A mixture of 15 g. of the picrate and 100 ml. of 5% sodium hydroxide was refluxed for 5 hours. The mixture was cooled and extracted with ether. A brown oil (7.8 g., 84% based on the amount of picrate used) was obtained, which solidified on standing (m.p. 32–38°). One recrystallization from absolute ethanol gave 6.2 g. (67%) of product, m.p. 34–36°. Further recrystallization did not improve the melting point.

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The Solubility and Transition Point of Lithium Chromate

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Data reported by earlier workers for the solubility of lithium chromate at 18,[1] 20[2] and 30°[3] are not consistent. Further, while the usual composition of the salt is the dihydrate, our observations confirm the findings of Retgers[4] that an anhydrous salt separates from the aqueous solution on boiling. It therefore seemed desirable to determine the solubility over the range 0 to 100°, and the temperature of transition between the dihydrate and the anhydrous salt.

Experimental

The material used for the solubility experiments was recrystallized $Li_2CrO_4 \cdot 2H_2O$, prepared from lithium hydroxide monohydrate and chromic anhydride. It was found to contain 99.85% $Li_2CrO_4 \cdot 2H_2O$ based on its hexavalent chromium content, 0.006% Cl and 0.021% SO_4. It was necessary to remove traces of trivalent chromium and insoluble matter from the solutions before the final crystallization; this was done by oxidation with a small amount of sodium hypochlorite and filtrations. The final product consisted of bright yellow crystals. Solubility[5] and transition point[6] were determined by previously described methods. The following results were obtained:

Temp., °C.	Solubility, wt. % Li_2CrO_4	Solid phase
0.7	47.27	$Li_2CrO_4 \cdot 2H_2O$
7.2	47.74	$Li_2CrO_4 \cdot 2H_2O$
10.4	47.89	$Li_2CrO_4 \cdot 2H_2O$
20.0	48.60	$Li_2CrO_4 \cdot 2H_2O$
29.8	49.62	$Li_2CrO_4 \cdot 2H_2O$
40.2	50.66	$Li_2CrO_4 \cdot 2H_2O$
50.1	52.10	$Li_2CrO_4 \cdot 2H_2O$
60.0	53.52	$Li_2CrO_4 \cdot 2H_2O$
70.0	55.27	$Li_2CrO_4 \cdot 2H_2O$
74.6		$Li_2CrO_4 \cdot 2H_2O + Li_2CrO_4$
75.1	56.17	Li_2CrO_4
80.0	56.34	Li_2CrO_4
90.0	56.57	Li_2CrO_4
100.0	56.82	Li_2CrO_4

The values when plotted yield smooth curves. For the dihydrate, the equation

$$S = 47.25 + 0.05037T + 0.0009143T^2$$

fits the observed data with an average deviation of 0.05% and a maximum deviation of 0.09%. For the anhydrous salt, the equation

$$S = 52.646 + 0.06265T - 0.0002096T^2$$

fits the data with an average deviation of 0.01% and a maximum deviation of 0.02%. Calculation of the concentration at the transition temperature gives: from the dihydrate equation, 56.10% Li_2CrO_4; from the anhydrous salt equation, 56.15% Li_2CrO_4.

A value of 56.12% Li_2CrO_4 is therefore reported for the solution concentration in equilibrium with the two solid phases at the transition temperature of 74.6°.

As might be expected from the relatively slight change of solubility of both phases with temperature and the oblique angle of intersection of the two solubility curves, the heat effect on transition is very small, and is estimated to be of the order of 1–2 kcal./mole, as contrasted with 15 kcal./mole reported[7] for the $Na_2CrO_4 \cdot 10H_2O$–$Na_2CrO_4 \cdot 6H_2O$ transition. It was necessary to heat and cool at rates in the order of 0.01°/minute to detect the thermal breaks, which were obtained at 74.6° on both heating and cooling.

Of the previous solubility determinations, only that of Schreinemakers,[3] who reported 49.94% Li_2CrO_4 at 30°, is in agreement with the present work.

An attempt was made to determine the temperature of the ice–dihydrate eutectic. This proved to be below −60°; equipment and measuring facilities were not available to investigate lower temperatures.

An unusual characteristic of the anhydrous salt is its ready solubility in the lower alcohols. Sodium chromate is soluble to the extent of only 0.35%[8] in methanol and even less in ethanol at room temperature. Other anhydrous chromates are virtually insoluble in alcohols. Anhydrous lithium chromate was prepared for study by slowly boiling a saturated solution of the dihydrate. The yellow crystals were 99.83% Li_2CrO_4. An approximate determination of the solubility of the salt in commercial absolute methanol and ethanol was made by rotating sealed containers containing these compounds with an excess of lithium chromate in a constant temperature bath for eight hours. The bottles were protected from light by a covering of black tape, since alcoholic solutions of lithium chromate, although stable for more than two months in the dark, were found to undergo decomposition fairly rapidly, with deposition of hydrous chromic chromate, when exposed to light. The following results were obtained:

Temp., °C.	Solubility, wt. % Li_2CrO_4 Methanol	Ethanol
0.5	13.4	1.6
24.4	15.7	1.8

The dihydrate is somewhat more soluble than the anhydrous salt, but its true solubility in alcohols cannot be determined, since the salt is dehydrated by these solvents.

Anhydrous lithium chromate was found to be insoluble in ether, and soluble only to the extent of about 25 p.p.m., as judged by color, in acetone. The low solubility in acetone explains the previously reported[5] decomposition of lithium dichromate to lithium chromate in acetone solution.

Density of the dihydrate and the anhydrous salt was determined by immersion in toluene in a pycnometer: Li_2CrO_4, $d^{25}{}_4$ 2.426; $Li_2CrO_4 \cdot 2H_2O$, $d^{25}{}_4$ 2.149.

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[8] This value is from unpublished data by E. A. Roche of this Laboratory.

The Reaction of Silver *n*-Perfluorobutyrate with *n*-Perfluoropropyl Iodide and with 1,2-Dibromo-1-chlorotrifluoroethane

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Several attempts were made to synthesize perfluorinated esters by the reaction of silver salts of perfluoro-fatty acids with perfluoroalkyl iodides, but without success.[1] In contrast to the ease of formation of esters by treating perfluoro-silver salts with *n*-alkyl iodides and diiodides,[2] the attempted preparation of *n*-perfluoropropyl-*n*-perfluorobutyrate by the reaction of silver *n*-perfluorobutyrate with *n*-perfluoropropyl iodide at 275–335°, in the absence of solvents, resulted in the formation of *n*-perfluorohexane, carbon dioxide and silver iodide according to the equation

$$CF_3CF_2CF_2I + CF_3CF_2CF_2CO_2Ag \longrightarrow n\text{-}C_6F_{14} + CO_2 + AgI \quad (1)$$

These results suggest a free radical mechanism with formation of $C_3F_7\cdot$ and $C_3F_7COO\cdot$. At the high temperature of the reaction, direct combination does not take place. The latter radical loses carbon dioxide, and the coupling product, C_3F_7–C_3F_7, is formed exclusively.

Experimental

The Reaction of *n*-Perfluoropropyl Iodide with Silver *n*-Perfluorobutyrate.—The reaction of perfluoropropyl iodide[1] and silver perfluorobutyrate[1] was carried out in nickel and silver pressure reactors at 275 and 335°, respectively. In both cases the only reaction products isolated were *n*-perfluorohexane, carbon dioxide and silver iodide in agreement with equation (1). Only possible traces of unreacted perfluoropropyl iodide were detected. *n*-Perfluorohexane boiled at 56°; mol. wt. found (Victor Meyer), 336; calcd., 338; known, b.p. 55.9–56.7°.[3]

The nickel reactor (100-cc. capacity) was of the rotating type and was partially filled with stainless steel balls. The silver reactor (16-cc. capacity) was filled with silver Raschig rings. Both vessels were equipped with Hoke valves. In a typical reaction, 7.5 g. (0.053 mole) of perfluoropropyl iodide was transferred *in vacuo* to the nickel reactor containing 8.4 g. (0.0262 mole) of finely powdered silver perfluorobutyrate. After heating this mixture at 275° for 10 hours, the Dry Ice-cooled reactor was opened to a similarly cooled glass collecting trap, and the temperature of the reactor was allowed to warm up slowly to *ca.* 25°. A large quantity of uncondensed carbon dioxide gas was collected in a barium hydroxide scrubber attached to the system. Finally all volatile products were transferred *in vacuo* to the collecting trap. This material (6.46 g.) was rectified in a micro fractionating column, and 5.65 g. (66% yield) of *n*-perfluorohexane, was collected. The yield of silver iodide was quantitative. A small scale run in the silver reactor at 335° for one hour, gave an almost quantitative yield of perfluorohexane.

At temperatures below 220° only a very slight reaction occurred in sealed Pyrex tubes. When anhydrous ethyl ether was used as a solvent, there were formed some *n*-perfluoropropyl hydride and a sizable fraction boiling at 70–100° which had a distinct ester odor and was only slightly soluble in water and dilute alkali (density < 1). No pure compound, however, could be isolated under these conditions.

The Reaction of 1,2-Dibromo-1-chlorotrifluoroethane with Silver *n*-Perfluorobutyrate.—The reaction of silver perfluorobutyrate with 1,2-dibromo-1-chlorotrifluoroethane (prepared by the photochemical bromination of chlorotrifluoroethylene) was carried out in glass and metal pressure reactors at temperatures of 100–200° and higher under a variety of conditions. The desired perfluorochloroester, trifluorochloroglycol diheptafluorobutyrate, was not obtained. When ethyl ether or dioxane was used as solvent, an insignificant amount of reaction occurred with some decomposition and loss of carbon dioxide. When an ethyl ether–heptafluorobutyric acid solvent mixture was employed, despite the formation of 50% silver bromide, evidence was found only for the formation of carbon dioxide, the olefin chlorotrifluoroethylene, and only possible traces of a higher boiling ester. Despite its reactivity, methanol was tried as a solvent because of its high solubilizing effect for the reactants. In this case the theoretical amount of silver bromide was isolated as well as a high yield of methyl *n*-heptafluorobutyrate,[4] b.p. 80–80.8° at 760 mm., n^{20}D 1.293, formed by reaction with the solvent.

In the latter case, 15.0 g. of the dibromide, 36.5 g. of the silver salt and 70 ml. of methanol were heated together at 100° for 5 hours in a sealed Pyrex bulb. There were formed 20.2 g. of silver bromide, traces of chlorotrifluoroethylene, and after washing and drying with calcium chloride, 18.18 g. of pure methyl *n*-heptafluorobutyrate.

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[1] The perfluorinated inner ester, perfluorobutyrolactone, is the only completely fluorinated ester to be described to date. See M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951); M. Hauptschein, C. S. Stokes and A. V. Grosse, *ibid.*, **74**, 1974 (1952).

[2] M. Hauptschein and A. V. Grosse, *ibid.*, **73**, 5139 (1951); also M. Hauptschein, unpublished results.

[3] T. J. Brice in J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 453. Also, J. H. Simons and W. H. Pearlson, 112th Meeting American Chemical Society, September, 1947.

[4] Minnesota Mining and Manufacturing Co. Brochure on Heptafluorobutyric Acid.

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Molecular Order in *n*-Heptane and *n*-Perfluoroheptane

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Molecules of *n*-perfluoroheptane are undoubtedly far less flexible than those of *n*-heptane by reason of the size of the fluorine atoms, hence they can be expected to pack in a somewhat more orderly, parallel array in the liquid state, especially at lower temperatures. The liquids should differ like dry and cooked spaghetti. We sought evidence for this in a difference between their entropies of vaporization like the differences previously found between liquids with differing order due to molecular geometry.[1] According to the "Hildebrand Rule" liquids composed of highly symmetrical molecules all have the same entropy of vaporization per mole, Δs^v, when compared at temperatures where they have the same gas volume, v^g, but any degree of order in the liquid, whether the result of molecular association or simply of geometrical shape, leads to a higher entropy of vaporization as this order is destroyed.

We have reliable vapor pressure equations for *n*-heptane[2] and for *n*-perfluoroheptane.[3] Instead of obtaining their entropies of vaporization graphically from the slope of log p *vs.* log T plots, as heretofore, we differentiated the vapor pressure equations to obtain $\Delta s^v = R(\mathrm{d} \ln p/\mathrm{d} \ln T)$. Selecting 25° as the temperature of comparison for the heptane, we calculated 15° as the temperature at which the perfluoroheptane would vaporize to the same volume, 403 liters, assuming ideal gases, which introduces no significant discrepancy. Table I gives the resulting figures for Δs^v, and shows an excess of 1.6 entropy units for the perfluoroheptane. This seems reasonable when compared with the

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[2] "Selected Values of Hydrocarbons," Circular of the National Bureau of Standards, C 461, 1947, p. 123.

[3] G. D. Oliver and J. W. Grisard, THIS JOURNAL, **73**, 1688 (1951).