served. Cromwell and Scott,[5] in spectrophotometric measurements of the heat of formation of the benzene–iodine complex, report no measurable temperature broadening of the ultraviolet absorption in benzene.

As the temperature is lowered below 0°, the coloration of the solutions of iodine in the alkyl iodides is observed visually to become deep brown and finally straw yellow in color in the solid state at liquid nitrogen temperature. Freed and Sancier[6] have observed a similar temperature shift at 77°K. for the propylene–iodine complex together with pronounced intensification of the absorption in the ultraviolet.

In the case of the pure alkyl iodides as solvents, an increase in temperature generally results in a decrease in the extinction coefficients in the region from 400 to 500 mμ and an increase in the region above 500 mμ. This increase for the long wave length region is quite pronounced, *e.g.*, at 550 mμ the molar extinction coefficient in propyl iodide increases from 250 at 5° to 500 at 99°.

The relative oscillator strength (taken here to be $f = \int_{400\ \mathrm{m}\mu}^{625\ \mathrm{m}\mu} \epsilon \, d\nu$; ν in cm.$^{-1}$) shows a surprisingly small temperature coefficient in spite of the fact that the absorption is much more intense in the propyl iodide solutions ($f'/f = 1.92$ at 25°). The coefficient corresponds to a change of 7.9% in going from 5 to 99° in the propyl iodide and 4.1% (extrapolated) for an equivalent temperature interval in the octane solution.

These observations might perhaps be adequately explained in terms of a shift in a solvation equilibrium (of the form $RI + I_2 \rightleftarrows RI \cdot I_2$) toward the left with increasing temperature. However this system seems to be somewhat more complicated, particularly in that the behavior of the extinction coefficient (and oscillator strength) does not more than qualitatively parallel the shift in maximum. Also the effect of temperature is unexpectedly low for the relatively large displacement of the maximum in these solutions. An alternate explanation along the lines suggested by Bayliss and Rees[7] seems worthy of consideration in this regard, *i.e.*, that the change in spectrum in the alkyl iodide solvents is due to a generalized solvation resulting in a perturbation of the normal iodine absorption.

(5) T. M. Cromwell and R. L. Scott, THIS JOURNAL, **72,** 3826 (1950).

(6) S. Freed and K. M. Sancier, *ibid.*, **74,** 1273 (1952).

(7) N. S. Bayliss and A. L. G. Rees, *J. Chem. Phys.*, **8,** 377 (1940); N. S. Bayliss, *Nature*, **163,** 764 (1949).

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Physical Properties of *cis*-1-Cyano-1,3-butadiene

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A recent literature survey at this Laboratory revealed a scarcity of physical property data on *cis*-1-cyano-1,3-butadiene. Several physical properties of high purity *cis*-1-cyano-1,3-butadiene (99.80 ± 0.08 mole %) were measured; the experimentally determined values are given in Table I together with conservative estimates of uncertainties wherever possible.

TABLE I

MEASURED PHYSICAL PROPERTIES OF *cis*-1-CYANO-1,3-BUTADIENE

F.p. for zero impurity, $T_{f0} \pm 0.04°$		−62.58
Heat of fusion, ΔH_F ±250 cal./mole		3028
Refractive index, n^{25}D ±0.0001		1.4835[a]
dnD/dt (25°)		−0.0005
Density, d^{25}_4 ±0.0002 g./ml.		.8578[b,c]
dd_4/dt (25°)		− .00087
Viscosity, η^{25} ±0.006 millipoise		5.973
dη/dt (25°)		−0.061
Flash point (Tag Closed Tester), °F.		95
Vapor pressure constants in Antoine	A	7.376
eq.[d] for temp. range 45–110°	B	1639
	C	230

Solubility: 1.5 wt. % soluble in water at 25°, and completely miscible with all common organic solvents

[a] H. R. Synder, *et al.*, THIS JOURNAL, **75**, 4742 (1953), report n^{20}D 1.4855. [b] *Ibid.*, report d^{26}_4 0.8541 and d^{1}_4 0.866. [c] D. D. Coffman, THIS JOURNAL, **57**, 1982 (1935), reports d^{20}_4 0.8644. [d] The Antoine equation is written as $\log_{10} P_{\mathrm{mm}} = A - (B/C + t)$.

The purity of the *cis*-1-cyano-1,3-butadiene used in this work was determined cryoscopically by the methods described by Taylor and Rossini.[1] The infrared spectrum (Baird double beam infrared spectrophotometer) of high purity *cis*-1-cyano-1,3-butadiene was also obtained; the spectrum was identical with the one published by Snyder, *et al.*, reference (*a*). The density value which Snyder, *et al.*, report for the density of the *trans* isomer of 1-cyano-1,3-butadiene is identical to the density value obtained in this work for the *cis* compound. Snyder also obtained higher density and refractive index values for the *trans* isomer than for the *cis*. This order is contrary to the usual order (*cis* higher than *trans*) for several other pairs of *cis* and *trans* compounds.

Experimental

Purification.—*cis*-1-Cyano-1,3-butadiene was purified by fractionation in a Smith column at 56 mm. The column was packed with glass helices and had 10–15 theoretical plates. A reflux ratio of 5:1 was maintained during the take-off of the high purity fraction boiling at 61°.

Freezing Points.—The freezing point for zero impurity (T_{f0}) and the actual freezing points (T_f) for several distillate cuts of *cis*-1-cyano-1,3-butadiene were ascertained from time–temperature cooling curves; these freezing curves were obtained with either equipment similar to the NBS freezing point apparatus[2] or with a Leeds and Northrup Automatic Stull Recorder.[3-5] The readability of the former is better than 0.001°, and the uncertainty of temperature measurements with the Automatic Stull Recorder is ±0.03°. In ascertaining the freezing points, liquid nitrogen was used as a constant temperature cooling medium, and the rate of cooling near the freezing point was approximately one degree per minute. A spiral Nichrome-wire stirrer which moved up and down in the freezing tube ensured equilibrium during freezing. It was never necessary to induce crystalliza-

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(1) W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards*, **32,** 197 (1944).

(2) A. R. Glasgow, A. J. Streiff and F. D. Rossini, *ibid.*, **35,** 355 (1945).

(3) D. R. Stull, *Rev. Sci. Instruments*, **16,** 318 (1945).

(4) Brochure, "Speedomax High-Precision Resistance Thermometer Recorder with Automatic Range Extension," Leeds and Northrup Company, Philadelphia, Pa.

(5) D. R. Stull, *Ind. Eng. Chem., Anal. Ed.*, **18,** 234 (1946).

tion, and only a small amount of supercooling (*ca.* 0.2°) was observed for high purity *cis*-1-cyano-1,3-butadiene. The value of T_{f0} given in Table I was obtained with each assembly of freezing point apparatus; this value is also an average value for eleven runs obtained with the Automatic Stull Recorder.

Heat of Fusion.—All experimental work to determine the heat of fusion was carried out on equipment similar to the NBS freezing point apparatus. The procedure and method employed for determining the heat of fusion from cryoscopic measurements have been described by Johnsen and Fitzpatrick.[6] For this work adiponitrile was used as the solute, and the heat of fusion was calculated from the equation[6]

$$\Delta H_F = \frac{NRT_{f0}^2}{(T_f - T_s) - (T_{f0} - T_f)}$$

where N is the mole fraction of adiponitrile in the solution to be frozen, R is the gas constant in cal./deg./mole, T_{f0} is the freezing point of *cis*-1-cyano-1,3-butadiene for zero impurity, T_f is the actual freezing point for the sample of the *cis*-1-cyano-1,3-butadiene before the addition of adiponitrile, and T_s is the freezing point for the sample after the addition of the solute. The mole fraction of adiponitrile varied from 0.032 to 0.045, and the average value for the heat of fusion listed in Table I was determined from the freezing point data of three runs which were believed to be satisfactory.

Vapor Pressure.—A dynamic method was used to obtain the summarized vapor pressure–temperature data given in Table I. The apparatus employed for these measurements is very similar to that described by Stull,[5] and consists of an ebulliometer (15-ml. capacity), a contacting manostat, and an Automatic Stull Recorder equipped with a platinum resistance thermometer. During ebullition, the pressure in the system was regulated by the contacting manostat at one of 14 fixed pressures which were previously calibrated with water. The equilibrium temperature of boiling was recorded in terms of resistance on the strip chart of the Automatic Stull Recorder. The uncertainty for the vapor pressure measurements is believed to be ±0.1 mm. The vapor pressure constants A, B and C listed in Table I were determined from a Cox Chart.

Refractive Index.—A Bausch and Lomb precision refractometer was used to measure the refractive index of high purity *cis*-1-cyano-1,3-butadiene at 26.0°, 28.7° and 31.0°. Water from a thermostatically controlled bath was circulated through the prism blocks of the refractometer. The temperature of the bath did not vary more than ±0.05° for any setting of the Merc-to-Merc regulator. (This bath was also employed for density and viscosity measurements.) The thermometers in the bath and in the refractometer were calibrated with a platinum resistance thermometer to ensure that all subsequent temperature readings would be accurate. The refractometer had previously been properly aligned with a "test plate," and the refractive index of water was always measured each day during this work to check the calibration of the instrument.

Density.—A Sprengel type pycnometer was used to determine the densities of high purity *cis*-1-cyano-1,3-butadiene at 26.2°, 30.8° and 34.0°. The volume of the pycnometer was determined from the weight of water it contained when filled at a constant temperature. All weights were reduced to vacuum, and duplicate runs were made at each temperature.

Viscosity.—Using an Ostwald viscosity pipet, the efflux times for both distilled water and high purity *cis*-1-cyano-1,3-butadiene were measured at 25° and 30°. Water was used as a standard liquid at both temperatures, and the coefficient of viscosity for *cis*-1-cyano-1,3-butadiene at each temperature was calculated from the usual relationship obtained from Poiseuille's law governing the flow of liquids through capillary tubes.[7]

Flash Point.—A Tag Closed Tester was used to determine the flash point of *cis*-1-cyano-1,3-butadiene. The procedure which has been recommended for this apparatus by the A.S.T.M.[8] was followed in order to obtain a standardized value. The purity of the sample used for the flash point test was approximately 95 mole per cent. Duplicate determinations were made, and the flash point of one run checked the other within 2°F.

Solubility.—A simple turbidimetric method was used to determine, qualitatively, the solubility of *cis*-1-cyano-1,3-butadiene in various organic solvents. *cis*-1-Cyano-1,3-butadiene from a graduated pipet was added dropwise to 1 ml. of solvent until either turbidity was apparent or until 1 ml. of *cis*-1-cyano-1,3-butadiene had been added. The value for the solubility of *cis*-1-cyano-1,3-butadiene in water was also confirmed by spectrophotometric analysis using both the Beckman quartz (model DU) and the Carey recording (model 11) spectrophotometers.

Solubility of Water in *cis*-1-Cyano-1,3-butadiene at its Freezing Point.—Three drops of water were added to a sample of high purity *cis*-1-cyano-1,3-butadiene of known T_f; the solution was then frozen to determine whether or not the addition of water produced any lowering of the freezing point, T_f. No depression of T_f was observed. The infinitesimal amount of water required to give a saturated solution of *cis*-1-cyano-1,3-butadiene and water at the freezing point of the former was not determined, as the error in reporting the cryoscopically determined purity on an anhydrous basis is probably no greater than 0.01–0.02 mole per cent.

Derived Properties

The derived properties listed in Table II were calculated from the experimentally determined physical properties given in Table I.

TABLE II

DERIVED PHYSICAL PROPERTIES OF *cis*-1-CYANO-1,3-BUTADIENE

B.p.,[a,b] °C.	(100 mm.)	74.9
	(760 mm.)	134.6
Heat of vapn., kcal./mole	(100 mm.)	9.73
	(760 mm.)	9.16
Crit. vol., cc./mole		285
Crit. press., atm.		49.3
Crit. temp., °K.		656
Compressibility factor Z	(100 mm.)	0.996
	(760 mm.)	0.980
Cryoscopic constant, $A°$, ±0.003 mole fraction/deg.		0.034

[a] Snyder, *et al.*, ref. *a*, Table I, report 32.5° (13 mm.). [b] H. R. Snyder, J. M. Stewart and R. L. Meyers, THIS JOURNAL, **71**, 1055 (1949), report 49.5° (31.5 mm.).

The boiling points at 100 mm. and 760 mm. pressure were calculated from the Antoine equation. The heats of vaporization at 100 mm. and 760 mm. were calculated from the smoothed vapor pressure data by an equation given by Rossini.[9] Since this equation involves the compressibility factor, Z, of the vapor in equilibrium with the liquid; the Z factors were calculated from the Berthelot equation of state. The constants in the Berthelot equation were determined from the critical properties of the vapor; the critical temperature, volume and pressure were approximated by empirical methods given by Hougen and Watson.[10] The cryoscopic constant, $A°$, for *cis*-1-cyano-1,3-butadiene which is used to calculate sample purities from freezing point data was obtained from the experimental values given in Table I for the heat of fusion and the freezing point for zero impurity.

Acknowledgments.—The author is indebted to W. F. Hamner and the Instrument Group for determining the infrared spectrum, and also for

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[6] Paper, "Freezing Point, Heat of Fusion, and Determination of Purity of Acrylonitrile," presented before the Division of Physical and Inorganic Chemistry, 1st Joint Meeting of the Southeast and Southwest Regional Sections of the American Chemical Society, New Orleans, La., Dec. 10–12, 1953.

[7] F. H. Getman and F. Daniels, "Outlines of Physical Chemistry," 7th Ed., John Wiley and Sons, Inc., New York, N. Y., 1946, p. 167.

[8] "1952 Book of A.S.T.M. Standards, Part 5, Fuels, Petroleum, Aromatic Hydrocarbons, Engine Antifreezes," American Society for Testing Materials, Philadelphia 3, Pa., 1953, p. 1.

[9] F. D. Rossini, "Chemical Thermodynamics," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 436.

[10] O. A. Hougen and K. M. Watson, "Chemical Process Principles, Part I, Material and Energy Balances," John Wiley and Sons, Inc., New York, N. Y., 1947, pp. 68–73.

running several spectral analyses during the course of this investigation. The author also wishes to thank S. E. J. Johnsen and K. M. Taylor for their assistance in the purification of *cis*-1-cyano-1,3-butadiene.

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Solid Solutions in the System Li_2SO_4–$(NH_4)_2SO_4$–H_2O[1]

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Although the alums generally belong to the cubic system there are three distinct internal arrangements of the structural units: α-, β- and γ-structures.[2] However, lithium aluminum alum is not cubic.[3] It would be interesting to determine whether it forms solid solutions with alums having the various internal structures. The acquisition of several well-formed ammonium aluminum alum crystals which contained significant amounts of lithium had led to the speculation that perhaps they contained lithium alum in solid solution.[4] A systematic study of the quaternary system Li_2SO_4–$Al_2(SO_4)_3$–$(NH_4)_2SO_4$–H_2O at 0° was therefore undertaken in connection with this and with the general question of whether lithium alum formed solid solutions with alums possessing the different internal structures. Since the ternary system Li_2SO_4–$(NH_4)_2SO_4$–H_2O at 0° had not been previously reported, a partial study of it was also necessary to determine the compositions of the isothermally invariant saturated solutions. A more detailed study of the system was made as a result of the discovery of solid solutions. Experimental evidence is presented below which indicates that the solid solutions are discontinuous and are actually between $Li_2SO_4 \cdot H_2O$ and $LiNH_4SO_4$. A few results of a study of the same system at 25° which substantiate the occurrence of solid solutions at a higher temperature also are given.

It appears that the occurrence of solid solutions in the system Li_2SO_4–$(NH_4)_2SO_4$–H_2O at various temperatures has been overlooked because of the limited data and the absence of any indication of solid solutions in the graphical representations. The diagram of the system at 30° reproduced in Mellor[5] is taken from an earlier report by Schreinemakers and Cocheret.[6] It shows four solid phases: $Li_2SO_4 \cdot H_2O$, Li_2SO_4, $LiNH_4SO_4$ and $(NH_4)_2SO_4$. The diagram commonly used as an illustration of a classical ternary isotherm,[7–9] is taken from a later report by the same investigators.[10] It indicates only three solid phases: $Li_2SO_4 \cdot H_2O$, $LiNH_4SO_4$ and $(NH_4)_2SO_4$. The two diagrams are based on the same table of data appearing in both of the above-mentioned reports. However, algebraic extrapolation[11] of the figures lends little support to the conclusion that $Li_2SO_4 \cdot H_2O$ is a solid phase in equilibrium with saturated solutions. In the later report[10] which also contains results of a study of the system at 50° there appears a brief mention by the authors that Li_2SO_4 does not exist as a pure solid phase at 30 and 50° but in solid solutions, the nature of which they did not investigate further. Two other references[12,13] to the ternary system at 20, 57 and 97° contain no mention of solid solutions. The presentation of results in these reports is fragmentary and pertains to the double salt $LiNH_4SO_4$.

Experimental Procedure

Anhydrous Li_2SO_4 was prepared from J. T. Baker reagent Li_2CO_3 which had been recrystallized by the method of Kraus and Burgess.[14] The final product was heated in platinum in a muffle furnace at 550–600° to remove the last traces of acid and water. Merck reagent $(NH_4)_2SO_4$ was used without further purification. It was pulverized and then dried for several hours at 105°.

Complexes of known compositions, totaling 50-60 g., were prepared in capped solubility tubes which contained two glass marbles to produce a grinding action during mixing. They were brought to equilibrium at 0° in a completely enclosed, well-insulated ice-water bath. The tubes were rotated end over end on a completely submerged wheel turned by a horizontal, motor-driven shaft which entered the bath through one of the sides.

The complexes were mixed 14–21 days before final analysis. In most cases the saturated solutions were first analyzed after 7 days, the mixtures rotated for an additional 48 hours, and the solutions then reanalyzed. Constancy of composition upon repetition of this process was used as a criterion of attainment of equilibrium. The procedure followed in the work at 25° was the same.

The saturated solutions were sampled by means of pipets fitted with filter paper, and analyzed by one of two methods. Complexes 1-7 inclusive of Table I were analyzed for ammonia by distillation into excess standard sulfuric acid,[15] and for lithium sulfate on separate samples by volatilization of ammonium sulfate after evaporation to dryness. Complexes 8-32 were analyzed for total sulfates by evaporation and drying, and for lithium sulfate by ignition of the residues. The first method was adopted for part of the work at 0° to shorten the time of analysis. The procedure of the second method was that employed in a similar study of solid solutions between ammonium sulfate and other alkali metal sulfates.[16] It gave slightly higher ammonium sulfate values, about 5 parts per 1000, than the first method presumably because the last traces of entrapped water were removed very slowly in the drying process. A tracer tech-

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[1] This work was supported in part by the National Science Foundation Grant G159.

[2] Primary references and a discussion of the criteria of isomorphism appear in Therald Moeller's "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1952, p. 541.

[3] An X-ray study of the structure of lithium alum is in progress. It appears to be monoclinic.

[4] J. A. N. Friend, private communication to H. A. Horan. The limited amount of material permitted an aluminum analysis only; calcd. % $Al_2(SO_4)_3$ in $NH_4Al(SO_4)_2 \cdot 12H_2O$: 37.7, found 37.0. The determined value should be higher than the calculated if solid solutions of lithium alum were involved.

[5] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green and Co., New York, N. Y., 1922, p. 706.

[6] F. A. H. Schreinemakers and D. H. Cocheret, *Chem. Weekblad*, **2**, 771 (1905).

[7] Farrington Daniels, "Outlines of Physical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 335.

[8] Louis Hammett, "Introduction to the Study of Physical Chemistry," McGraw-Hill Book Co., New York, N. Y., 1952, p. 282.

[9] "International Critical Tables," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1928, p. 388.

[10] F. A. H. Schreinemakers and Cocheret, *Z. physik. Chem.*, **59**, 645 (1907).

[11] A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4306 (1931).

[12] C. Spielrein, *Compt. rend.*, **155**, 347 (1912).

[13] C. Spielrein, *ibid.*, **157**, 46 (1913).

[14] C. A. Kraus and W. B. Burgess, THIS JOURNAL, **49**, 1227 (1927).

[15] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Third Ed., The Macmillan Co., New York, N. Y. 1952, p. 537.

[16] C. Calvo and E. Simons, THIS JOURNAL, **74**, 1202 (1952).