would be preferred reference liquids. In absence of pressure, glass-stoppered tubes would suffice; but sealed tubes are recommended because of the requirement of vigorous shaking to observe the colors.

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